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RELATIONSHIPS BETWEEN ORGANO-MINERAL SUPPLY AND EARLY DIAGENESIS IN THE LACUSTRINE ENVIRONMENT: A STUDY OF SURFICIAL SEDIMENTS FROM THE LAC DU BOUCHET (HAUTE LOIRE, FRANCE)

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Abstract — The relationships between organo-mineral composition and early diagenetic processes in surface (< 50 cm) sediments from the Lac du Bouchet (Haute Loire, France) are presented. Parallel pore-water studies reveal downcore increases in dissolved organic carbon, inorganic carbon and CH_4, illustrating the dominant methanogenetic degradation, but also highlighting regions of enhanced degradation due to sulphate reduction (confirmed by solid phase sulphur and pyrite distributions). Three sedimentary facies are observed: IA (0–25 cm) where the majority of compaction and degradation of the organic matter by diagenesis occurs in the absence of any significant change in the type of organic material or sedimentation rate; IB (25–40 cm) characterised by an increased grain size and diatom abundance; II (below 40 cm), whose base dates at 2500 ± 350 BP (i.e. within the Sub-Atlantic) shows high organic carbon contents and large grain size.

Autochthonous amorphous organic matter is the dominant petrographical organic component, whereas pedogenetic (allochthonous) amorphous organic matter is slightly enriched in facies II and IA. This is coincident with the disappearance of the spores and pollen and suggests a greater continental runoff from the surrounding basin at these times. Proportions of kaolinite, chlorite and illite content do not vary greatly, indicating that the detrital input has not changed significantly over the last 2500 years. Downcore decreases in the Si/Al curve (proxy for biogenic silica) parallel those of total organic carbon suggesting the dissolution of solid phase silica over time. The anthropogenic deforestation and consequent greater nutrient runoff into the oligotrophic lake encouraged an increased production of diatoms around 30 cm. The increased sedimentation rate at the beginning of the Sub-Atlantic (facies II), as a result of greater continental runoff due to installation of present climatic conditions, enhanced the preservation of the organic material by reducing the dia-genetic effects and by increasing the proportion of diagenetically inert and relatively resistant organic matter. These findings underline the critical role that bulk sedimentation rate and the nature of organic matter play in the final determination of sediment composition, both in terms of input and in post-depositional degradation. Copyright © 1996 Elsevier Science Ltd

INTRODUCTION

There has been much work completed on maar lakes in Europe over the past decade, particularly within the framework of the EUROMAARS program. Parallel studies of organo-mineral sedimentation have been developed by the research group GdR 942 of CNRS (e.g. Bertrand *et al.*, 1992; Lallier-Vergès *et al.*, 1993; Sifeddine *et al.*, 1996). Maar lakes represent a highly specific sedimentary environment: they are relatively recent, their catchment areas are very restricted, and they often lack any riverine input (Bonifay and Truze, 1987). Thus, sedimentation should be relatively constant depending on the stability of the rainfall sensitive water column and a well defined and constant catchment basin ensuring homogeneity of detrital input; and climate change (e.g. temperature variation) which may trigger changes in vegetation, sedimentation pathways with respect to erosion factors,

aeolian input and the quality and quantity of organic material. European maar lakes, being situated in the temperate belt and typically between 700 and 1300 m altitude, are particularly susceptible to climate change (Bonifay and Truze, 1987) and may even serve to amplify any early and subtle changes in palaeoclimate. Realising the potential of such a situation, workers have studied the proportions of vegetal components in the sediments over time and have illustrated the link between sedimentation and climatic variation (e.g. Reille and de Beaulieu, 1988; Lallier-Vergès *et al.*, 1993).

The Lac du Bouchet is a maar crater lake some 28 m deep, situated in the Devès volcanic Massif (15 km SW of Le Puy; 44°55′N, 3°47′E) at 1205 m altitude (see Fig. 1, Sifeddine *et al.*, 1996). Water column composition is dominantly influenced by the surrounding basaltic basin and from rainfall (Truze, 1990). It displays relatively constant and sufficiently rapid sedimentation over the

past 120 ka (Creer *et al.*, 1986; Thouveny *et al.*, 1990; Thouveny, 1991) to have recorded European climatic variations (Bonifay *et al.*, 1987). Thus, Lake Bouchet represents an excellent example to observe the interaction between the effects of early diagenesis and climate change on the sediment record. Moreover, there have been very few high resolution studies of the topmost part of the sediment column, particularly on early diagenesis. This study is an attempt to characterise and measure, with a centimetric resolution, the relationship between the organo-mineral sedimentation and the effects of early diagenesis in the upper 50 cm.

SAMPLING AND METHODS

Three new sediment cores (S1, S3 and S4), each approximately 50 cm in length, were recovered by divers (October 1992) by manual insertion of PVC tubes into the sediment, which allowed good recovery and preservation of the sediment–water interface. Once ashore, the supernatant water was removed by syringe and the cores were flushed with N_2 (to retard any further oxidation of the surface sediments) before being transported upright to the laboratory in an isothermic container. There, cores were sliced in half lengthwise and logged for changes in texture, colour and grain size. Subsequently, the cores were sampled (centimetric) after the uppermost 3 cm of sediment were removed by syringe, due to their extremely high water contents.

RESULTS AND DISCUSSION

General Characteristics and Chronostratigraphy of the Sediments

The sediments are broadly homogeneous grey/green silty clays. Three facies were distinguished by slight changes in colour (7.5 YR 3/2–10 YR 2/2) and texture, which were confirmed by subsequent chemical analysis. Unit II (below 45 cm) corresponds to unit II as described by Sifeddine *et al.* (1996); unit IB corresponds to between approximately 25 and 45 cm, and unit IA between the surface and around 25 cm.

