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# **Spatial variations in nutrient utilization, production and diagenesis in the sediments of a coastal upwelling regime (NW Africa): Implications for the paleoceanographic record**

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## **ABSTRACT**

A biogeochemical study of recent (multicores) sediments of the northwest African slope was undertaken to understand how the sediment composition varies with respect to the location of core sites relative to the centers of coastal upwelling, and how this has affected the palaeoceanographic record. Sedimentary organic carbon contents are inversely correlated with the nitrogen isotopic composition ( $\delta^{15}\text{N}$ ), high  $\text{C}_{\text{organic}}$  concentrations and low  $\delta^{15}\text{N}$  occurring at proximal (shallow) sites and the opposite at distal (deep) ones. These spatial differences are interpreted to result from higher relative nutrient utilization and a decrease in production as waters are advected offshore from the zone of upwelling. Highest  $\text{C}_{\text{organic}}$  contents also correlate positively with highest concentrations of redox-sensitive elements (U, Mo and S) that are fixed diagenetically in the sediments.

These results suggest that the sedimentary regime at a fixed position depends on the spatial location of the productive areas relatively to a given core site. Downcore records of Zr/Al, Ti/Al, mean grain size of the terrigenous fraction,  $\delta^{15}\text{N}$ ,  $\text{C}_{\text{organic}}$ , biogenic Ba, U, Mo and sulfur at a single site on the slope are interpreted to reflect glacial-interglacial changes in the core location relative to the coastline (sea-level effect), and hence changes in production as the area of coastal upwelling moved on- and offshore as sea-level changed, as well as undoubtedly changes in upwelling intensity through wind forcing. Further studies are needed to fully understand the interrelationships of all these processes, which are required for building more reliable paleoceanographic-paleoclimatic records.

## **1. Introduction**

Although they represent only 10% of the total surface of the ocean, continental margins play a significant role in the global cycles of carbon and nitrogen (Walsh, 1991). Biological production in the coastal ocean is generally high because of large inputs of nutrients by

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ivers, by cross-shelf flow of bottom waters, and/or by coastal upwelling. Upwelling of CO<sub>2</sub> and nutrient-rich oceanic waters causes both the degassing of CO<sub>2</sub>, which acts as a source of C to the atmosphere, and enhanced biological production (the biological pump), which acts as a sink of C through exportation in deep waters and sediments. This is the reason why great attention has been attached to these systems, especially in order to understand how the biological pump efficiency varied with time during the late Quaternary in response to upwelling intensity and hence nutrient availability and utilization, and how this could be implicated in the atmospheric CO<sub>2</sub> changes.

Oceanic productivity is sensitive to climatic variability, which influences circulation, water column stability, upwelling intensity, water discharge and sea-level changes. For instance, nowadays, maps of the distribution of organic carbon in oceanic sediments are similar to maps of the distribution of primary production in the surface waters (see Degens and Mopper, 1976; Romankevich, 1984) and maximum values are located mainly in continental margin areas (shelves and slopes), especially in regions where coastal upwelling occurs. In addition, during these times of high sea-level, cross-shelf transport of organic matter is particularly important, within giant filaments or plumes in surface and subsurface waters, or within nepheloid layers of resuspended sediments at depths (Van Camp *et al.*, 1991; Gabric *et al.*, 1993; Anderson *et al.*, 1994). Because of glacial low sea-level stands, shelves were uncovered. As a consequence, the location of upwelling cells, the extension and repartition of productive areas as well as the modalities for organic particle sedimentation changed. During these glacial times, lateral advection of particular organic material from coastal areas to open ocean was limited compared to interglacial periods.

Therefore, glacial-interglacial paleo-biogeochemical records in deep-sea cores integrate such conditions and changes, thereby complicating paleoceanographic reconstructions. Several studies have shown that paleo-biogeochemical signals recorded in sediment cores are primarily linked to changes in production during the Late Pleistocene (Pedersen, 1983; Sarnthein *et al.*, 1987; Lyle, 1988; Shimmield and Mowbray, 1991; Shimmield, 1992; Schneider *et al.*, 1996; Dean *et al.*, 1997; Ganeshram and Pedersen, 1998; Schubert *et al.*, 1998). This is particularly true in the case of upwelling systems because they are strongly affected by atmospheric circulation (i.e., wind forcing).

The purpose of this paper is to decipher the paleo-biogeochemical variability over the last 150,000 years in a sedimentary record at mid-slope depth in a major upwelling regime. To do this, we first examine modern sedimentation and processes off NW Africa using a set of multicores recovered over a range of depths and distances from the productive upwelling area. We focus on the distribution and behavior of various geochemical and isotopic indices of nutrient utilization, export production, diagenetic intensity and redox conditions, and lithogenic input. These results are then used to interpret the palaeoceanographic record recovered from the mid-slope in order to identify the mechanisms involved in building the sedimentary record and to constrain the paleoceanographic construction.

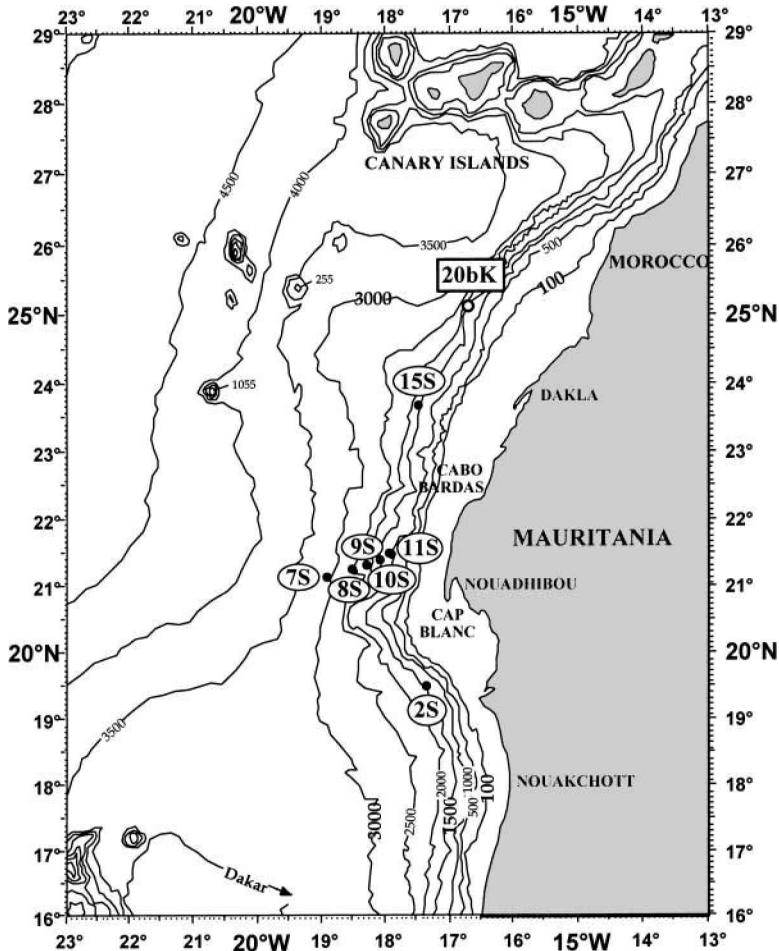


Figure 1. Location map of the study area showing bathymetry and the core locations. Cores 15S, 11S, 10S, 9S, 8S, 7S and 2S are multicores, and core 20bK is a piston-core.

