

Sedimentological and geochemical investigation of an oligotrophic environment on the Cape Verde abyssal plain, NE Atlantic

Early diagenesis
Oligotrophy
Abyssal environment
Fe, Mn
Rare earth elements
Diagenèse précoce
Oligotrophie
Environnement abyssal
Fe, Mn
Terres rares

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ABSTRACT

Near surface sediment was sampled in a 33 cm long box-core recovered from 4973 m water depth in the Cape Verde abyssal plain (CV2 site) of the NE Atlantic Ocean, an area characterized by low biological productivity. The measurements of ²³⁰Th and ²³¹Pa excess activities combined with micropaleontological observations has yielded an average rate of sediment accumulation of the order of 0.6 cm 10⁻³ yr for the whole section and 1 cm 10⁻³ yr for the Holocene. ²¹⁰Pb excess activities and estimates of coefficients of recorded bioturbation indicate a relatively low intensity of burrowing activity in the sediments which may contribute to the low degree of dissolution during post-glacial times. Solid phase contents of Fe, Mn and rare earth elements (REE), as well as the extractible fractions of Fe and Mn, have been analysed in bulk sediment subsamples and the results used to estimate authigenic fluxes. The low authigenic fluxes indicated are the result of very low diagenetic mobility of Fe and Mn in a well oxygenated sediment core with little organic carbon. Thus, solid phase geochemistry can be used as a marker to retrace variations in sedimentary regimes since the last glacial maximum: *i.e.* influence of aeolian detrital input, sedimentation breaks (hiatuses) and dissolution cycles due to changes in corrosive bottom water circulation. In the case of deep water sites such as CV2, oligotrophy would certainly appear to be of primary importance in the control of physical and chemical variations with depth in slowly accumulated sediments.

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RÉSUMÉ

Étude sédimentologique et géochimique d'un milieu abyssal oligotrophe : site CV2, Atlantique NE

Une carotte a été prélevée par 4973 m de profondeur dans la plaine abyssale du Cap Vert, en Atlantique Nord-Est, dans une zone de faible productivité. Les excès de ²³⁰Th et ²³¹Pa et l'analyse micropaléontologique révèlent un taux de sédimentation faible : 1 cm 10⁻³ ans pour l'Holocène. L'excès de ²¹⁰Pb et la mesure d'un coefficient de bioturbation enregistrée témoignent d'une activité biologique relativement faible : cela contribue à la bonne préservation des carbonates. Le fer, le manganèse et les terres rares mesurés dans le sédiment total, ainsi que Fe et Mn extractibles, permettent de discuter de la mobilité, très réduite, de ces éléments dans une colonne sédimentaire bien oxygénée et très pauvre en matière organique. Ils peuvent donc être utilisés pour retracer les événements qui ont marqué l'histoire de ce milieu de sédimentation depuis le dernier maximum glaciaire : variations des apports éoliens, hiatus sédimentaire, changements dans l'hydrographie abyssale. En définitive, l'oligotrophie apparaît comme un facteur de première importance, déterminant l'évolution physique et chimique des sédiments déposés en milieu abyssal.

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INTRODUCTION

Numerous studies have concentrated on the breakdown of organic matter and the associated remobilization of certain solid phase constituents in anoxic (*e.g.* Aller, 1980*a* and *b*) and suboxic (*e.g.* Froelich *et al.*, 1979) deep water sediments. However, rather less work has been carried out on abyssal sediments, where pore waters are in communication with well oxygenated bottom waters and where the very low inputs of organic material and slow accumulation rates inhibit the formation of anoxic conditions.

The area defined by the CV2 site (Seabed programme of CEA-CNEXO) is situated on the Cape Verde abyssal plain and extends between latitudes 19°10'–19°28'N and longitudes 29°34'–29°57'W. This area (*see* Fig. 1) is characterized by a hilly topography and succession of NNE-SSW oriented scarps, with water depths comprised ranging 4 730 and 5 100 m.

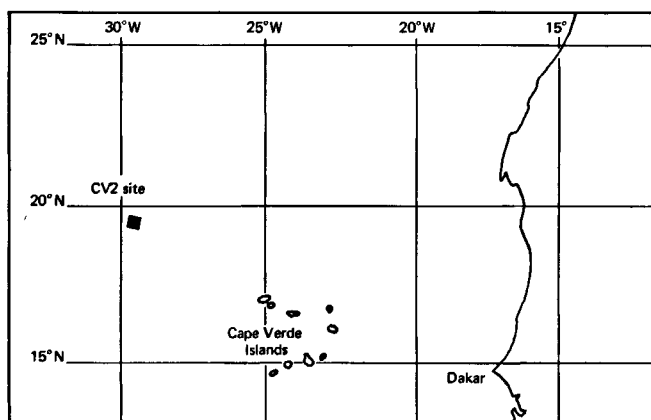


Figure 1

The CV2 site in the North-East Atlantic Ocean.

Localisation du site CV2 en Atlantique Nord-Est.

During cruises Seabed 1 and Seabed 2 of the N/O "Jean Charcot" in October and November 1980, many geophysical, geological, hydrological and biological data were collected which contribute to a better understanding of oceanographic properties in this part of the eastern basin of the North Atlantic. These data have been compiled and summarized by Auffret *et al.* (1982*a*; 1982*b*). The main characteristics include the observation of 3.5 cm s^{-1} currents above the seabed, the scarcity of fauna collected in all size classes compared with other higher productivity areas of the North Atlantic (Sibuet, 1982) and the generally pelagic conditions of sedimentation. In addition, recent measurements of dissolved oxygen (Sørensen, Wilson, 1984) and nutrient salts (Boust, in preparation) in sediment pore waters show that the available oxidizing species such as O_2 , NO_3 , NO_2 , are only partly consumed even at depth of 10 m beneath the sediment/water interface.