Water contents decrease (in cores S1, S3 and S4) from around 92% at the surface to 77% at 40 cm before increasing again to around 85% in facies II (Fig. 1). Conversely, sediment density increases with depth from approximately 0.07 g cm^{-3} at the surface to around 0.25 g cm^{-3} at 40 cm, before decreasing again to values of around 0.10 g cm^{-3} in unit II. The distribution in the upper 40 cm is consistent with compaction during sedimentation, the majority of which occurs in unit IA (0–25 cm) as sediment densities are relatively constant during unit IB (Fig. 1). The large decrease in density observed in unit II suggests a very different rate of deposition and/or type of material to that in the upper 40 cm.

Radiocarbon dates (^{14}C) from total organic matter were obtained for core S3 which placed all sediments within the Sub-Atlantic period (i.e. < 2500 ± 350 BP) and allowed calculation of sedimentation rates, assuming
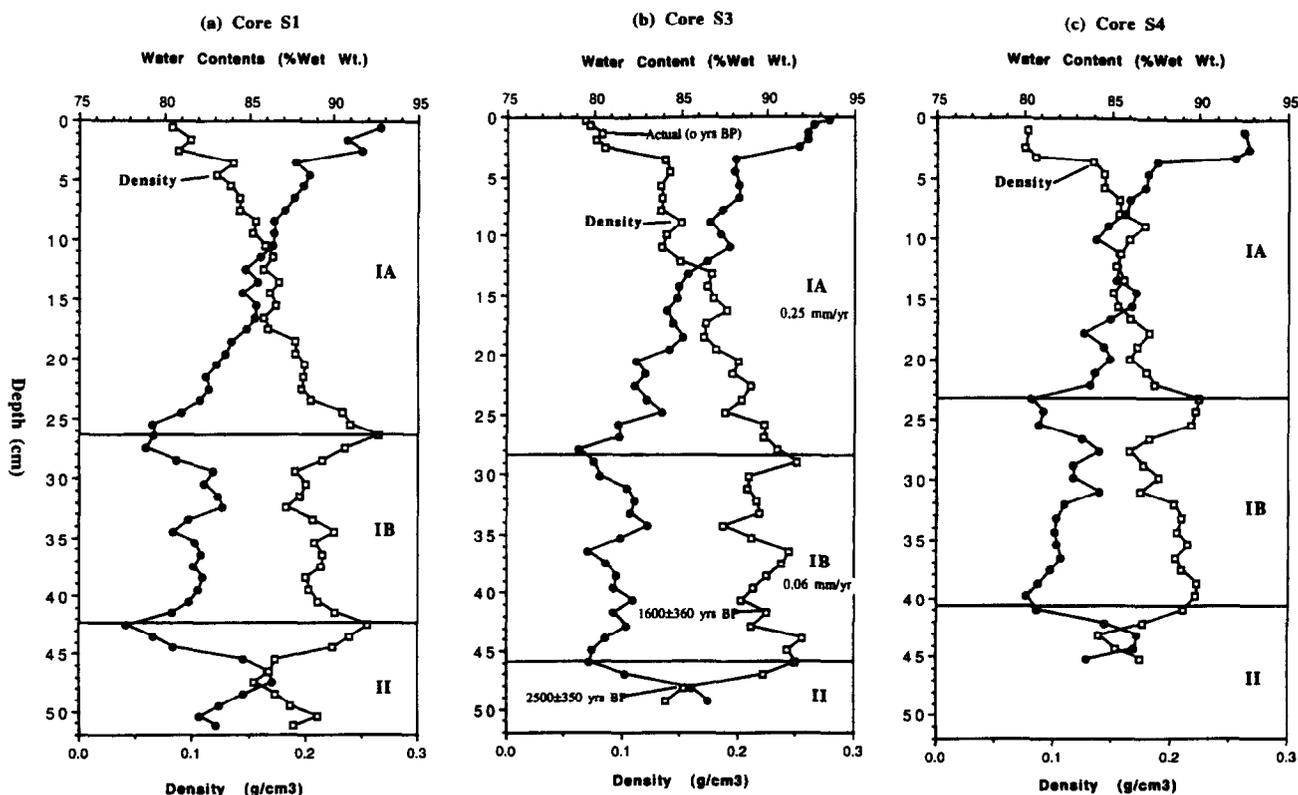

FIG. 1. Variations in the water content (% wet weight) and sediment density (g cm^{-3}) with depth (cm) in cores S1 (a), S3 (b) and S4 (c). Note also units IA, IB and II together with the ^{14}C dates and sediment accumulation rates (mm a^{-1}).

constant accumulation rates between dates (Fig. 1b). The sedimentation rate of 0.25 mm/year between 41.5 cm and 3.5 cm is consistent with previous estimates for Lac du Bouchet sediments (e.g. Creer *et al.*, 1986; Bonifay *et al.*, 1987). However, the sedimentation rate of 0.06 mm a⁻¹ between 48.5 and 41.5 cm is considered to be unrealistically low and is, most likely, the result of either a hiatus or the presence of reworked sediment with an age considerably older than the time of sedimentation. It is as a result of these doubts that the fluxes of the organic and mineral fraction are not discussed. Further ¹⁴C dating is being completed which may allow greater confidence in the assessment of sediment fluxes.

Study of the Mineral Fraction

Granulometry

The sediment from core S1 was treated with H_2O_2 to dissolve the organic fraction of the sediment before determination of the mineral grain size distribution using a Coulter laser sedigraph. The variation with depth of the four main grain size classes (Table 1) is shown in Fig. 2a.