## 2. Materials and methods

During the SEDORQUA cruise in March 1994, multicores (2S, 7S, 8S, 9S, 10S, 11S and 15S) and a piston-core (20bK) were recovered from the northwest African margin (Fig. 1). The multicores were retrieved off Cap Blanc (21°N) at water depths of 1000, 1200, 1525, 2002, 2530, 3010 and 1407 m (Table 1). Core 20bK is located farther north (25°N) on the mid-slope at 1445 m depth (Fig. 1; Table 1). The multicores were subsampled on board at 0.5 cm intervals from 0 to 4 cm, and then at 1.0 cm intervals. Core 20bK was sampled at 2.5 cm intervals throughout. All the samples were stored frozen and then dried and homogenized by grinding for chemical and isotopic analysis. The sediments consisted of hemipelagic silty-clayey nanno and foram ooze. Visual and X-ray examination showed that core 20bK does not contain turbidites and/or hiatuses.

Table 1. Location, depth and type of the cores studied.

Core	Latitude	Longitude	Depth (meters)	Type
15 S	N 23°43.6	W 17°15.6	1000	Multitube
11 S	N 21°28.9	W 17°57.3	1200	Multitube
10 S	N 21°25.0	W 18°04.7	1525	Multitube
9 S	N 21°19.8	W 18°15.1	2002	Multitube
8 S	N 21°14.8	W 18°25.5	2530	Multitube
7 S	N 21°11.4	W 18°51.5	3010	Multitube
2 S	N 19°29.4	W 17°16.9	1407	Multitube
SU94-20bK	N 25°01.7	W 16°39.2	1445	Piston-core

Organic carbon ( $C_{\text{organic}}$ ) and total sulfur (S) determinations were made by the total combustion of homogenized samples using a LECO C-S 125 analyzer. Precisions were better than  $\pm 5\%$ . For  $C_{\text{organic}}$ , the sediment was treated with hydrochloric acid prior to analysis to remove calcium carbonate. Total nitrogen determinations were made with a Carlo Erba CHN analyzer.

For Mn, U and Mo determinations on the multicores, sediment subsamples were totally digested in a hot mixture of concentrated HCl,  $HNO_3$  and HF. Mn, U and Mo were determined using an Elan 5000 Perkin-Elmer-Sciex ICP-MS (Inductively Coupled Plasma-Mass Spectrometer). Calibration was effected using standard solutions with known metal concentrations. Quantitative recovery for the method was confirmed by analyses of international reference materials (marine sediments: MESS-2 and BCSS-1; rocks: GS-N and BE-N). The precision of the analyses was better than  $\pm 5\%$ .

Aluminium, Ti, Zr, Mo and U concentrations on piston core 20bK were determined by X-ray fluorescence spectrometry. For major element determinations, glass discs were prepared by fusing 1 g of bulk sediment with a La-Li tetraborate flux (Norrish and Hutton, 1969). For minor element determinations, 3 gram subsamples were formed into briquettes with a boric acid backing in a hydraulic press (Shimmiel, 1985). A wide range of international rock standards were used for calibration, and the precision was  $\pm 3\%$ .

Grain-size distributions were determined on the lithogenic fraction using a Malvern 2600 E laser sizer after removing  $CaCO_3$ , the main biogenic fraction in these sediments. The method is based on the near-forward scattering of a laser beam by particles suspended in water (McCave and Syvitski, 1991).

Nitrogen isotope ratios were determined on dried, ground bulk sediment using a Carlo Erba CHN analyzer interfaced directly to a VG prism mass spectrometer. The nitrogen isotope ratio is reported in the  $\delta$  notation as:

$$\delta^{15}N(\text{‰}) = \frac{{}^{15}N/{}^{14}N_{\text{sample}} - {}^{15}N/{}^{14}N_{\text{standard}}}{{}^{15}N/{}^{14}N_{\text{standard}}} \times 1000$$

where the standard is atmospheric nitrogen. The precision of these measurements is better than  $\pm 0.3\text{‰}$ . We assume that the isotopic composition of total nitrogen primarily reflects

that of organic matter, rather than inorganic nitrogen (ammonium), which constitutes a minor proportion of total nitrogen (see also Calvert *et al.*, 1992; Farrell *et al.*, 1995; Ganeshram *et al.*, 1995).

Prior to carbon isotopic composition determination, sediments were decarbonated using HCl 0.6N. We checked that the decarbonation process had no effect on carbon isotope composition by comparing  $\delta^{13}\text{C}$  values of sedimentary organic matter free of carbonate before treatment and after treatment with HCl solutions at different concentrations. Carbon isotope ratios were obtained from a VG Optima mass spectrometer coupled with a Carlo Erba NA 1500 elementary analyzer. Carbon isotope ratio results are reported in the  $\delta$  notation versus PDB, with an absolute precision of 0.1‰.

The  $\delta^{18}\text{O}$  stratigraphy for core 20bK (Fig. 5) was determined using samples of the planktonic foraminifera *Globigerina bulloides* at 5 cm intervals (for details see: Bertrand *et al.*, 1996; Martinez *et al.*, 1996).

### 3. Present-day characteristics of the study area

On the northwest African margin, coastal upwelling is induced by the Trade Winds blowing mainly from northeast (Barton *et al.*, 1977; Mittelstaedt, 1983; Van Camp *et al.*, 1991). Between 20N and 25N, upwelling occurs throughout the year and seasonally over much wider latitudes (Schemainda *et al.*, 1975; Fütterer, 1983). Nitrate concentrations in the surface waters show the highest values off Cap Blanc, both during winter and spring-summer (Fig. 2). Nitrates reach concentrations higher than  $16 \mu\text{M l}^{-1}$ , similar to those of central waters that upwell from depths of 100–200 m in this area (Schemainda *et al.*, 1975; Minas *et al.*, 1982), or in other coastal upwelling systems (e.g., Angola Basin: see Holmes *et al.*, 1996). One upwelling cell can be observed in surface nitrate distributions over the shelf and the shelf-break, and another one farther offshore (Fig. 2). This distribution results from the formation of a hydrological front south of Cap Blanc which favors the off-shoreward deviation of the Canary Current and that transports recently upwelled nutrient-rich waters offshore at a velocity of 4–5 km/day (Barton *et al.*, 1977; Mittelstaedt, 1983; Gabric *et al.*, 1993). According to other studies, the two-cell upwelling system occurs when the wind stress is particularly strong (Barton *et al.*, 1977; Minas *et al.*, 1982, 1986). As the upwelled water is advected offshore, nutrients are gradually consumed by phytoplankton. As a consequence, they become progressively more nutrient-depleted as waters age and travel far from the locus of upwelling (Fig. 2). These cells correspond well with the two patches of high primary production observed in Figure 2. High biomasses and elevated primary production occur during the whole year with maximal values during June and July because of more favorable winds. The most productive area is located off Cap Blanc (Fig. 2) (Schemainda *et al.*, 1975) and extends several hundred km offshore, especially off Cap Blanc within plumes or “giant filaments” as seen in satellite imagery (Van Camp *et al.*, 1991; Gabric *et al.*, 1993). These “giant filaments” persist throughout the year (Van Camp *et al.*, 1991; Gabric *et al.*, 1993), but with substantial seasonal and interannual variability (see the satellite imagery of sea-surface temperature and chlorophyll *e* concen-