The core described in this study (KG40) was collected at 19°13'75N and 29°45'94W at 4973 m water depth; the total sediment section recovered was 33 cm long. Solid phase analyses (natural radionuclides, Fe, Mn, and REE) were obtained from core sediment sub-sam-

ples. Geochemical variations with depth are also interpreted in the light of changing sedimentation in the studied area from uppermost Pleistocene to Holocene times. The aim of these investigations is to evaluate the influence of oligotrophic conditions on the postdepositional geochemical behaviour of the studied elements.

APPARATUS AND ANALYTICAL METHODS

Sediment cores were obtained by use of an USNEL-type box-corer of large surface sampling area (0.25 m^2) as described by Hessler and Jumars (1974). A side plate of this box-corer is removable to allow direct observation of the sediment section.

A sub-core was obtained by forcing a 5 cm diameter PVC tube down into the contents of the box, thus providing sub-samples for subsequent geochemical solid phase analyses. The sub-core was also used for shore-based photographic and descriptive studies (sedimentological structures, burrow textures and colour descriptions; optical mineralogy and other observations on smear slides).

Sediment sub-samples were taken as 1 cm thick slices at selected depths in the core. For each depth interval, carbonate contents were measured by volumetric calcimetry and organic carbon contents were analysed on an automatic "LECO" W.R.12 machine. The $>63 \mu\text{m}$ grain size fraction was estimated by sieving the sediments under flowing water. The activities of natural γ -emitting radio-nuclides were measured on an H.P. Ge detector, using methods described by Yokoyama and Nguyen (1980). Two processes account for the ^{230}Th and ^{231}Pa activities that are measured in near-surface sediment samples. Firstly, decay of the parent isotopes ^{238}U and ^{235}U dissolved in the water column gives rise to the insoluble daughter products ^{230}Th and ^{231}Pa which are then incorporated into the sediment section. The excess activities of ^{230}Th and ^{231}Pa are defined as the difference between total measured activity and the theoretical activity in equilibrium with the naturally occurring parents ^{238}U and ^{235}U . Such excess activities are seen to decrease as a function of time, with half-lives of $7.52 \times 10^4 \text{ yr}$ and $3.25 \times 10^4 \text{ yr}$ respectively. Thus, this method allows the estimation of sediment accumulation rates in the oceanic environment.

^{210}Pb excess activities were also measured in order to estimate the depth to which sediment has been mixed over the last 100 years (Aller, 1977). The decay of ^{226}Ra contained in the sediment, and of atmospheric ^{222}Rn , both give rise to ^{210}Pb , the excess activity having a half life of 22 years.

Solid phase iron and manganese were analysed by atomic absorption spectrophotometry, after HF acid digestion of sample aliquots. Amorphous or cryptocrystalline oxy-hydroxide coatings rich in Mn and Fe were selectively extracted with 0.3N HCl at 95°C for 30 min. (Malo, 1977).

REE analyses were obtained by neutron activation of 100 mg samples aliquots (Osiris facility at Saclay; neutron flux of $3 \times 10^{13} \text{ n cm}^{-2} \text{ s}^{-1}$ for 15 min.). Measurements were performed by γ -spectrometry (Philipot, 1970).

RESULTS AND DISCUSSION

Core description; estimations of sediment accumulation rate and intensity of bioturbation

The decrease in ^{230}Th and ^{231}Pa excess activities with depth (see Fig. 2) yields a log-linear regression with very low correlation coefficient ($r^2=0.5$). Despite the scattering of analytical points, both ^{230}Th excess and ^{231}Pa excess methods indicate comparable accumulation rates of $0.5 \text{ cm } 10^{-3} \text{ yr}$ and $0.7 \text{ cm } 10^{-3} \text{ yr}$ respectively. Sediment accumulation rates have also been determined on a Kullenberg core recovered from the same site (KS06), and the ^{230}Th excess method applied to the topmost 2 m yields an average accumulation rate of $0.36 \text{ cm } 10^{-3} \text{ yr}$ (Colley, unpublished data). Nannofossil biostratigraphy applied to the same core yields an average accumulation rate of $0.3 \text{ cm } 10^{-3} \text{ yr}$ over the past 460 000 years, which breaks down into $0.26 \text{ cm } 10^{-3} \text{ yr}$ for NN21 and $0.32 \text{ cm } 10^{-3} \text{ yr}$ for NN20 (Muller, pers. comm. and Weaver, unpublished data).

The study of planktonic foraminifera in the $> 150 \mu\text{m}$ fraction of the KG40 core sub-samples, carried out by C. Pujol, has led to the identification of the Pleistocene-Holocene boundary at about 11 cm, where carbonate contents reach their maximum value (Fig. 3A-3B). The topmost 11 cm of the core are characterized by the abundance of the species *G. menardii* and sinistrally coiled forms of *G. truncatulinoides*, which are indicators of warmer water conditions. Beneath 11 cm, the cold water tropical form *G. inflata* increases in abundance until the minimum carbonate content at around 18 cm which could represent the last glacial maximum (Würm glacial stage 3 at 18 000 B.P.). Carbonate dissolution would be expected to reach a maximum during the last glacial stage, so the relative preservation of resistant forms such as *G. eggeri* beneath 18 cm would support the hypothesis that the Pleistocene-Holocene boundary occurs somewhere between 18 cm-11 cm. This would suggest that sedimentation rates during the past 18 000 years have been rather higher (*i.e.* $1 \text{ cm } 10^{-3} \text{ yr}$) than the average accumulation rate calculated for the whole core ($0.6 \pm 0.1 \text{ cm } 10^{-3} \text{ yr}$) and, in any case, much higher than the rate of $0.26 \text{ cm } 10^{-3} \text{ yr}$ indicated for NN21 in KS06. The estimate of $1 \text{ cm } 10^{-3} \text{ yr}$ for pelagic sedimentation during post-glacial times is closely in agreement with results obtained from near-surface sediments of the Madeira abyssal plain (Weaver, Kuijpers, 1983).