Generally, unit I is dominated by the clay and silt fractions whereas unit II is characterised by an abundance of the coarser fraction (Fig. 2a). However, an increase in the coarse grain size is observed in unit IB around 30 cm, consistent with an increase in the diatom abundance as observed in smear slides under light microscopy. There is a marked increase in the silt fraction relative to the clay at around 10 cm (unit IA) and, conversely, a sharp increase in the clay/silt ratio towards the end of unit IB at 28 cm (Fig. 2b). However, the clay/silt ratio is relatively constant throughout the core (Fig. 2b), suggesting a relatively constant detrital input.

Clay mineralogy

Kaolinite, chlorite and illite, observed in the organic free (H_2O_2 treated) sediment using X-ray diffractometry, are present in approximately equal proportions (Figs 3a–c), with kaolinite being especially well crystallised. Below 15 cm, kaolinite and illite tend to vary in opposition and the ratio between the two minerals increases markedly around 18 cm and 30 cm depth (Fig. 3d). Moreover, the kaolinite/illite ratio tends to increase from 25 cm to the surface, possibly indirectly indicating some

TABLE 1. The Four Main Grain Size Classes in Core S1

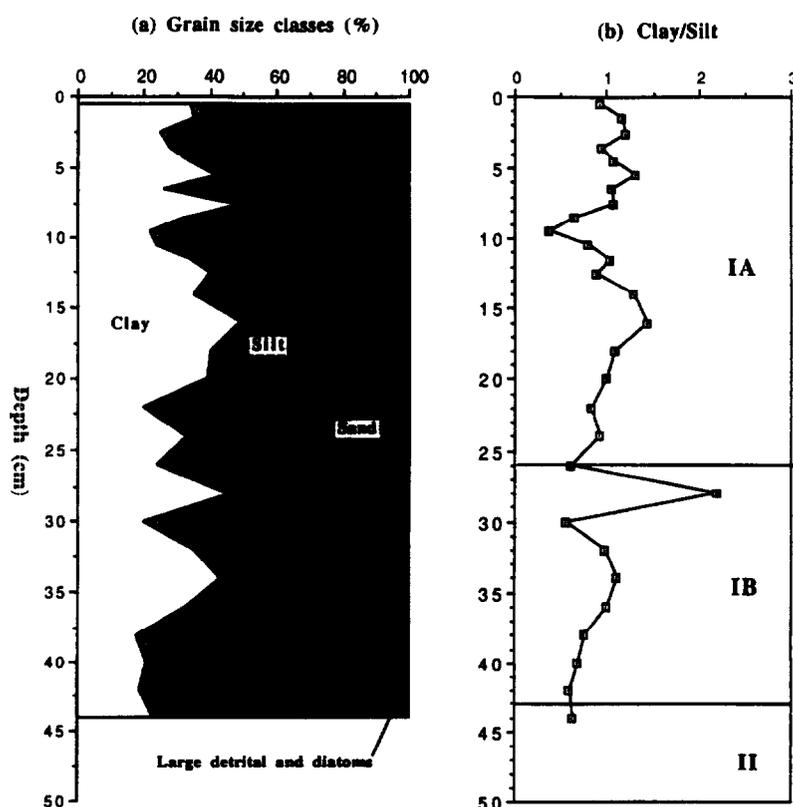| Class	Size	Type
Class 1	1–6 μm	Clays
Class 2	15–40 μm	Silt
Class 3	40–200 μm	Sand and biogenic particles (mainly diatom fragments)
Class 4	> 200 μm	Ligno-cellulosic debris and diatoms

FIG. 2. (a) variations in the four main sediment grain size classes of organic-free sediment (H_2O_2 treated), and (b) variations in the clay/silt ratio with depth (cm) in core S1.
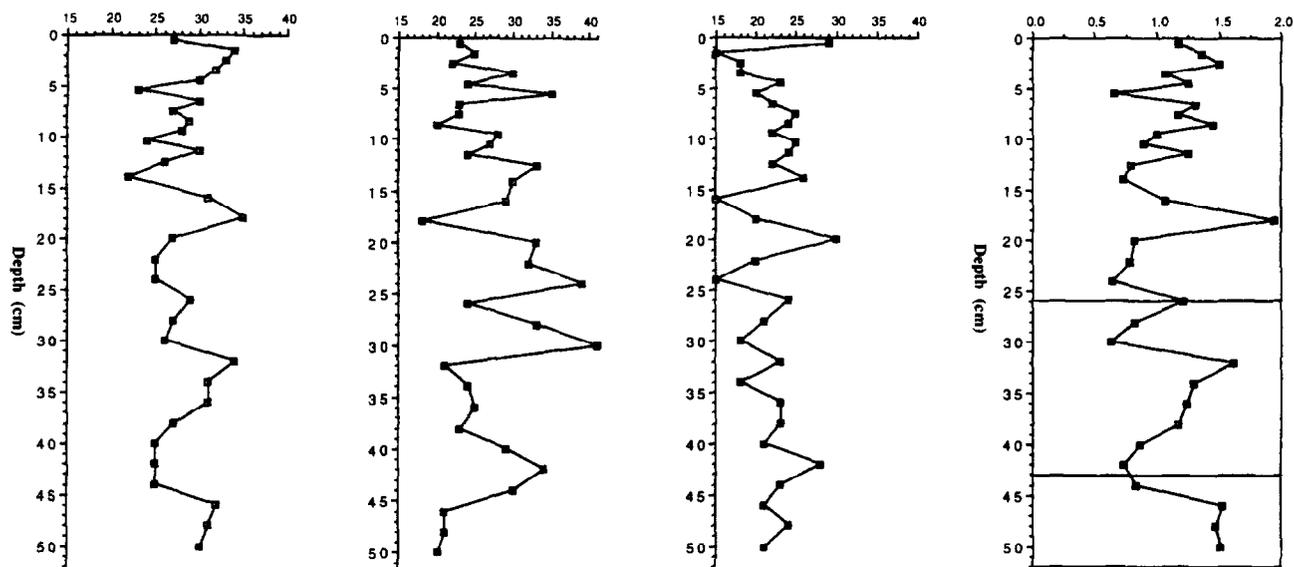
FIG. 3. Variations in sediment mineralogy with depth (cm); (a–c) downcore changes in the proportions of kaolinite, illite and chlorite and, (d) illustrating variations in the kaolinite/illite ratio.