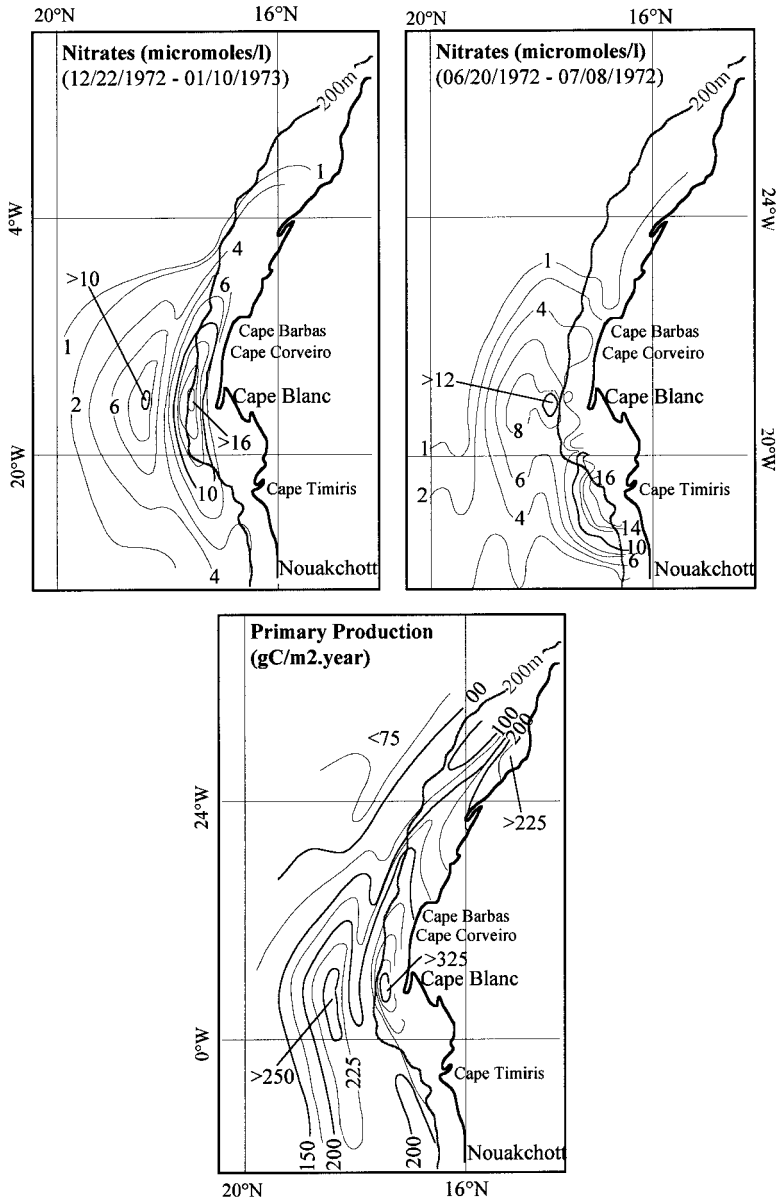


Figure 2. Maps showing the surface waters distribution of nitrate (in  $\mu\text{M l}^{-1}$ ) in the NW African coastal upwelling during an upwelling event in winter and summer (upper panels), and the mean annual primary production (in  $\text{gC m}^{-2} \text{year}^{-1}$ ) (redrawn from Schemainda *et al.*, 1975).

tration in Van Camp *et al.*, 1991, and Gabric *et al.*, 1993). They extend from coastal sites to the open ocean, the area of high productivity.

This current-induced offshore transport of biological production leads to a peculiar sedimentation. Indeed, present-day sedimentation over the shelf does not record the export

production, but instead, most of the biogenic fluxes are exported and accumulate in a depocenter at water depths of 1000–2000 m. This is also due to strong hydrodynamic processes which occur over the shelf (Fütterer, 1983) because of strong winds. Strong winds can also reduce primary production in this area by producing a deep mixed layer that limits light availability for phytoplankton population (Huntsman and Barber, 1977).

#### 4. Results and discussion

##### *a. Nitrogen isotope records: Spatial variations in nutrient availability and utilization*

The reconstruction of the history of planktonic production using  $\delta^{15}\text{N}$  is based on biological fractionation of  $^{14}\text{N}$  and  $^{15}\text{N}$ , whereby preferential uptake of  $^{14}\text{N}$  by plankton results in organic matter that is enriched in the light isotope and a residual dissolved nutrient pool that is correspondingly enriched in  $^{15}\text{N}$  (Wada and Hattori, 1991). This is confirmed by the general observation of an inverse relationship between the near-surface nitrate concentration and the  $\delta^{15}\text{N}$  signature of particulate organic matter in the water column and at the sediment-water interface (Wada and Hattori, 1976, 1991; Altabet and François, 1994b). This relationship is ascribed mainly to variations in relative nitrate utilization (biological uptake relative to physical supply), and hence, production (Altabet *et al.*, 1991; François *et al.*, 1992; Altabet et François, 1994a, b; Holmes *et al.*, 1996, 1998).

The  $\delta^{15}\text{N}$  values in cores 7S, 9S and 11S range between 3.7 and 6.7‰ (Fig. 3). The values become heavier with distance from shore and with water depth, the lightest values (4.5‰) being found in core 11S and the heaviest values (around 6.5‰) occurring in core 7S. The main factors that can account for these are related to: (i) changes in  $\delta^{15}\text{N}$  of the subsurface nitrate source; (ii) nutrient availability and utilization by phytoplankton; (iii) degradation during sinking between surface and deep waters, and diagenesis at the sediment-water interface and during burial. We can exclude the effect of an input of terrigenous organic matter, with light  $\delta^{15}\text{N}$  (Peters *et al.*, 1978), since petrographical observations (Martinez, 1997; Lallier-Vergès, unpublished data) and biomarkers (Ternois *et al.*, 2000; Sicre *et al.*, 2000) indicate that the organic input is mainly planktonic.

Denitrification, a microbially-mediated process that converts  $\text{NO}_3^-$  to  $\text{N}_2\text{O}$  and  $\text{N}_2$  during the degradation of organic matter, often occurs in the water column near continental margins where high production and subsequent sinking of organic matter leads to enhanced consumption of oxygen, intensifying the oxygen minimum zone (OMZ). This process could lead to isotopically heavy sedimentary  $\delta^{15}\text{N}$  values because denitrification occurs with a large isotopic fractionation, producing isotopically light  $\text{N}_2$  and  $\text{N}_2\text{O}$  that are largely lost to the atmosphere, and isotopically heavy residual nitrate (Cline and Kaplan, 1975; Liu and Kaplan, 1989). Supply of some of this nitrate to surface waters by upwelling and its utilization by plankton would then enrich the particulate organic matter in the heavy isotope (Cline and Kaplan, 1975; Saino and Hattori, 1987; Liu and Kaplan, 1989). Denitrification is not a major influence on the northwest African margin, however, because  $\text{O}_2$  concentrations are too high for nitrate reduction to occur at intermediate depths, except locally on rare occasions (Minas *et al.*, 1982). Furthermore, the observed sedimentary  $\delta^{15}\text{N}$  values are much lighter than those observed at sites where denitrification is known to be





(submitted; cited in Holmes *et al.*, 1997) noted a +1.6‰ enrichment between sediment traps and underlying sediments, and Ganeshram (1996) reported that sediment trap  $\delta^{15}\text{N}$  values from intermediate waters were the same as those in the upper 30 cm of sediments off northwestern Mexico. It appears, therefore, that a water column degradation effect is regionally variable, and is likely to be smaller compared with oceanic water depths. However, this does not exclude a stronger water-column degradation of the organic matter during its transport to be partly responsible for the  $\delta^{15}\text{N}$  differences between shallow and deep sites (see also the following, Section b). No sediment trap data are available in this area to further address this question.