The sediment core is composed of biogenous marly oozes that can be divided into four lithological units according to the facies criteria of Auffret and Pastouret (1978) and the classification of bioturbation structures compiled by Berger *et al.* (1979; see Fig. 3).

Unit I (0-6 cm): Sedimentation appears to be mainly pelagic with limited influence from continental detritus. Carbonate contents increase from 60-70% and organic matter contents decrease from 0.24-0.11% with increasing depth. Foram tests are fragmented and show traces of active dissolution especially near the sediment/water interface. This unit is particularly homoge-

neous, with a loose consistency typical of the "mixed layer" described by Berger *et al.* (1979).

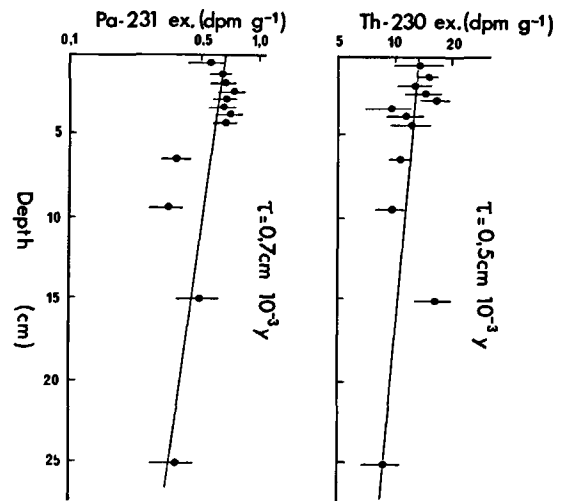


Figure 2
Decrease in ^{230}Th and ^{231}Pa excess activities with depth in the KG40 core.

Droites de décroissance des activités du ^{230}Th en excès et du ^{231}Pa en excès en fonction de la profondeur dans la carotte KG40.

Unit II (6-12 cm): Sedimentation is pelagic with the biogenous fraction representing 70-80% of the whole sediment. Organic carbon contents reach a low and stable value of 0-10% which is maintained to the base of the core. There is no evidence for dissolution of the foram tests and several burrows (planolites) are observed in a homogeneous matrix. This unit corresponds to a transitional mixed layer.

Unit III (12-19 cm): Carbonate contents decrease in this unit, reaching a minimum of 50% at 18 cm (last glacial maximum). The $> 63 \mu\text{m}$ fraction is made up mainly of fragmented foram tests. There is generally mottled appearance due to the presence of numerous burrow structures. This unit shows the best preservation of bioturbation and corresponds to a transition between units II and IV.

Unit IV (19-33 cm): Carbonate contents remain between 55-60% dropping to a minimum of 40% at the base of the core where coarse ($> 63 \mu\text{m}$) material accounts for only 10% of the bulk sediment. Foram debris shows an advanced stage of carbonate dissolution. There is some mottling and an absence of any sedimentary structures-features typical of a buried "historical" layer.

Two factors must be taken into the account to explain the preservation of carbonate material at this abyssal site.

Firstly, the bathymetry of the Eastern basin of the North Atlantic and its adjoining ridges, flanks and plateaux is such as to prevent any important breakthrough of cold, CO_2 rich corrosive bottom waters during interglacial periods. The only possible passage for Antarctic bottom waters across the Mid-Atlantic ridge at equatorial latitudes is afforded by passways such as the Vema (Vangriesheim, 1980), Chain and Romanche (Metcalf *et al.*, 1964; Worthington, Wright, 1970) fracture zones. An increase in dissolved oxygen

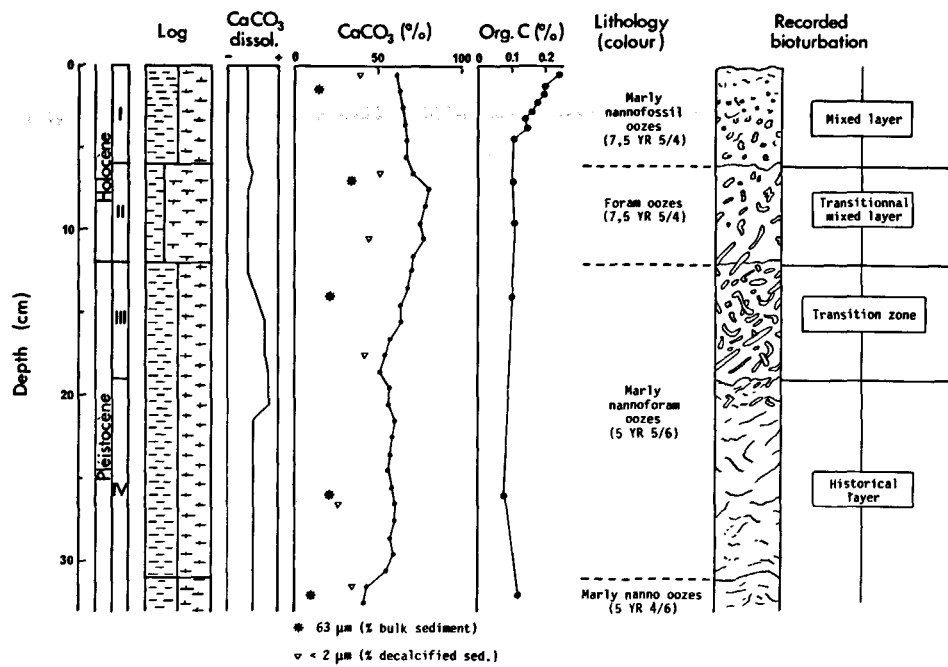
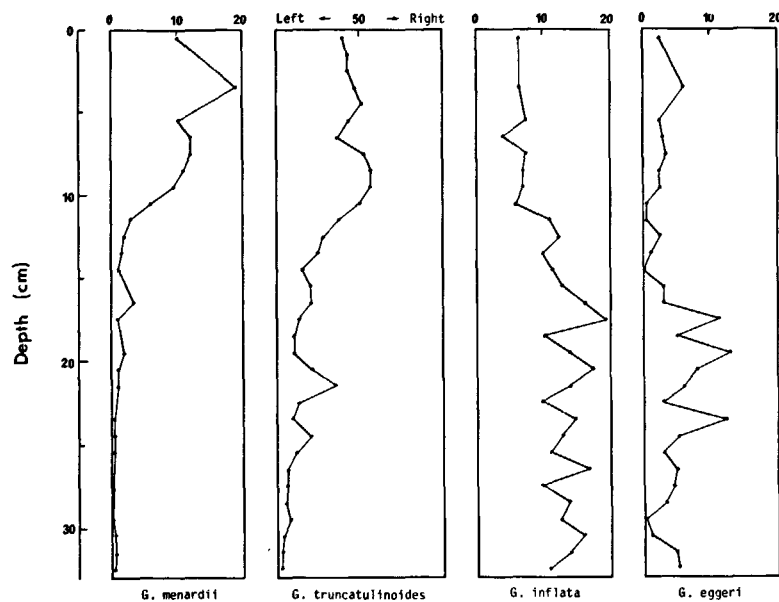