slight variation in the lithological input. However, generally, the input of the detrital mineral fraction has not varied significantly over the last 2500 years.

Mineral geochemistry

The alkali–basaltic and pyroclastic nature of the terrigenous material in Lac du Bouchet sediments has been previously documented (Negendank *et al.*, 1991). Close inspection of smear slides, under light microscopy, confirmed these findings with detrital material being dominated by quartz and feldspars with some obvious amphiboles, olivines and glass shards. Major element chemistry was completed on bulk sediment samples using energy dispersive spectrometry (EDS). Al and Si vary in parallel between 12 and 14% and between 23 and 25% respectively (Fig. 4a), consistent with the detrital nature of both elements. However, in the upper 5–10 cm of sediment and around 30 cm, the two elements vary in opposition (Fig. 4a). The Si/Al ratio, thought to be a proxy for biogenic silica (Patience, 1992; Lallier-Vergès *et al.*, 1993) decreases downcore (Fig. 4b) whilst the dissolved silicate in the pore waters increases with depth (Jézéquel *et al.*, on-going studies), consistent with the progressive dissolution of the amorphous biogenic silica during sedimentation. The gradual downcore decrease of the Si/Al ratio is, however, interrupted around 30 cm by a sharp increase due to a greater percentage of diatoms (biogenic silica), as observed in smear slides (*Acnanthes* spp. and *Coconeis* spp.) and as described by Pailles (1989). This peak is also present in the P/Al profile (Fig. 4b) and may reflect an increase in the input of phosphorus rich organic material. Thus, both the Si/Al and P/Al peaks indicate an increase in the autochthonous productivity in the lake at this time perhaps as a result of an increased input of biologically limiting nutrients from the surrounding basin due to anthropogenic deforestation and the consequent greater soil erosion.

Iron sulphides are known to precipitate in sediments during bacterial sulphate reduction. However, in these sediments, the profiles of S and Fe are very different (Fig. 4c, d). Iron and titanium however do vary in parallel (Fig. 4c), suggesting the presence of titanomagnetite (confirmed from ongoing TEM studies) and/or ilmenite, consistent with the alkali–basaltic nature of the surrounding catchment area and illustrating that the majority of the iron is present in the mineral (and non-pyritic) phase. The occurrence of titanomagnetite is consistent with palaeomagnetic studies over the last decade (e.g. Creer *et al.*, 1986, 1990). Sulphur decreases downcore from surface values around 0.6% at the surface to approximately 0.2% at 40 cm (Fig. 4d). In addition, there is a dramatic increase in S to around 1% at 3.5 cm depth coincident with an equally marked increase in the DOC (cf. Figs 4d and 8b). Moreover, pyrite was observed in the palynofacies slides at this level, and in unit II where there is also an increase in the solid phase S. These results suggest that an enhanced degradation due to sulphate reduction is taking place at present in the uppermost part of the Lac du Bouchet series in addition to the dominant methanogenetic type of diagenesis.