Diagenesis at the sediment-water interface and during burial in the first decimeters of the sediments could also alter the primary signal of  $\delta^{15}\text{N}$  formed in the water column. Altabet *et al.* (1997), in a study in the Equatorial Pacific, found that  $\delta^{15}\text{N}$  often increases with depth in the upper 5 cm of the sediment as total N concentration decreases, and acid hydrolysis of the most labile fraction in the laboratory leaves a fraction that is always depleted in  $^{15}\text{N}$ . Sigman *et al.* (1999) showed that  $\delta^{15}\text{N}$  of diatom-bound organic matter in Southern Ocean sediments, which is probably protected from degradation in the opal matrix, is 2–4‰ lighter than bulk sediment  $\delta^{15}\text{N}$ . Accordingly, the sedimentary nitrogen pool is composed of a  $^{15}\text{N}$ -enriched labile fraction (which can be removed with perchloric acid treatment) and a  $^{15}\text{N}$ -depleted refractory one which is protected from alteration. This could explain the  $\delta^{15}\text{N}$  offset between sinking particles, surface sediment and buried sediment, as well as regional differences in this effect because of the different relative contributions of the refractory and labile fractions, the degree of degradation and the original type or quality of the organic matter settling to the sea floor. Off NW Africa, we find no significant downcore changes in  $\delta^{15}\text{N}$ , as also found by Ganeshram (1996) off NW Mexico, suggesting that there has not been a large isotope fractionation effect due to microbial degradation at these sites (see also the following, Section b.).

On the northwest African margin, surface water nutrient concentrations are high in coastal waters and they decrease seaward (Fig. 2; Schemainda *et al.*, 1975; Huntsman and Barber, 1977; Minas *et al.*, 1982, 1986), as is commonly observed in coastal upwelling systems (see Hutchings *et al.*, 1995; Holmes *et al.*, 1996, 1998). Such an offshore gradual diminution in surface water nutrient concentrations (see Fig. 2: approximately from 15 to less than  $1 \mu\text{M l}^{-1}$  of nitrates) is observed only during and just after an upwelling event. During periods of relaxation, surface waters become depleted in nutrients and present then more homogenous concentration (2 to  $5 \mu\text{M l}^{-1}$  of nitrates). Therefore, we can reasonably assume that surface nutrient concentrations at the site of core 7S are generally depleted relative to those at core 11S, and that this would be imprinted in the  $\delta^{15}\text{N}$  signals, since sedimentary signals integrate both periods of upwelling events and relaxation for several years. Thus, there is less relative utilization of nutrients at site 11, leading to a lighter  $\delta^{15}\text{N}$  signal, and more utilization of isotopically heavy nitrate (due to offshore advection of upwelled waters) at site 7, where we find heavier isotopic values.

Since the sediments of the NW African margin are similar in constitution (silty-clayey

carbonate ooze, with approximately 2% organic carbon) to those of the equatorial Pacific, off NW Mexico and off the Angola margin, where diagenetic effects are not as severe as observed in the Southern Ocean, we assume that the offshore change in  $\delta^{15}\text{N}$  can be first interpreted as a relative increase in nutrient utilization in the same direction (see also the following, Section b.).

*b. C<sub>organic</sub>, N and C/N ratio: Export production and preservation*

$\text{C}_{\text{organic}}$  contents decrease from shallower to deeper sites onto the slope, with mean values for cores 11S, 10S, 9S, 8S and 7S of 2.80, 2.89, 2.42, 1.60 and 0.97 wt. %, respectively (Fig. 3). In the latitudinal transect, mean  $\text{C}_{\text{organic}}$  is higher at site 11S than at sites 2S (2.17%) and 15S (1.26%). This indicates that present-day upwelling and production is much more important off Cap Blanc, as previously concluded by Schemainda *et al.* (1975) and Fütterer (1983). The same observations can be made for N contents, which correlate significantly with  $\text{C}_{\text{organic}}$  contents (Fig. 3). The atomic  $\text{C}_{\text{organic}}/\text{N}$  ratio, determined from the slope of the linear regression, is similar for all the cores and close to 7, which is typical of autochthonous (planktonic) organic material (see Meyers, 1997, and references therein). In addition, whereas cores 11S, 9S and 7S present similar C/N ratios,  $\delta^{15}\text{N}$  values become heavier from site 11 to site 7 (Fig. 3). Thus, there is certainly little fractionation between  $\text{C}_{\text{organic}}$  and N during transport through the water column and initial diagenetic reactions on the sea floor, lending support to the assumption that there has been a relatively small diagenetic effect on the  $\delta^{15}\text{N}$  values of the sediments in this region, and/or that this diagenetic effect is hidden by the relative nutrient utilization effect (see above, Section a). On the basis of sediments trap data from different oceanic regions, an empirical relationship was shown by Suess (1980) between the flux of particulate organic matter and water depth. This relationship predicts that most degradation occurs in the first 1000 m of the water column. According to this assumption, a recent study of Pierre *et al.* (1994) shows that nutrient recycling from organic matter mineralization occurs at similar rates and predominantly in the upper 900 m layer in the oligotrophic, mesotrophic and eutrophic zones of the northeast Atlantic (NW African margin offshore Cap Blanc). Therefore, below 1000 m water depth, the remaining organic particles fall down to the bottom with only minor transformation. In addition, our study area is under eutrophic to mesotrophic conditions, in which the transfer to the bottom is known to be favored by larger fecal pellets and aggregates than in oligotrophic conditions, and that the export production that reaches the sediments at the different sites is of similar constitution.

$\text{C}_{\text{organic}}$  concentrations and  $\text{C}_{\text{organic}}/\text{N}$  ratios show small downcore changes in the first 2–3 cm and minor variations deeper than 3 cm in cores 9S, 7S, 15S and 2S. Such profiles appear to be characteristic of continental margin environments where input of refractory material is generally high, and because most of the degradation occurs in the water column (Suess, 1980; Carpenter, 1987; Smith *et al.*, 1987; Anderson *et al.*, 1994). Alternatively, this could result from a rapid diagenesis of the remaining labile organic matter shortly after deposition in the first cm of the sediment-water interface, and that would not be seen here at

the resolution used. Larger exponential downcore decreases in  $C_{\text{organic}}$  concentrations have been observed in situations where a relative large fraction of the organic matter is labile, marine organic matter (Grundmanis and Murray, 1982; Murray and Kuivila, 1990).

$C_{\text{organic}}$  contents decrease from the shallowest (11) to the deepest site (7). The decrease in the concentration in  $C_{\text{organic}}$  and total nitrogen with increasing water depth may be due to an offshore decrease in primary production, as can be seen in satellite imagery (see Fig. 2; Van Camp *et al.*, 1991; Schemainda *et al.*, 1975), as well as to a concomitant decrease in the input of advected organic material from the shelf. This would be consistent with a major offshore increase in nutrient utilization as shown by the downcore  $\delta^{15}\text{N}$  records and the negative relationship between  $\delta^{15}\text{N}$  and  $C_{\text{organic}}$  contents (Fig. 3).

### c. Trace metal and sulfur distributions: redox conditions

The distributions of trace metals and total S in the multicores are linked to the sedimentary redox conditions (Fig. 4). A surface manganese-rich layer is observed in cores 11S, 9S and 7S; the layer is thinnest (1.5 cm) in core 11S, intermediate in thickness (2 cm) in core 9S, and thickest (4 cm) in core 7S, where the Mn concentration is higher (800 ppm) than in the other two cores (300 ppm). Concentrations are more or less constant below this surficial layer. The surficial enrichments correspond well with the depth of oxygen penetration into the sedimentary column (Jorissen *et al.*, 1998), and are due to the upward diffusion of reduced pore water Mn derived from the bacterial reduction or the reductive solution of buried  $\text{MnO}_2$  and/or  $\text{MnOOH}$  (Froelich *et al.*, 1979). Such oxyhydroxide phases have a marked sorptive capacity for many trace elements (Balistrieri and Murray, 1986; Shimmield and Price, 1986). For example, relatively high concentrations of Mo are found in the Mn-rich superficial layers in the multicores, as is also found in other continental slope settings where a relatively constant Mo/Mn ratio of 0.002 has been found (see Shimmield and Price, 1986).