Figure 3

A) Lithological facies (after Auffret, Pastouret, 1978) and bioturbation structures (after Berger et al., 1979) in the KG40 core.

Faciès lithologiques (selon Auffret, Pastouret, 1978) et figures de bioturbation (selon Berger et al., 1979) dans la carotte KG40.



B) Vertical distribution of some planktonic foraminifera (> 150 µm fraction).

Distribution verticale de quelques foraminifères planctoniques (fraction supérieure à 150 µm).

in bottom waters from profiles taken at the CV2 site would appear to indicate the presence of Antarctic bottom waters (Vangriesheim, Madelain, 1982), but the influence of such water masses must be rather limited judging by the deep level of the lysocline in the Eastern basins of the North Atlantic compared with the Western basins (i.e. 4500 m on the Sierra Leone Rise; Bremer, Lohmann, 1982; 5000-5200 m on the Angola and Cape Verde abyssal plains; Berger, 1968).

Secondly, the low intensity of burrowing activity is probably responsible for the good preservation of burrow structures and would explain the relative lack of carbonate dissolution of buried foram tests. Vertical mixing throughout the core is probably rather limited because the carbonate content profile shows well-defined maxima and minima with a fine structure reflecting fluctuations in both dissolution and biogenous/terrigenous inputs (Fig. 3).

The intensity of bioturbation B has been evaluated in this study by use of the equation:

$$B \text{ (cm } 10^{-3} \text{ yr)} = \tau \times \frac{\text{Surface area of burrows}}{\text{Total surface area of core}} \times 100,$$

where τ is sediment accumulation rate (cm 10^{-3} yr). This assumes that the recorded bioturbation is homogeneous and has proceeded at a constant rate; in this case $B = 9 \text{ cm } 10^{-3} \text{ yr}$, a value which is much less than other estimates of burrowing activity obtained from abyssal sites (e.g. $B = 30 \text{ cm } 10^{-3} \text{ yr}$ for the Meriadzek plateau; Mauviel, 1982).

Measurements of ^{210}Pb excess activity have provided an estimate of the depth to which surface mixing processes have penetrated. Since there is no detectable ^{210}Pb excess except in the 0-1 cm interval, it can be concluded that mixing processes are very superficial and only concern the topmost centimetre over a period of 100 years (approximately $5 \times$ half-life of ^{210}Pb excess). This mixing rate ($\leq 1 \text{ cm } 10^{-2} \text{ yr}$) is of the same order of magnitude as the intensity of bioturba-

tion B derived from burrow measurements; such a low intensity of surface layer mixing is in agreement with the remarkable scarcity of fauna (Sibuet, 1982), the low supply of organic carbon from the water column (Raymont, 1980) and the low primary productivity. Total flux of deposited organic carbon is estimated to be $2 \text{ mg cm}^{-2} 10^{-3} \text{ yr}$ (Khrpounoff, 1982), 5 to 10 times lower than in Demerara Abyssal plain or on Meriadzek Plateau (Mauviel, 1982).

In the short term (100 years), shallow and weak mixing processes imply that biogenic carbonate material is progressively buried and thus cut off from communication with corrosive bottom waters at the sediment/seawater interface. Furthermore, the scarcity of benthic infauna (*e.g.* holothuroids and echinoids; Hammond, 1981) which might facilitate the fragmentation of carbonate tests and assist dissolution, is an observation that is in conformity with the lack of dissolution in Unit II (6-12 cm).

The mineralogy of the non-carbonate fraction has been studied by optical microscopy on smear slides made up from decalcified residues. There appears to be little significant variation of mineralogy with depth in the core. Etched grains, such as volcanic glass shards and iron-rich oxide-hydroxide alteration products, constitute only a small proportion of the detrital component. Quartz grains (10 μm maximum size) are also observed, some showing an angular form, along with plagioclase (examples of albite twinning) and amphibole. X-ray diffraction studies of cores from the CV2 site show a remarkable invariability of the clay mineral suite throughout the upper Pliocene and Pleistocene (Maillet, 1982; Carpenter, unpublished data).

The $<2 \mu\text{m}$ fraction is dominated by illite, smectite and kaolinite with small quantities of chlorite, palygorskite and dolomite.