Study of the Organic Fraction

Rock eval pyrolysis

Determination of the total organic carbon (TOC), hydrogen index (HI: mg HC/g C-org) and oxygen index (OI: mg CO_2/g C-org) by rock eval pyrolysis can give an indication as to the maturity or degree of degradation of sediments. There is a strong positive correlation between the variations in TOC and HI in all three cores with the profiles in core S3 (Fig. 5a) being very similar to those in cores S1 and S4. TOC in core S3 decreases during units IA and IB from surface values of around 12% to approximately 6% at the base of unit IB (40–45 cm).
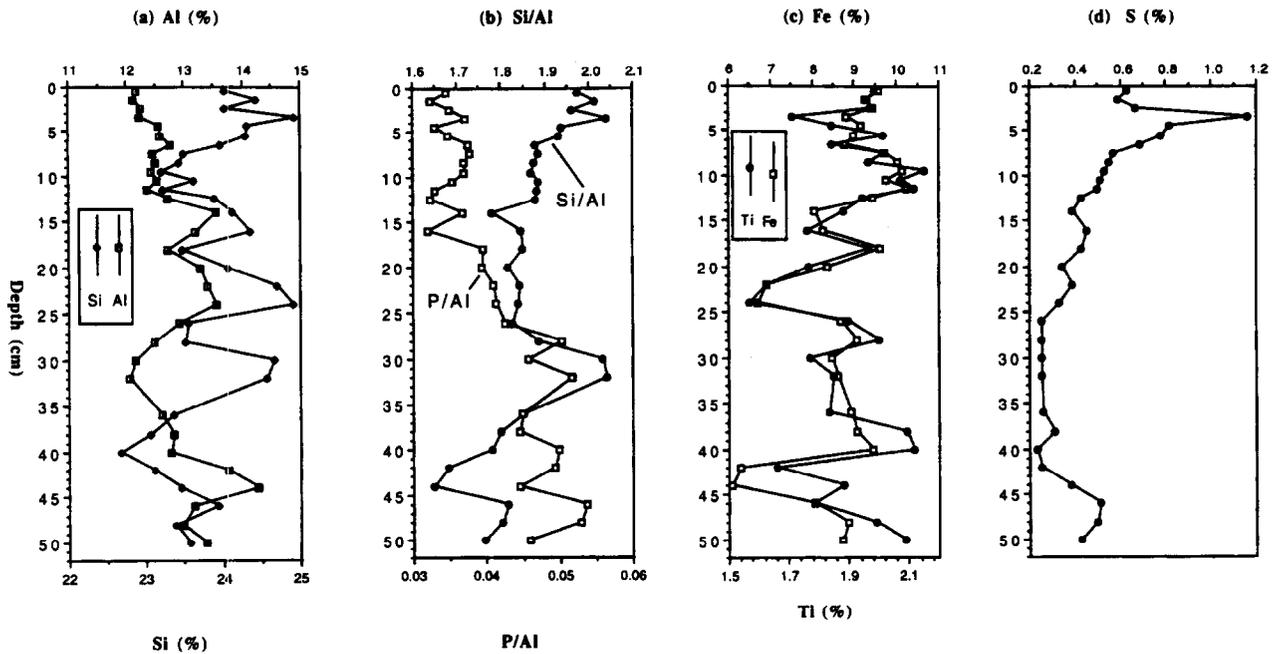
FIG. 4. Variations in mineral geochemistry (Al, Si, Si/Al, P/AL, Fe, Ti and S) with depth (cm) in bulk (total) sediment samples from core S1.
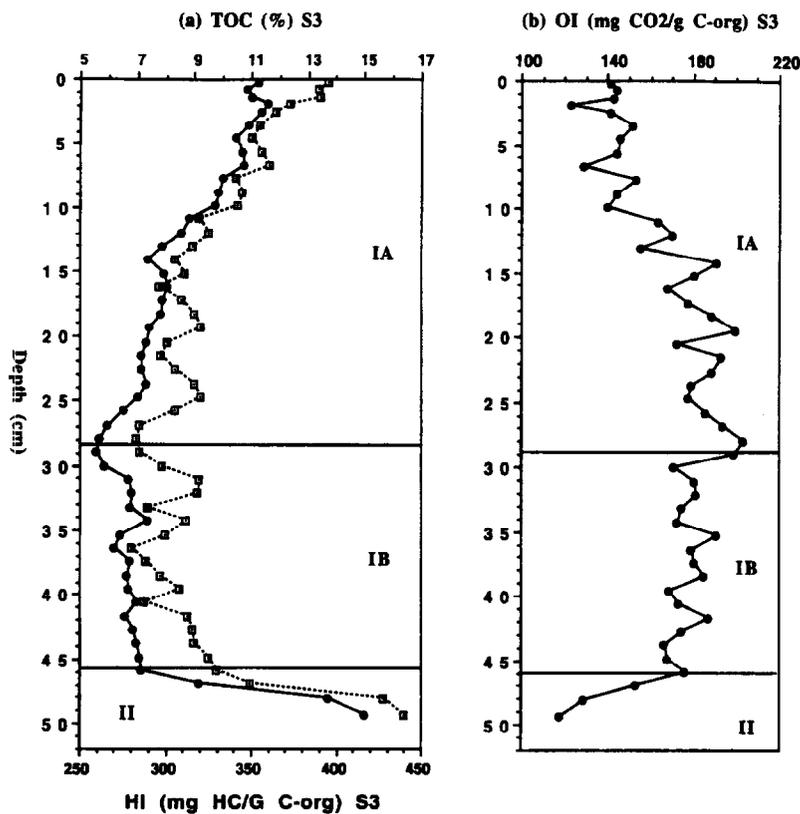

FIG. 5. Rock eval pyrolysis results of bulk sediment samples from core S3 vs depth (cm); (a) TOC — total organic carbon (solid circles) and HI — hydrogen index (mg HC/g TOC, hollow squares); (b) OI — oxygen index (mg CO₂/g TOC, solid circles).

Subsequently, in unit II, TOC increases rapidly to values close to those at the surface (Fig. 5a). Similarly, the HI varies between 250 and 450 mg HC/g C-org (Fig. 5a) and indicates an increase in the proportion of HC in the organic material in facies II and a decrease in HC, with depth, due to diagenesis in the upper 40 cm. The OI

profile in core S3 closely mirrors the HI curve, increasing downcore to around 45 cm depth before decreasing sharply in facies II (Fig. 5b). This distribution together with the parallel profiles of HI and TOC are consistent with the methanogenetic diagenesis resulting in a progressive oxidation of the organic matter.

Palynofacies

Several types of isolated organic material (palynofacies) have been recognised using transmitted light microscopy in Lac du Bouchet sediments (e.g. Sifeddine *et al.*, 1992, 1996). Of these, the important variations within the sediments are as follows: greyish amorphous organic material (G-AOM) is always dominant varying from between 46 and 60% of the total organic fraction (Fig. 6a). G-AOM is thought to be of phytoplanktonic origin due to its ultralaminar structure observed under STEM (Largeau *et al.*, 1991; Boussafir *et al.*, 1994); pedogenetic reddish amorphous organic material (R-AOM — observed in abundance in smear slides prepared from soil samples collected from the surrounding basin) displays increases during unit IA around 10–15 cm and in unit II below 40 cm (Fig. 6b); spores and pollen also increase in abundance in unit II and disappear between 10 and 15 cm where the R-AOM increases (Fig. 6c).