Below the horizon of Mn-enrichment, U, Mo and S contents gradually increase downcore. This is a clear indication of the establishment of suboxic (no  $\text{O}_2$ , no  $\text{H}_2\text{S}$ ) and anoxic (sulphidic:  $\text{H}_2\text{S}$  present) conditions at depth. Pyrite framboids can be observed under the microscope, and S/Fe ratios typical of pyrite indicate that sulphur enrichment occurs as a result of sulphate reduction (Lallier-Vergès *et al.*, 1998). The gradient between oxic and anoxic conditions in the sedimentary column leads to a net downward diffusive flux of dissolved elements that are known to precipitate under reducing conditions. This is particularly the case for U and Mo (Fig. 4), leading to subsurface metal enrichments significantly higher than crustal abundances (Bertine and Turekian, 1973; François, 1988; Klinkhammer and Palmer, 1991; Calvert and Pedersen, 1993; Crusius *et al.*, 1996).

Trace metal and S enrichments are similar in the two shallowest cores 11S and 9S, with maxima of around 4 ppm U, 1.2 ppm Mo and 0.6% S, whereas the deepest core 7S presents lower enrichment. At the two shallowest sites (11 and 9), Mo and S enrichment are rather well correlated (except for the surficial Mo peak) due to coprecipitation of Mo with Fe sulphides or the surface adsorption of thiomolybdate species (Helz *et al.*, 1996).

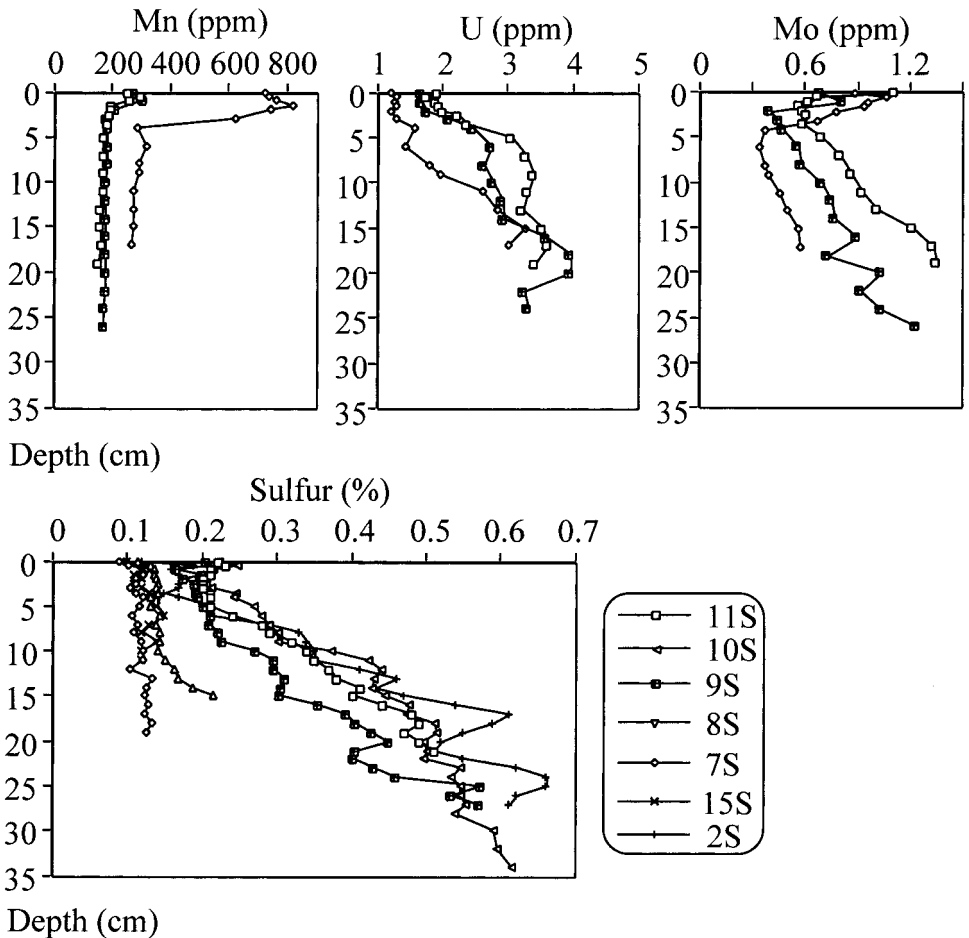


Figure 4. Records of manganese (ppm), uranium (ppm), molybdenum (ppm) for multicores 11S, 9S and 7S, and sulfur for all multicores 15S, 11S, 10S, 9S, 8S, 7S and 2S.

Sulphur, U and Mo concentrations at depth are higher when organic carbon is higher, whereas the opposite is the case for Mn. This is probably due to the combination of a higher organic carbon input and higher sedimentation rate at shallower water depth which leads to the burial of a larger proportion of organic matter to be degraded under suboxic-anoxic conditions. This will cause a more intense recycling of Mn and at the same time a greater diffusive flux of metals and sulphur into the sediment.

*d. Grain-size of the lithic fraction: Relationships with eolian particles and organic sedimentation*

Lithogenic sediment supply to the northwest African margin is dominated by aeolian input from the Sahara via the Trade Winds (Milliman, 1977; Sarnthein *et al.*, 1981).

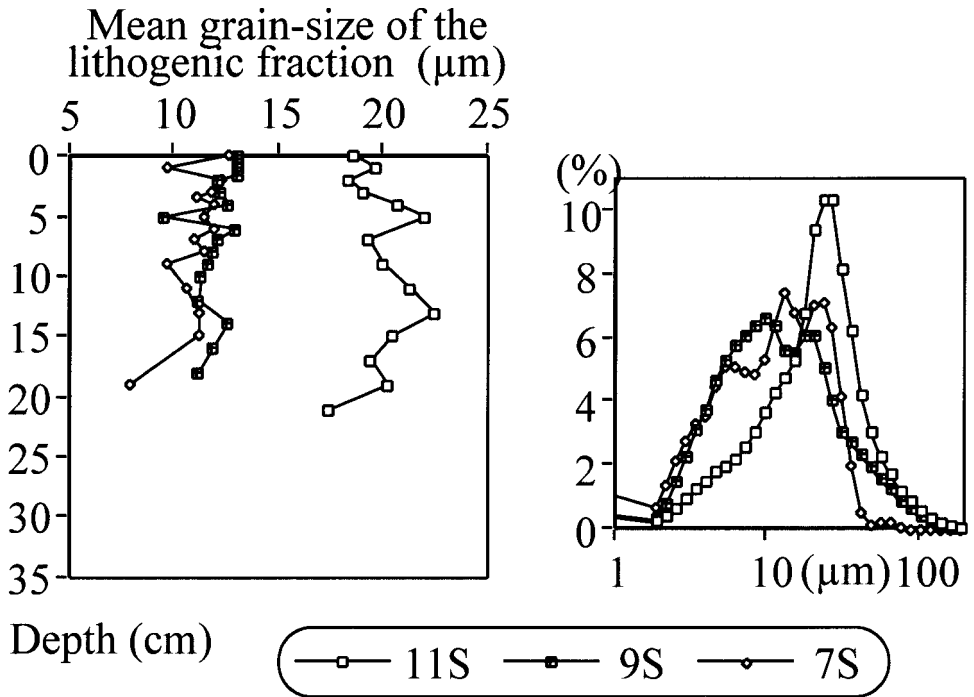


Figure 5. Left: Mean-grain size of the terrigenous fraction (determined on carbonate-free sediment) for cores 11S, 9S and 7S. Right: Selected corresponding frequency curves for each core indicating the dominant modes.