Scandium contents at five different levels in the core KG40 have been measured by neutron activation methods. These results, expressed on a carbonate free basis (*see* Table 1), are comparable with average shale abundances ($13 \mu\text{g g}^{-1}$; Wedepohl, 1971) or average crustal rocks ($22 \mu\text{g g}^{-1}$; Taylor, 1964). The highest carbonate free Sc content ($30 \mu\text{g g}^{-1}$) is found at 7 cm depth; this extreme value could be explained by a relative enrichment in fine particles which contain less quartz than average Saharan dusts (*i.e.* at quartz contents of 15-20%, Saharan dust contains: $13 \mu\text{g g}^{-1}$ Sc, Glacuum, 1978; $17 \mu\text{g g}^{-1}$ Sc, Rahn, 1976) or even average shale (quartz content: 20%; Wede-

pohl, 1971). At the 7 cm interval, the $<2 \mu\text{m}$ fraction accounts for 51% of the carbonate-free sediment—a maximum for the core. It is possible to estimate an accumulation rate for non carbonate detrital material in the Holocene section of core KG40, assuming an average carbonate content of 70% for Unit II, where post-depositional dissolution is minimal. The value obtained is $0.3 \text{ cm } 10^{-3} \text{ yr}$, a detrital accumulation rate similar to model derived estimates proposed by Jaenicke (1977) on the basis of atmospheric circulation and transport of Saharan dust. A minimum value of $16 \mu\text{g g}^{-1}$ Sc is recorded for the 32 cm interval, where carbonate dissolution appears to have been very important ($\text{CaCO}_3=43\%$). However, the $<2 \mu\text{m}$ fraction at this level accounts for over 40% of the non carbonate material, thus suggesting that the presence of quartz-rich, fine particles might explain the strong dilution of Sc contents compared with the 7 cm interval.

The minor component of glass shards and altered ferromagnesian minerals could well reflect the influence of local volcanic activity, whereas the greater part of the detrital fraction is derived from Saharan dust that may become more quartz-rich during glacial epochs.

Fe and Mn geochemistry

Distribution of Fe and Mn between carbonate, lithogenous and extractible components

Contents of Fe and Mn in bulk sediment sub-samples vary between 1-2.5% and 0.05-0.12% respectively (Fig. 4A, 4C), this variation being inversely proportional to carbonate content since these elements are

Table 1
Scandium contents in the bulk sediment (a) and in the non-carbonaceous fraction (b).
Teneurs en scandium dans le sédiment total (a) et dans la fraction non-carbonatée (b).

Profondeur (cm)	CaCO_3 (%)	Sc (a) ($\mu\text{g g}^{-1}$)	Sc (b) ($\mu\text{g g}^{-1}$)
7	71	8,7	30
11	78	4,8	22
18	54	10,0	22
27	60	7,6	19
32	43	9,3	16

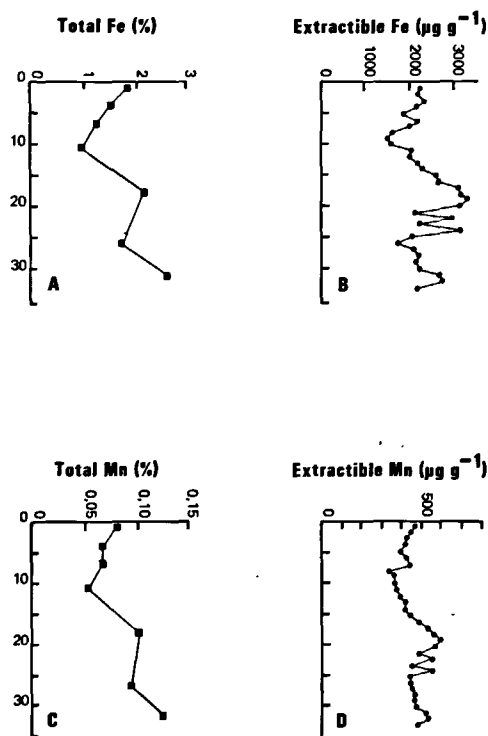


Figure 4

Fe and Mn profiles versus depth; A: Total Fe; B: extractible Fe; C: Total Mn; D: extractible Mn.

Profils de Fe et Mn; A : Fe total; B : Fe extractible; C : Mn total; D : Mn extractible.

mostly contained within the lithogenous component. Linear regressions of Fe against CaCO_3 ($r^2=0.99$) and Mn against CaCO_3 ($r^2=0.95$) yield non-zero intercepts at $\text{CaCO}_3=0\%$ which correspond to the end member compositions of the non carbonate fraction (lithogenous component) viz: $4.7 \pm 0.2\%$ Fe and $0.22 \pm 0.02\%$ Mn. These values, when compared with

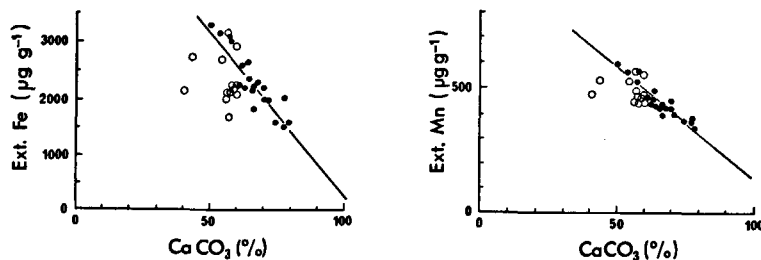


Figure 5

The relationship between extractable Fe or Mn and carbonate content; ● : 0-20 cm, ○ : 21-33 cm. Relations Fe extractible-carbonates et Mn extractible-carbonates.

average shale containing 4.8% Fe and 0.085% Mn (Wedepohl, 1971) indicate no detectable excess Fe and an excess of $1350 \mu\text{g g}^{-1}$ Mn.