The coincidence of the disappearance of the spore/pollen and the increased input of the pedogenetic R-AOM around 10–15 cm suggests that precipitation increased and, consequently, promoted greater erosion of the surrounding basin at this time as there is also a decrease in the clay/silt ratio at this point (suggesting subtle changes in the terrigenous input at this time).

Chemistry of isolated organic matter

Hydrogen, oxygen, carbon and nitrogen were analysed in total organic matter (TOM) isolated from the sediment by acid (HCl-HF) treatment. Values are expressed as %TOM. All four elements decrease with depth during the first 25 cm below which values remain relatively constant (Fig. 7a, b). Carbon contents decrease from surface values of around 40% to approximately 20% in unit II at the base of the core, whilst oxygen, hydrogen and nitrogen vary similarly with values of 15–20%, 3–6% and 1.5–3% respectively (Fig. 7a, b). This distribution of the H and C (i.e. no increase in facies II) is in contrast with that observed in the HI results.

The H/O ratio (atomic) decreases in the topmost 25 cm consistent with the oxidation of the organic material. The increase in this ratio around 35 cm is thought to be the result of changes in the diagenetic regime resulting from increased biogenic productivity (diatoms) and consequent changes in the sedimentation rate. The C/N ratio (atomic), however, decreases from around 13.5 at the surface to approximately 9 at 25 cm before increasing again to values close to those at the surface in units IB and II (Fig. 7c). The marked increase at 3 cm corresponds to increased values of solid phase S and dissolved organic carbon, and is further proof of an enhanced degradation at this level. The increase in the C/N ratio in the first 3 cm is consistent with the results from Lac d'Aydat, where the sedimentation rate is known to be considerably greater than at Bouchet (Sarazin *et al.*, 1992). Below the peak at 3 cm however, the downcore decrease in the C/N ratio more closely resembles the profile observed in the marine environment (e.g. Müller, 1977), where sedimentation rates are generally considerably slower. Moreover,
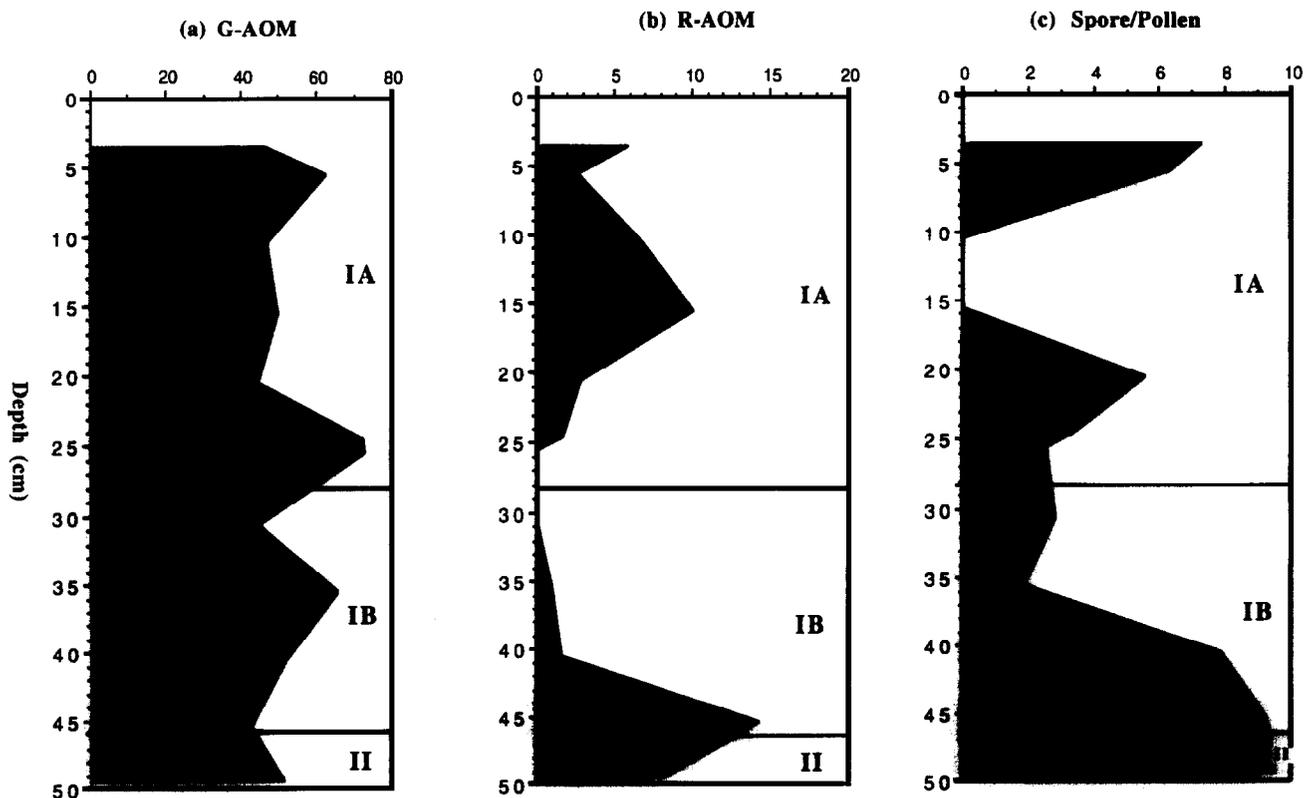

