Early diagenesis of organic matter from higher plants in a malagasy peaty marsh. Application to environmental reconstruction during the Sub-Atlantic

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The purposes of the present work were to examinate the morphological features and chemical composition of organic matter (OM) from a peaty marsh, in order to derive information on biological sources and on the changes in depositional conditions that occurred during the last 2300 years.

The studied site, Tritrivakely, is a maar (a former volcanic crater lake) about 600 m wide and 50 m deep, located on Ankaratra Plateau. The maar is presently occupied by a peaty marsh with abundant Cyperaceae. The waterbody is shallow, fluctuating from 0 to 2 m. The study was concerned with the uppermost meter of peat which has accumulated for 2300 years B.P. in the maar. The Cyperaceae living in the marsh were also studied for comparison.

Experimental

Rock-Eval analyses (TOC, HI) and LECO CNS analyses (C/N) were performed every 5 cm on bulk peat and also on living Cyperaceae. Identification and quantification of peat constituents were obtained by light microscopy. Gas chromatography analyses of easily hydrolysable sugars and of cellulose were realized after hydrolyses with HCl 0.5N and HCl 12N, respectively. Lignin analyses were performed after a CuO attack by Capillary Electrophoresis (Maman *et al.,* 1996). Furthermore, the chemical composition of the insoluble material, isolated after lipid and sugar removal, was studied through gas chromatography-mass spectrometry identification of the products released via off-line pyrolyses of this material.

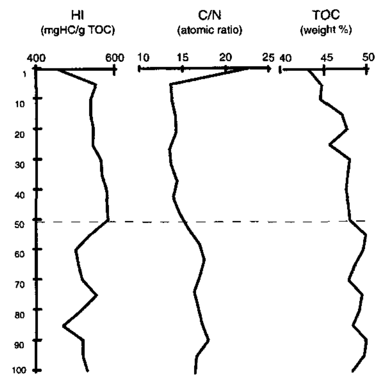

FIG. 1. Geochemical parameters *vs* depth.

Results and discussion

The evolution of the geochemical parameters (Fig. 1) along the core indicates that (i) the quantity of accumulated OM was always important (TOC between 43 and 50%), and (ii) two parts can be distinguished in the series, likely reflecting changes in the conditions of peat sedimentation. Between 1 and 50 cm, the accumulated OM is characterized by high hydrogen indexes (HI) and low C/N ratios, suggesting a substantial algal contribution. In contrast between 50 and 100 cm, the contribution of the OM derived from higher plants was higher, as shown by relatively low k HI values and high C/N ratios.

Two sources of OM were evidenced from light microscopy studies: an aquatic source including algae like *Botryococcus* and diatoms and a paludal source comprising ligno-cellulosic tissues from Cyperaceae and reddish amorphous OM. The latter fraction is derived from plant tissues which lost their structure during early diagenesis (Bourdon *et al*, 1997). This reddish amorphous OM was predominant from the first cm and all along the series suggesting that extensive early diagenesis alterations occurred during the incorporation of senescent plant debris in peat.

Studies on sugars and lignin showed that both types of compounds were highly altered as soon as plant death (Fig. 2). Nevertheless a small and rather constant quantity survived in the peat all along the studied series.

The cinnamic/vanillic and the (xylose + glucose + arabinose)/total sugars ratios can be considered as reflecting inputs from Cyperaceae markers and thus used as markers of paludal conditions in the marsh. The evolution of these ratios all along the core confirmed the hypothesis of a mid core change in environmental conditions that affected peat deposition. Higher values between 50 and 100 cm than in the upper part of the core suggest that conditions were drier in the first part of the series.

So as to test whether the composition of the insoluble, sugar-free, OM fraction can also related to the differences in sources, reflected by the above petrographical and bulk geochemical data, two samples belonging to the upper (32 cm) and lower part (80 cm) of the core, respectively, were selected for pyrolytic studies. The insoluble material, obtained after lipid extraction and sugar hydrolysis was pyrolysed at 400°C under a helium flow. Mass balances indicates that the bulk of released products corresponds to volatile compounds. However, the latter are relatively more abundant in the case of the 80 cm sample, in agreement with higher contribution of ligno-cellulosic material. The trapped, medium volatility, products were analysed by GC-MS. They are dominated by n-alkane/n-alk-1-ene doublets, up to C15 and C18, reflecting the algal contribution and also comprise substantial amounts of lignin-derived phenolic compounds. These compounds are dominated by phenol and methyl phenols but vinylphenol, which can be considered as a marker of monocotyledon plants like Cyperaceae (Saiz-Jimenez and de Leeuw, 1986), occurs in significant amount as well. The presence of methoxyphenols in the two pyrolysates shows that early diagenesis did not result in alteration of all lignin-derived moieties. The pyrolysate from the 80 cm sample, when compared to the 32 cm one, exhibits a higher relative abundance of phenolics with respect to normal hydrocarbons. Such a difference is consistent with the larger contribution of remains from higher plant tissues in the former sample, inferred from petrographic and bulk geochemical resuts.

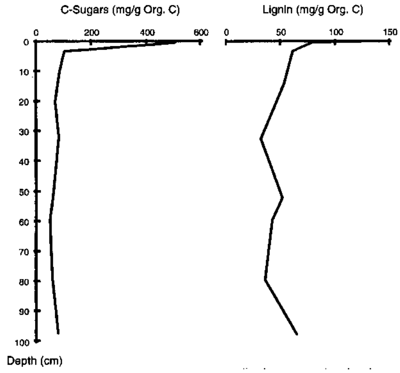

FIG. 2. Quantity of sugars and lignin *vs* depth.

Conclusion

The OM from Cyperaceae which accumulation results in peat formation, underwent important, early diagenetic, changes just after plants death. Such changes are reflected by a large alteration of the basic components of the ligno-cellulosic cell walls (cellulose, hemicellulose and lignin). Due to this loss of structural components, the bulk of the ligno-cellulosic tissues is transformed into reddish amorphous OM. This major component of peat which seems to be chemically stable records information about Cyperaceae abundance.

Comparison between Cyperaceae markers and algae markers allowed to distinguish two periods for organic sedimentation, with a limit that probably occurred at 1000 years B.P.

The first period, 2300 to ~1000 years B.P., was a peaty phase where the water column was minimal. The second period, between $\approx$ 1000 years and the present time, corresponded to a waterlogged marsh, with a longer lasting, if not permanent, water column.

The environmental variation recorded in the peat accumulation in Tritrivakely marsh correspond probably to a regional climatic change occurring around 1000 years B.P.

References

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