Chemical leaching of these samples produced $1500\text{--}3300 \mu\text{g g}^{-1}$ Fe and $350\text{--}600 \mu\text{g g}^{-1}$ Mn (extractible component; see Fig. 4B, 4D). The contents of extractible Fe and Mn are inversely proportional to carbonate content, but the correlation is somewhat better for the first 20 cm ($r^2=0.8\text{--}0.9$ respectively) than for the whole group of samples ($r^2=0.3\text{--}0.6$ respectively; see Fig. 5). From 0-20 cm, the well defined correlations of extractible Fe and Mn against CaCO_3 lead to an estimate of the compositions of extractible components in pure carbonate and lithogenous phases. End-member CaCO_3 contains $330 \pm 50 \mu\text{g g}^{-1}$ extractible Fe and $130 \pm 20 \mu\text{g g}^{-1}$ extractible Mn; values which agree very well with results obtained by selective leaching of carbonates in other cores of the CV2 site (i.e. $300\text{--}600 \mu\text{g g}^{-1}$ extractible Fe and $200\text{--}400 \mu\text{g g}^{-1}$ extractible Mn; Boust, in prep.). At $\text{CaCO}_3=0$, the pure lithogenous component contains $6000 \pm 500 \mu\text{g g}^{-1}$ extractible Fe and $1000 \pm 100 \mu\text{g g}^{-1}$ Mn.

An important hiatus is observed near 20 cm in the profiles of extractible Fe and Mn (Fig. 4B and 4D), but this discontinuity appears to have no relation with variations in carbonate content. Beneath 20 cm, contents of extractible Fe and Mn are much less for any given CaCO_3 content than values observed in layers above the hiatus. The presence of numerous

burrows in Unit III would appear to explain the variability and interdigitation of extractible Fe and Mn contents, especially between 19 and 24 cm where material from Unit III has been mixed into Unit IV. These observations suggest that there has been an important change in sedimentary regime after the deposition of the "historical" layer (Unit IV).

Calculation of authigenic fluxes of Fe and Mn

The chemical leaching methods used in this study are not sufficiently selective to permit the extraction of a pure authigenic end-member which corresponds to the composition of amorphous oxy-hydroxide coatings. More selective extraction methods (Förstner, Stoffers, 1981) have permitted the separation of the authigenic component from other fractions of the sediment and suggest that 25% of the extractible Fe and 85% of the extractible Mn are contained within authigenic phases (Boust *et al.*, 1984). This would indicate that, in the present core, only $1500 \mu\text{g g}^{-1}$ Fe and $850 \mu\text{g g}^{-1}$ Mn in the non-carbonate phase are of authigenic origin. Assuming an average CaCO_3 content of 67% for the 0-20 cm interval, a density of 1 g cm^{-3} and an accumulation rate of $1 \text{ cm } 10^{-3} \text{ yr}$, authigenic fluxes of 4×10^{-10} and $2 \times 10^{-10} \mu\text{mole cm}^{-2} \text{ s}^{-1}$ can be calculated from the estimated excesses of $700 \mu\text{g cm}^{-3}$ Fe and $400 \mu\text{g cm}^{-3}$ Mn respectively.

These fluxes can be compared with diffusive fluxes that have been calculated from pore water data in suboxic sediments (Froelich *et al.*, 1979). Using a simple diffusion model, the diffusive flux, F_E , of an element E is directly related to the product of the diffusion coefficient, D_E , and the pore water concentration gradient, $d[E]/dz$, viz:

$$F_E = -D_E \times \frac{d[E]}{dz}$$

Table 2

Diffusive and authigenic fluxes of Fe and Mn in some Atlantic abyssal sediments; theoretical and field data used for the estimates of diffusive fluxes; 1) Froelich *et al.*, 1979; 2) Carpenter *et al.*, 1983; 3) Thomson *et al.*, 1984, using constant flux method; 4) KG40 core, deduced from leaching experiments; 5) Berner, 1980; 6) Bender, 1971; 7) estimated from pore water profiles.

Flux authigènes et flux diffusifs de Fe et Mn dans quelques sédiments atlantiques abyssaux; données utilisées pour les calculs de flux diffusifs.

	Diffusive fluxes $\mu\text{M cm}^{-2} \text{ s}^{-1}$		Authigenic fluxes $\mu\text{M cm}^{-2} \text{ s}^{-1}$	
	Romanche ⁽¹⁾ Chain Fracture Zones	Nares ⁽²⁾ Abyssal Plain	Nares ⁽³⁾ Abyssal Plain	Cape Verde ⁽⁴⁾ Abyssal Plain
Fe	-6×10^{-9}		1.5×10^{-9}	0.4×10^{-9}
Mn	-3×10^{-9}	-2.1×10^{-9}	0.8×10^{-9}	0.2×10^{-9}
$D_{\text{Fe}} (\text{cm}^2 \text{ s}^{-1})$	$3 \times 10^{-6(5)}$			
$D_{\text{Mn}} (\text{cm}^2 \text{ s}^{-1})$	$1.5 \times 10^{-6(6)}$	1.3×10^{-6}		
$d[\text{Fe}^{2+}]/dz (\text{M cm}^{-4})$	$2 \times 10^{-9(7)}$			
$d[\text{Mn}^{2+}]/dz (\text{M cm}^{-4})$	$2 \times 10^{-9(7)}$	1.6×10^{-9}		

Table 3

Rare-earth elements and scandium contents in a hypothetical <math> <4 \mu\text{m}</math> non-carbonaceous fraction (see text for calculation method) and in shales: 1) Piper (1974); 2) Wedepohl (1971); all values in $\mu\text{g g}^{-1}</math>. Teneurs en terres rares et en scandium dans une hypothétique fraction non-carbonatée inférieure à $4 \mu\text{m}</math> (cf. texte pour la méthode de calcul) et dans les shales; teneurs en $\mu\text{g g}^{-1}</math>.$$$