FIG. 6. Variations in the palynofacies with depth (cm) in core S3; (a) G-OAM — greyish amorphous organic material; (b) R-OAM — reddish amorphous organic material; (c) spores and pollen.
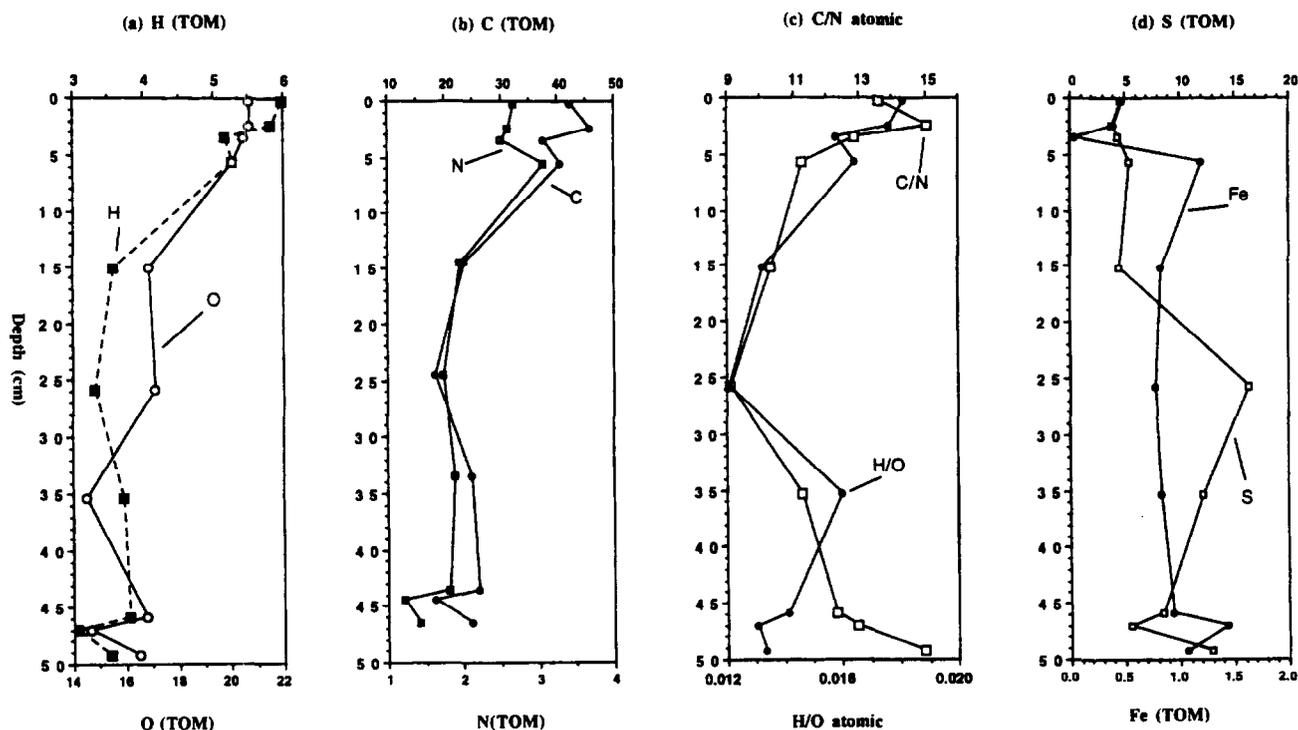
FIG. 7. Variations in the chemistry (C, N, H, O, S and Fe) of the total isolated organic matter (TOM) with depth in core S3.

the process of preferential degradation (loss) of C relative to N, resulting from the association of NH_4^+ with clay minerals has already been observed in surficial marine sediments (Lallier-Vergès and Alberic, 1990). Thus, perhaps the downcore decrease in the C/N ratio results from a combination of the very slow sedimentation rates observed at Bouchet and an association between the clay minerals and NH_4^+. Moreover, the increase in the C/N ratio in unit II is interpreted as reflecting a decrease in the rate of degradation resulting from a rapid increase in sedimentation rate.

As with bulk sediment chemistry, the profiles of sulphur (TOM) and iron (TOM) do not vary in parallel (Fig. 7d), confirming that iron occurs in several forms and not exclusively as iron sulphides. Indeed, the marked increase in S at 25 cm (Fig. 7d) is not accompanied by a similar increase in the Fe suggesting an increase in the input of S-bearing organic compounds at this level coincident with the increase in abundance of the diatoms (biogenic silica). It is perhaps the change in the diagenetic conditions at this time due to the increased productivity and consequent increased sedimentation rate that encouraged the preservation of these S-compounds.

Pore-Water Chemistry

To better understand the diagenetic framework in which the sediments are being deposited, parallel studies of pore-water chemistry (dissolved organic carbon, inorganic carbon and methane) were completed. The pore-waters were sampled using 'dialysers' which penetrate approximately one meter of sediment and allow equilibration (over a period of several weeks) of *in situ* pore-waters through permeable membranes every centimetre.

The dialyser is subsequently recovered and the 'pore-waters' from each cell are recovered.

Dissolved inorganic carbon (ΣCO_2) and dissolved organic carbon (DOC) both increase with depth in the dialyser (Fig. 8a, b): the former increased from around 1.5 mM at the surface to approximately 2.5 mM at the base (i.e. -90 cm), whilst DOC increases from approximately 0.2 mM at the surface to around 0.5 mM at the base. However, this relatively gradual increase in DOC is interrupted, at 10 cm, by a sharp increase to over 0.5 mM (Fig. 8a) which coincides with an increase in solid phase S, suggesting the presence of an accelerated, sulphate reduction type of sediment degradation. Similarly, methane increases gradually with depth from values close to 0 mM at the surface to around 1 mM at 90 cm depth (Fig. 8a). These profiles and relatively elevated concentrations highlight the dominance of methanogenetic degradation processes in these sediments.