Particulate material carried to the ocean consists mainly of quartz and feldspar in the size range 10–50  $\mu\text{m}$  (Wefer and Fischer, 1993). Mean grain-size of the lithic fraction in the three cores (Fig. 5) is fairly constant, suggesting that the lithic fraction input has remained constant over the period of sedimentation recovered, but the grain size is different at the three sites: core 11S contains coarser sediment, while cores 7S and 9S are finer grained. Modal analysis of the terrigenous fraction of core 11S shows that it is well sorted, with a predominant mode around 20–30  $\mu\text{m}$  which is typical of aeolian dust in this area (Wefer and Fischer, 1993; Grousset *et al.*, 1998). For core 9S, other distinctive modes occur at around 10, 20 and 25  $\mu\text{m}$ , whereas for core 7S modes appear at around 6, 15 and 25  $\mu\text{m}$ . These results indicate a decreasing ability for winds to carry coarse material with increasing distance from the source area (Prospero and Carlson, 1972; Prospero, 1996; Rea, 1994). We cannot exclude the possibility that some of the lithic grains have been carried to the slope indirectly and not only by aeolian transport pathways. For example, a possible indirect way is through surficial or mid-depth plumes which develop at the shelf break and which generally carry fine-grained material, such as clays. In addition, grain by grain transport of coarse particles from the shelf to the slope is also possible (Fütterer, 1983).

The sediments at the mid-slope site (core 11S) have the highest  $C_{\text{organic}}$  contents and also contain the coarsest lithic particles, whereas the opposite is observed at the deeper site (core 7S) (Figs. 3 and 5). Previous work has demonstrated that the organic content of marine sediments is controlled by supply and preservation and also by sediment texture, finer-grained sediments generally containing more organic matter than coarser ones. Some authors have proposed that this observation is the result of the hydraulic equivalence between clay-fine silt and the organic material via winnowing and sorting (Shimmield *et al.*, 1990; Calvert and Pedersen, 1992; Pedersen *et al.*, 1992; Calvert *et al.*, 1995), whereas others have proposed that this association could be due to the greater absorption of organic material on the larger surface areas of fine-grained particles (Hedges and Keil, 1995 and references therein). The latter hypothesis has recently been challenged by Ransom *et al.* (1997) who were unable to find evidence of such organic monolayers in sediments from the western North American continental margin. On the northwest African margin, sediment reworking is significant, especially over the shelf where turbulence prevents settlement of fine particles, thereby favoring advection to the slope (Fütterer, 1983). This effect is also seen on other continental margins, such as in the Middle Atlantic Bight (Anderson *et al.*, 1994), the eastern Arabian Sea (Calvert *et al.*, 1995) and in the Oman Margin (Shimmield *et al.*, 1990; Pedersen *et al.*, 1992). In all these areas, in spite of different environmental settings (bathymetry, river versus aeolian inputs, etc.), a  $C_{\text{organic}}$  maximum is observed on the upper or middle slope. On the northwest African margin, this organic depocenter between 1000 and 2000 m depth (Fütterer, 1983) is induced by the interplay of several different factors: production over the shelf; resuspension and advection to the slope, which carries indirectly more refractory material; production at the shelf break (which extends several hundreds km offshore within plumes and filaments), which carries materials more directly to the slope; and aeolian inputs of lithic particles whose size decreases seaward.

*e. Palaeoceanographic implications: Sea-level and upwelling intensity influence*

It is well documented that coastal upwelling systems have been affected at different frequencies and their locations have changed as a result of climatic forcing (see Summerhayes *et al.*, 1995). For example, in the Arabian Sea and off the northwestern and the southwestern African margins such variations have been interpreted to result from changes in wind forcing. Thus, periods of enhanced favorable wind stress led to enhanced upwelling intensity and plankton production (Müller and Süess, 1979; Prell and Van Campo, 1986; Sarnthein *et al.*, 1987; Shimmield and Mowbray, 1991; Shimmield, 1992; Martinez *et al.*, 1996; Schneider *et al.*, 1996; Holmes *et al.*, 1997).

*i. A comparison of past and modern conditions.* Proxies of past wind-stress, e.g. mean grain size, Ti/Al and Zr/Al ratios (see Peterson *et al.*, 1995), obtained in core 20bK (Fig. 6) show strong glacial-interglacial contrasts, with higher values during glacial periods, such as Stages 2 and 6. Furthermore, the mean grain size and the size frequency distributions

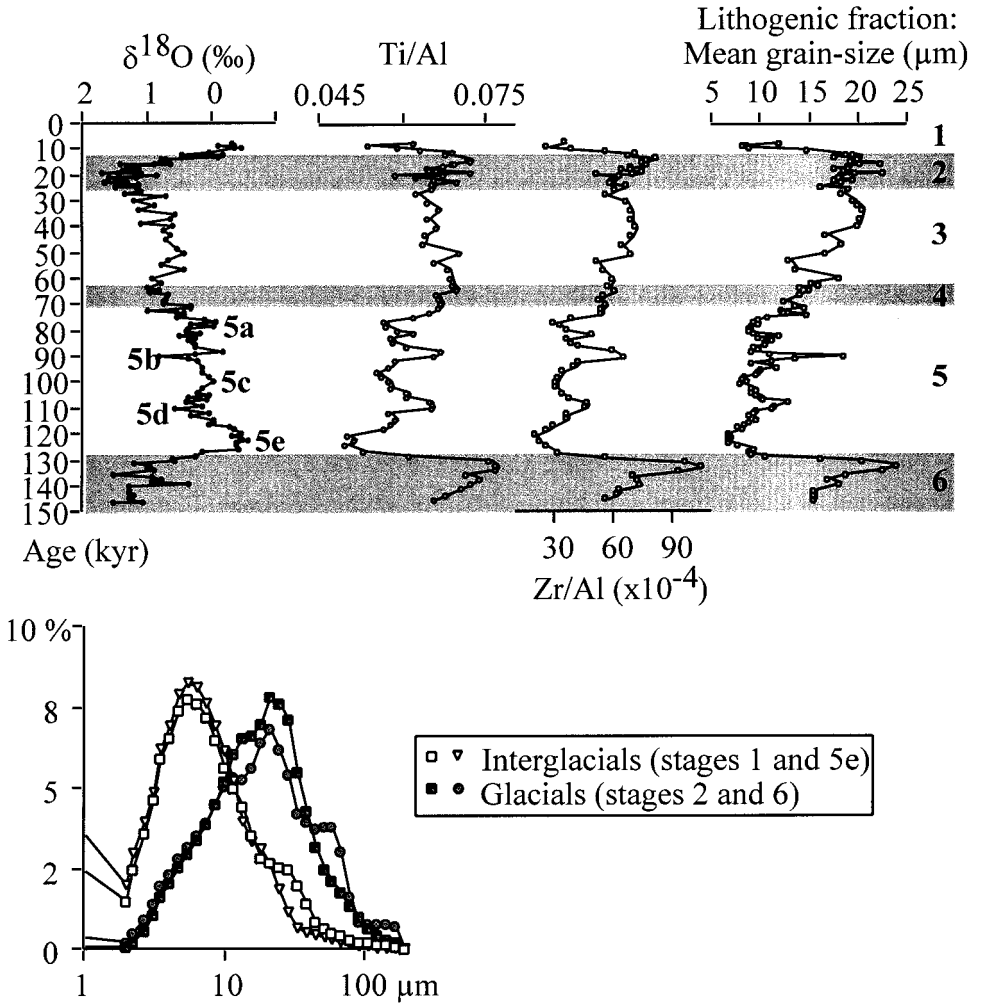


Figure 6. Records versus age (kyr) for piston-core 20bK of  $\delta^{18}\text{O}$  of planktonic foraminifera *Globigerina bulloides*; of different parameters related to the terrigenous fraction (Ti/Al, Zr/Al, mean-grain size), as well as selected frequency curves showing the dominant modes for glacial (stage 2 and 6) and interglacial (stages 1 and 5e). Shaded areas represent glacial stages.

during glacial stages are quite similar to those observed in the Holocene at site 11S, whereas interglacial values and distributions are quite similar to those at site 7S.