	La	Ce	Nd	Eu	Tb	Yb	Sc
Hypothetical <math> <4 \mu\text{m}</math> non-carbonaceous fraction	150 ± 40	250 ± 100	160 ± 60	5 ± 1	4 ± 1	$11,5 \pm 0,5$	40 ± 10
Average shale	$41^{(1)}$	$83^{(1)}$	$38^{(1)}$	$1,6^{(1)}$	$1,23^{(1)}$	$3,53^{(1)}$	$13^{(2)}$

Taking the concentration gradients and diffusion coefficients of Fe^{2+} and Mn^{2+} quoted in Table 2, diffusive fluxes can be calculated which are an order of magnitude greater than the authigenic fluxes for the CV2 site. Furthermore, the constant flux method applied to surface oxic sediments of the Nares abyssal plain, yields authigenic fluxes (Thomson *et al.*, 1984) which are four times greater than CV2 fluxes calculated from a chemical speciation model. These relatively low authigenic fluxes for the CV2 site are very probably related to the very low productivity of the water column compared to other pelagic sites. The diffusive fluxes are only relevant for suboxic sediments where Fe and Mn are mobilized into the pore waters near the sediment/water interface, so it is unlikely that redox controlled diffusive processes have been important at the CV2 site since the deposition of the "historical" layer (Unit IV). This conclusion is supported by the recently observed oxic character of pore waters to at least 2 m (Sørensen, Wilson, 1984) and the low concentrations of dissolved Fe and Mn in pore waters extracted at all depth down to 15 m ($<0.45 \mu\text{M Fe}$, $<0.9 \mu\text{M Mn}$). There is also good experimental evidence for the highly oxidized character of the sediment solids at the CV2 site— Co^{2+} in solution (as ^{60}Co) is fixed onto these sediments by autocatalytic adsorption thus demonstrating Co^{3+} species formation (Guegueniat *et al.*, in prep.) and chemical determinations of the Fe redox state show 95% of total Fe as Fe^{3+} (Carpenter, pers. comm.).

It might be possible to explain the short decrease of

extractable Fe and Mn contents below 20 cm as the result of remobilization during a period of less oxic conditions that prevailed sometimes after the deposition of Unit IV 18 000 years ago. But, in this case, an average deficit of 26% extractable Fe would correspond to a diffusive flux of $-5 \times 10^{-10} \mu\text{M cm}^{-2} \text{s}^{-1}$. Such a flux is comparable to the authigenic flux calculated for the interval 0-20 cm but is ten times less than the fluxes quoted for suboxic sediments in Table 3. The hypothesis of preferential mobilization of Fe^{2+} cannot be supported, since Mn^{2+} is always more mobile in the suboxic zone of present day sediments (Froelich *et al.*, 1979) and the observed deficit of extractable Mn in Unit IV of KG40 is not sufficient (6%) to account for such a phenomenon. The particular characteristics of the "historical" layer (Unit IV) of KG40, including the deficits in Fe and Mn, were probably acquired during or shortly after the deposition of the 33-20 cm interval. The conditions that prevailed prior to 11 000 B.P. favoured the dissolution of carbonate material and were characterized by greater input of quartz-rich windborne dust. Thus, Unit IV was deposited under conditions very different to the present day. Even if some modifications have taken place during the first 18 000 years, they have left no record in the overlying Unit III. The behaviour of Fe and Mn is not incompatible with the hypothesis of an important hiatus at 20 cm, especially if the particular characteristics of Unit IV are considered to be acquired after deposition of this unit.

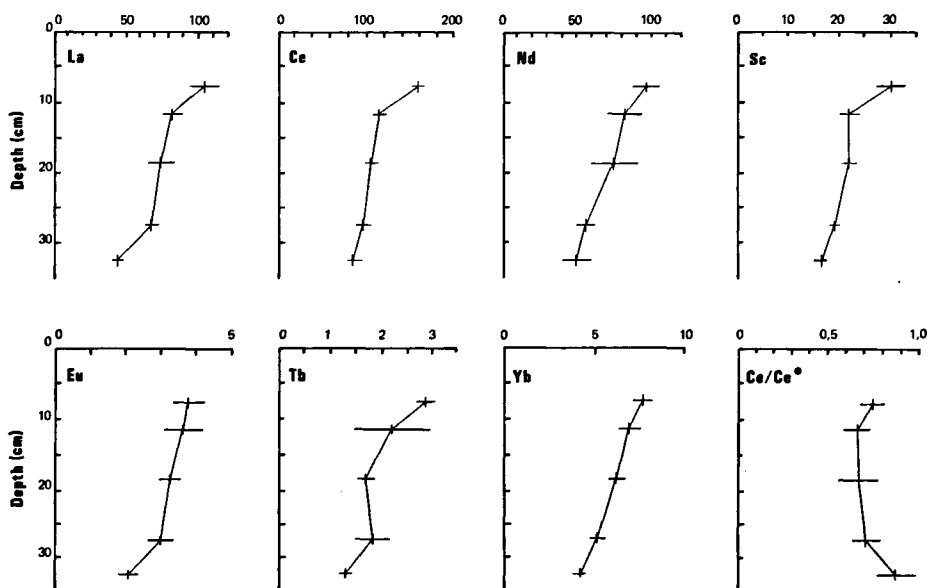


Figure 6

Rare-earth elements, scandium and cerium anomaly profiles in the non-carbonaceous fraction (carbonate-free basis estimation; values in $\mu\text{g g}^{-1}</math>).$

Profils de terres rares, de scandium et d'anomalie en cérium dans la phase non-carbonatée.