INTERPRETATION AND CONCLUSIONS

A successful sampling strategy allowed good recovery of the sediment-water interface and accurate correlation between cores (Fig. 1).

The definition of the current dominance of methanogenetic degradation, as indicated by pore-water chemistry (elevated CH_4, DOC and ΣCO_2 concentrations), is confirmed by sediment chemistry. This degradation is considerably less intense than in Lac d'Aydat (Sarazin *et al.*, 1992) which is almost certainly due to the oligotrophic nature of Bouchet, the resistant quality of the organic matter and in particular, the very slow sedimentation rates throughout the upper part of the core (< 40 cm).
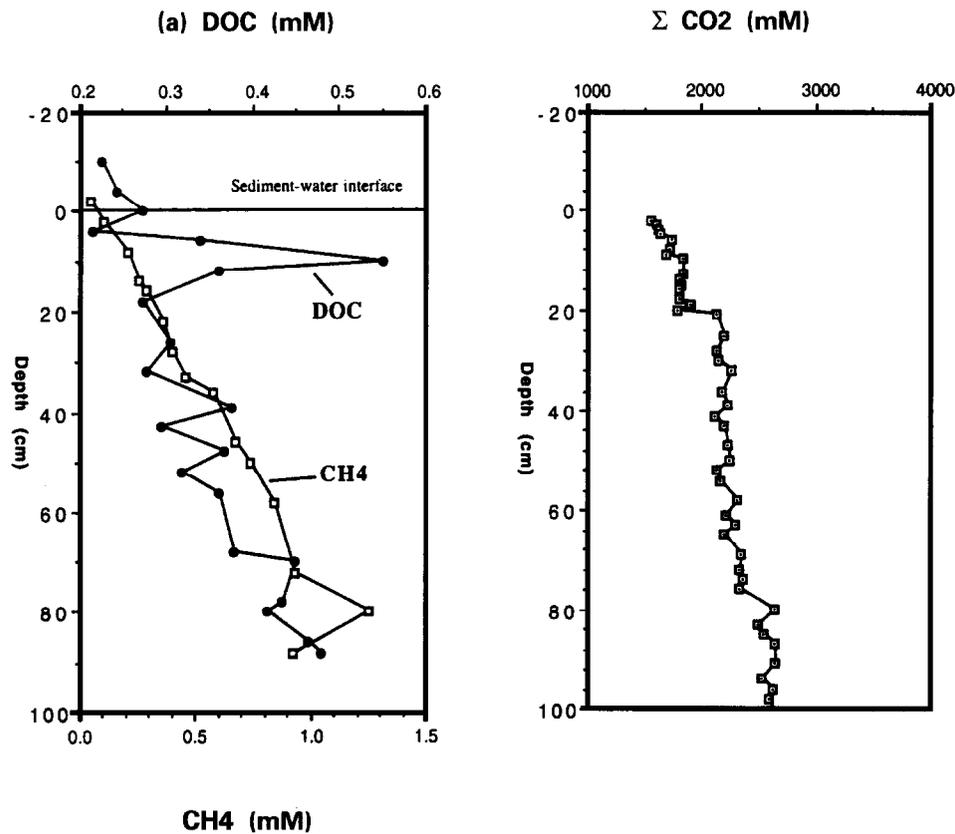
FIG. 8. Variations in pore water chemistry with depth (cm) in the 'dyalyser': (a) dissolved organic carbon (DOC) and methane (CH_4) profiles; (b) the dissolved inorganic carbon ($\Sigma\ CO_2$) curve.

Three distinctive facies are observed in the upper 50 cm of sediment, all of which is of Sub-Atlantic age (< 2500 BP). In facies IA (< 25 cm), the sediment composition is dominated by the methanogenetic degradation which, at the surface, occurs in parallel with an enhanced sulphate reduction type of diagenesis. Moreover, it is in this region that the majority of the compaction takes places and where diagenesis of the mineral phases is highlighted by the dissolution of the biogenic silica and by slight changes in the clay mineral proportions, especially visible in the uppermost 15 cm. Facies IB (25–40 cm), however, is characterised by an increased biological productivity (siliceous) probably induced by increased runoff of nutrient elements from the surrounding basin due to anthropogenic deforestation (as observed by Pailles, 1989), especially in light of the oligotrophic nature of the lake waters. In facies II, at the base of the cores (below 40 cm), the sedimentation rate is thought to be greater resulting in the organic matter containing relatively elevated HIs, low OIs and higher TOC content. These changes in organic matter composition are the result of the installation of the present climatic conditions at the beginning of the Sub-Atlantic.

Thus, it appears that palaeoclimate variations and even anthropogenic effects such as deforestation dramatically affect the rate of sediment diagenesis, and in particular this can be because of the change in the bulk accumulation rates. The increased sedimentation rate recorded at the beginning of the Sub-Atlantic (facies II), interpreted as the result of greater continental runoff by Sifeddine *et*

al. (this volume), is associated with changes in the composition of the organic matter and better preservation of this material. This result is interpreted as a reduction in the rate of diagenesis due to both the resistant nature of organic matter and the decreased residence time in contact with the oxic waters. Similarly, in facies IB (around 1600 BP), an anthropogenic deforestation induced greater nutrient element run-off from the surrounding basin and enhanced productivity in the oligotrophic lake waters. These findings show that the bulk sedimentation rate and the nature of organic matter (degree of pre-depositional degradation) play a dominant role in the final determination of the sediment composition.

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