Glacial-interglacial  $\delta^{15}\text{N}$  and  $\delta^{13}\text{C}$  changes are also significant (Fig. 7).  $\delta^{13}\text{C}$  record parallels  $C_{\text{organic}}$  variations and reflect mainly the  $\text{CO}_2$  biological limitation for phytoplankton (Bentaleb et al., 1996). Glacial and interglacial  $\delta^{13}\text{C}$  values are similar to those obtained for eutrophic and meso/oligothrophic sites in the same area, respectively (Bentaleb, 1994).  $\delta^{15}\text{N}$  values show opposite variations: Stages 2, 3, 4 and 6 having lighter





are typical of marine planktonic material, (3) terrestrial organic biomarkers are constant and at the lowest level (Ternois, 1996). In addition, any single relationship can be observed between  $\delta^{15}\text{N}$ ,  $\delta^{13}\text{C}_{\text{organic}}$  and  $\text{C}_{\text{organic}}/\text{N}$  ratio signals (see Fig. 6 and 7), for instance, during Stage 2 or during Stage 5 where variations in  $\delta^{15}\text{N}$  are not accompanied by concomitant changes in  $\delta^{13}\text{C}_{\text{organic}}$  (Fig. 6). Second, diagenetic effects and hence differential preservation between glacial and interglacials can be ruled out because the  $\text{C}_{\text{organic}}/\text{N}$  ratios do not vary significantly. In addition, Zegouagh *et al.* (1999) have shown that the organic matter in core 20bK is similar in composition regardless of the climatic period. Third, as discussed previously, denitrification is not observed on the northwest African margin; if it had occurred during glacial, then the heavier  $\delta^{15}\text{N}$  values should be accompanied by productivity-dependent indicators ( $\text{C}_{\text{organic}}$  and biogenic barium; see Ganeshram *et al.*, 1995), whereas the opposite is observed. That is to say, the heavier values correspond to lower  $\text{C}_{\text{organic}}$  and biogenic barium concentrations (Fig. 7) (see below), as well as in some other areas (Calvert *et al.*, 1992; Farrell *et al.*, 1995; Holmes *et al.*, 1997). The mean glacial  $\delta^{15}\text{N}$  values are in fact similar to the Holocene values at site 11S (around 4.5‰), and interglacial values are similar to those at site 7S (around 6.5‰) (see Fig. 3 and 7).

Glacial stages are characterized by higher  $\text{C}_{\text{organic}}$  fluxes and contents, as well as by higher N and bio Ba contents. Since preservation was similar during glacial and inter-glacials, and since a major change of terrestrial organic input is excluded, glacial/interglacial changes in organic contents can be interpreted to variations in the supply of organic matter to the sea floor. Furthermore, advection of  $\text{C}_{\text{organic}}$  during glacial times is excluded since shelf sediments do not record any productivity-dependent parameters. A direct comparison between the paleoceanographic record and the Holocene sediment as represented by the multicores indicates that glacial  $\text{C}_{\text{organic}}$  concentrations correspond quite well with those at site 11S, and interglacial ones with those at site 7S.

An enhanced biogenic input during glacial periods is also confirmed by the biogenic barium content which generally increases at these times. It is now accepted that biogenic Ba (barite) can be a useful tool for paleoproductivity reconstruction (Dymond *et al.*, 1992; Gingele and Dahmke, 1994; François *et al.*, 1995), and that periods of enhanced production are accompanied by enhanced sedimentary barite content. We rule out significant barite remobilization (von Breyman *et al.*, 1992) because there is a strong covariance between  $\text{C}_{\text{organic}}$ , barite and other production indicators, such as benthic foraminifera (Guichard, 1997) and biomarkers (Ternois *et al.*, 2000; Sicre *et al.*, 2000).

Trace metals, such as U and Mo, and pyritic sulphur can be useful indicators of past sedimentary redox conditions and, indirectly, of the quantity and the quality of the organic input to the sediment. We have shown already that U, Mo and S are enriched in subsurface anoxic horizons of the multicores and that these enrichments are higher when organic material contents are higher and the intensity or extent of diagenesis is higher. These three elements also increase in concentration in core 20bK during glacial, suggesting that the redox boundary in the near-surface sediment was shallower at these times. Bottom water anoxia is excluded because of the abundance of benthic foraminifera and ostracods

throughout the core record (Guichard, 1997). The shallower redox boundary would have steepened the pore water concentration gradients during glacials, thereby increasing the diffusive flux of the metals and S into the sediment. The depth at which an element is fixed can be evaluated using Fick's law and the element flux (or mass accumulation rate) (see François *et al.*, 1993; Crusius *et al.*, 1996). As an example, we estimate the flux of authigenic U ( $F_U$ ) by first correcting the total U for the lithogenous contribution using the lowest U/Al value ( $U/Al_{\min}$ ) in the core as representative of the contribution of the nonauthigenic fraction:

$$U_{\text{authigenic}} (\text{mol g}^{-1}) = U_{\text{total}} - (Al \times U/Al_{\min}).$$

This gives then a minimum  $U_{\text{authigenic}}$  concentration and  $U_{\text{authigenic}}$  flux from the product of the U concentration and the mass accumulation of the sediment and hence a maximum depth for U reduction ( $Z_U$ ):

$$F_U (\text{mol cm}^{-2} \text{ s}^{-1}) = U_{\text{authigenic}} \times \text{MAR}$$

(for details concerning MAR calculation and results, see Martinez *et al.*, 1996; Bertrand *et al.*, 1996).  $F_U$  must also equal the diffusive flux of U along the pore water gradient. We assume, as a first approximation, a linear pore water gradient from the seawater concentration at the sediment-water interface ( $1.3 \times 10^{-11} \text{ mol/cm}^3$ ) to  $0 \text{ mol/cm}^3$  at the depth of U reduction (see François *et al.*, 1993).