Rare earth element (REE) geochemistry

REE analyses were performed on five sub-samples taken at 7, 11, 18, 27 and 32 cm depth. Since the REE contents of biogenic carbonates are about ten times less than those of shale (Spirn, 1965), or less (Elderfield *et al.*, 1981), the present data (see Fig. 6) are expressed on a carbonate free basis. Overestimation (+10% for 80% CaCO₃ assuming carbonate REE contents is 0) of carbonate free REE abundances cannot account for their decrease from top to bottom. The simplest explanation for the REE vs depth profiles in Figure 6 is that the REE being relatively more concentrated in the clayey fraction, the downcore variation is a function of grain size distribution in the lithogenous component. This hypothesis is favoured by the carbonate free Sc data in Table 1, which also show a downcore dilution independent of CaCO₃ content. Even if it is clear that downcore variation in lithogenous REE is controlled by factors within the sedimentary matrix (*i.e.* increased quartz dilution with depth), it is still possible that diagenetic remobilization has had some influence on the observed REE patterns (*e.g.* nodule bearing sediments, Elderfield, Greaves, 1981; Elderfield *et al.*, 1981). Although the possibility of sedimentary reworking (slumps, turbidites) cannot be completely discounted, it is most likely that the observed variations in grain size distribution reflect changes in the lithogenous supply (*i.e.* source term dominated by Saharan windborne dust).

A linear regression established between carbonate free REE contents and the proportion of <4 µm grain size fraction in the decalcified residue has led to an estimate of the REE abundances in a hypothetical lithogenous end-member clay (*i.e.* 100% sediment particles <4 µm; Table 3). The REE contents of this end-member clay are compared to average shale composition (Piper, 1974) and the results are presented as an abundance pattern in Figure 7 (Coryell *et al.*, 1963).

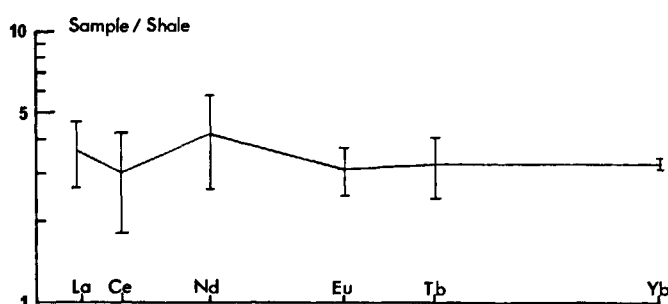


Figure 7
Shale normalized REE pattern of the <4 µm non-carbonaceous fraction (see text for calculation).
Spectre normé aux shales des terres rares contenues dans la fraction non-carbonatée (détails du calcul dans le texte).

The REE pattern shows: 1) an absence of fractionation with respect to shales, thus suggesting that the sediment particles are ultimately derived from the erosion of continental crustal rocks; 2) an absolute enrichment factor of 3x shale, reflecting the abundance of aluminosilicates in the 4 µm fraction attested by the shale normalized enrichment factor of Sc (3x); 3) a slight

deviation of normal shale-type composition represented by a poorly significant negative Ce anomaly ($Ce/Ce^* = 0.8$) calculated by $Ce/Ce^* = 3 Ce_N / (2 La_N + Nd_N)$, where Ce^* is the theoretical concentration of Ce when strictly trivalent and Ce_N , La_N , Nd_N are concentrations of Ce, La, Nd normalized to shale.

It is difficult to know whether this anomaly has been inherited from the source area or whether it has been acquired during or after sedimentation. Ce anomalies of the same magnitude have been observed in bottom waters from the Madeira abyssal plain at 28°N, 26°W (Elderfield, Greaves, 1982), but the same authors also show the existence of a negative Eu anomaly which is not detected in sediments of the CV2 site. According to observations of present-day atmospheric circulation, Saharan dust is mainly expelled over the North Atlantic between latitudes 10°-25°N (Coudé-Gaussens, Rognon, 1983), so the influence of windborne dust should be more marked at the CV2 site than in the Madeira abyssal plain. This is in contradiction with the absence of an Eu anomaly in the KG40 core, since Sahara aerosols typically display a negative Eu anomaly (Elderfield, Greaves, 1982). If Antarctic bottom waters at the CV2 site were devoid of an Eu anomaly, then it might be possible to confirm the influence of advective flow on sedimentary regimes at this site.

The negative Ce anomaly cannot be considered as resulting from a diffuse loss of Ce^{4+} during post-depositional diagenesis because of the low solubility of Ce^{4+} which makes it less mobile than the other REE^{3+} . Therefore, the solid phase Ce anomalies recorded in oceanic sediment cores are probably representative of REE geochemistry of the water column through which the sediment particles have fallen. The REE patterns obtained for the KG40 core (see Fig. 6) show significantly lower Ce/Ce^* values in Unit IV which was deposited during the last glacial maximum. Thus, the formation of Ce^{4+} would be favoured during glacial periods because of the influence of cold Antarctic or North Atlantic bottom waters.

The Ce anomalies might allow a better understanding of palaeo-geochemical conditions than have prevailed in the deep-sea environment.

CONCLUSION

The multi-disciplinary approach presented in this study has permitted a reconstruction of the sedimentological and geochemical conditions that have prevailed during the deposition of an uppermost Pleistocene-Holocene sediment section accumulated on the Cape Verde abyssal plain. Not only trophic inputs but also sediment accumulation rates are shown to be relatively low. Both factors have played an important role in the preservation of climatic events and associated geochemical indicators in the core record. Low productivity and the resulting scarcity of benthic fauna have contributed to the low intensity of bioturbation in post-glacial sediments, so carbonate test material has not been fragmented and permeability has remained fairly high in near-surface sediments. In such a pore-water environment, where oxidizing species (O_2 , NO_3) are only slightly consumed by the small amounts of organic matter present, Fe, Mn and probably REE have not

been significantly remobilized by diagenetic processes. Consequently their concentration vs depth profiles can be used to re-trace variations in the original sedimentary regimes.

In this way, the presence of a sedimentation hiatus is reflected in the break in extractible Fe and Mn profiles. The influence of different bottom water masses can be characterized by Ce anomalies. These various conclusions show that low productivity of the water column (oligotrophic conditions) has a direct effect on the physical and chemical processes which take place beneath the sediment/water interface.

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