$F_U (\text{mol cm}^{-2} \text{ s}^{-1}) = (D \times C)/Z_U$ , with, D: pore water diffusion coefficient for U ( $3 \times 10^6 \text{ cm}^2 \text{ s}^{-1}$ ; Klinkhammer and Palmer, 1991); C: concentration of U in seawater ( $1.3 \times 10^{11} \text{ mol cm}^{-3}$ ). Therefore:

$$F_U = U_{\text{authigenic}} \times \text{MAR} = (D \times C)/Z_U, \text{ and we can solve for } Z_U:$$

$$Z_U = (D \times C)/(U_{\text{authigenic}} \times \text{MAR}).$$

The mean of the  $Z_U$  for two different periods, for example Stages 2 and 5, can be estimated using the mean  $U_{\text{authigenic}}$  fluxes for these time periods. The result gives a maximal  $Z_U$  of around 2 cm (below the interface) during Stage 2, and around 10–15 cm during Stage 5. These results clearly demonstrate that redox fronts were compressed and moved up to the interface during glacials. These calculations give results that are close to the direct measurements on the multicores. Thus, U increases at about 1–2 cm in core 11S, similar to the depth of U reduction calculated for glacial Stage 2. On the other hand, the calculated interglacial  $Z_U$  is greater than the measured one in core 7S, possibly due to the fact that we calculate a maximum  $Z_U$  value.

ii. *Paleoceanographic reconstruction.* We have previously suggested that the glacial benthic conditions at site 20b were similar to the modern conditions encountered at site 11 (proximal site), whereas interglacial conditions were similar to those encountered at site 7 (distal site). At the latitude of Cap Blanc the shelf is narrower than at 25N; the present

distance of core-site 7S from the coast (190 km) is broadly similar to the distance of core 20bK from the coast during Stage 5e, and core 11S is roughly the same distance from the coast (approximately 70 km) as was core 20bK during the LGM. As the present-day production on the northwest African margin occurs mainly over the shelf and the upper slope and gradually decrease seaward around 25N (Van Camp *et al.*, 1991; Gabric *et al.*, 1993), site 20b must have been closer to the productive area during Stage 2 due to lower sea level and the consequent offshore displacement of the productive areas.

How do the changes in paleogeography influence or control the sedimentary record on this continental margin? What were the dominant controls: wind stress and upwelling intensity variations, or sea-level and the relative location of the productive areas with respect to the core site? Are both of them important? For example, do the increases in the mean grain size and Ti/Al and Zr/Al ratios reflect an enhanced wind stress or do they reflect changes in sea-level and the proximity of lithogenic sources (dune fields)? Similarly, do the lighter  $\delta^{15}\text{N}$  values reflect a decrease in relative nutrient utilization because of enhanced upwelling intensity and nutrient availability or because of changes in the location of upwelling centers relative to the core-site?

As a consequence of the offshore displacement of the coastline during glacials, aeolian sediment sources were closer to core site 20bK. Thus, the transport of coarser grained particles could have been consequently enhanced. Indeed, the modal distribution of grain-sizes during glacials is similar to that observed at site 11S, whereas inter-glacial distributions are similar to those at site 7S. We, therefore, conclude that glacial terrigenous material is coarser because sources of materials are closer. Although other studies mainly based on deep ocean core sites suggest a major control of grain size changes by changing wind stress (Sarnthein *et al.*, 1981; Rea, 1994; Matthewson *et al.*, 1995; Balsam *et al.*, 1995; Martinez *et al.*, 1996; Grousset *et al.*, 1998), this does not exclude the possibility that sea level and source proximity variations could explain at least part of the variations observed in our records (Fig. 5: Mean grain size, Ti/Al, Zr/Al) (see Ruddiman *et al.*, 1989).

During inter-glacials, biological production occurs mainly over the shelf and the upper slope, and gradually decreases several hundreds km offshore, as can be seen on contemporary satellite imagery (Van Camp *et al.*, 1991; Gabric *et al.*, 1993). We have shown on the bathymetric transect of multicores that the nitrogen isotopic composition becomes heavier and that, concomitantly, organic carbon content decreases as the sites are more distant from the center of upwelling (from core 11S to core 7S). We have attributed this observation to a relative increase in nutrient utilization as waters move offshore. Therefore, in core 20bK, glacial  $\delta^{15}\text{N}$  was lighter than inter-glacial values because the core site was closer to the upwelling center over the shelf break instead of over the shelf. During glacials, the core site was near the productive area, where nutrients were not as extensively utilized; on the other hand, during interglacials the site was farther away from the production center where most of the upwelled nutrients have been used so that the remaining pool was isotopically heavier. This mechanism is similar to that proposed earlier to explain the differences between cores 11S, 9S and 7S.

Therefore, it seems at first glance that sea-level changes and, hence, core-site position relative to the locus of the upwelled waters could produce the observed downcore records. This would not involve changes in upwelling intensity and thus production. However, such changes have recently been proposed by Bertrand *et al.* (2000) who have developed a numerical model to explain why most of the sedimentary  $\delta^{15}\text{N}$  profiles from coastal upwelling areas show the heaviest values during deglaciation. Their simulation shows that the invasive waters over the shelf cause an initial increase and then a decrease in  $\delta^{15}\text{N}$  because of nutrient recycling over the shelf. Because their simulation does not take into account upwelling intensity changes, this is taken as evidence for a sea-level impact on the  $\delta^{15}\text{N}$  record.

How could sea-level changes have affected production-induced sedimentary properties such as  $C_{\text{organic}}$ , biogenic barium and trace metals? We know from present-day conditions that there is a significant transport of organic material from the shelf toward the slope depocenter. During glacial times, this process did not occur since the shelf was exposed and could not have exported fine-grained material, including organic matter. Thus, changes in  $C_{\text{organic}}$  contents between glacials and inter-glacials in core 20bK are better explained by changes in production intensity; a shorter distance of the core-site from the productive areas during glacials in comparison to inter-glacials emphasizes this difference. During inter-glacials, the greater distance led to a greater fraction of advected, more degraded and refractory material to be buried; during glacials, a larger fraction of fresher material directly carried from the water column to the sediment could have been buried, leading to enhanced diagenetic reaction and consequently a higher trapping efficiency of trace metals.

Our results demonstrate that the development of the paleoclimatic-paleoceanographic record of 20bK depends on a large number of parameters, principally sea-level and upwelling intensity changes. The main difficulty in our case is that they both act in the same direction, that is to say that they will have an additive effect on the sedimentary record. But they could have acted with their own periodicity. For example, a lower sea-level and an increased upwelling intensity should both result in lower  $\delta^{15}\text{N}$  values. It is obvious that sea-level changes during the Late Quaternary have played an important role in controlling sedimentation on continental margins, especially those with modern wide shelves. But it is evident that atmospheric changes (e.g., wind stress and direction, latitudinal extension of the Trade Winds) also occurred during the Late Quaternary and also controlled the upwelling intensity and hence the sedimentary record. Further studies are needed to fully understand the wide range of interrelated processes which are conducive to the building of the paleoceanographic-paleoclimatic records.

## 5. Conclusions

A multi-proxy approach has been used to study recent sedimentation on the northwest African margin where strong coastal upwelling occurs. First, there are strong biogeochemical differences between the modern sediments from a set of multicores recovered along a latitudinal and bathymetric transect off Cap Blanc. Nutrient gradients along this transect

are recorded in the  $\delta^{15}\text{N}$  of the underlying sediments and reflect increased nutrient utilization from the onshore to the offshore sites; shallower sites have more  $^{15}\text{N}$ -depleted isotopic compositions than deeper ones. Consequently, the shallower sites also have higher organic carbon and trace-metal contents that reflect the proximity of productive areas (over the shelf) and the coastline. Differential preservation of the deposited organic matter does not seem to be an important influence on the bulk organic composition of the sediments.

A downcore study has demonstrated that the sedimentary regime at the core site depends on its position relative to the locus of upwelling and production. This has strong implications for understanding the palaeoceanographic record in the same area, since sea-level changes will induce changes in the proximity of the core site to the productive areas (over the shelf during interglacials and over the shelf-break and the slope during glacials). We interpret changes in  $\delta^{15}\text{N}$ ,  $C_{\text{organic}}$  and grain-size as being influenced both by sea-level changes and upwelling intensity (through wind stress). Further studies are needed to fully understand all these processes which have different effects on the formation of paleoceanographic-paleoclimatic records, especially on continental margins.

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