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Optical and geochemical study of organic matter in present oxic sediments (equatorial North Pacific Ocean NIXO area)

Figured organic matter
oxic sediments
palynofacies
amino acids

Matière organique figurée
sédiment oxique
palynofaciès
acides aminés

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ABSTRACT

Optical (palynofacies) and geochemical (C, N, amino acids) study of surface sediments from the equatorial North Pacific Ocean, which are deposited in an oxic environment and characterized by ferromanganese nodule occurrence, revealed figured remains of pelagic, benthic and terrestrial organic matter. These organic remains consist of a residual organic fraction, related to alteration phenomena. The scarcity of amorphous organic matter contrasts markedly with anoxic sediments. Amino acid comparison between hand-picked figured organic elements and bulk sediments indicates that coarse components have distinct compositions, some being biologically active sites; the preserved amino acid content of bulk sediments being mostly related to fine fractions as clays.

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RÉSUMÉ

Étude optique et géochimique de la matière organique figurée de sédiments oxiques actuels (Pacifique Nord-équatorial : zone Nixo).

L'étude optique (palynofaciès) et géochimique (C, N, acides aminés) des sédiments superficiels du Pacifique nord-équatorial, déposés dans un environnement oxique et caractérisés par la présence de nodules polymétalliques, a révélé la présence de restes figurés de matières organiques pélagiques, benthiques et terrestres. Il s'agit d'une matière organique résistante aux phénomènes d'altération. Leur pauvreté en matière organique amorphe oppose ces sédiments aux dépôts anoxiques. L'analyse des acides aminés du sédiment et des constituants organiques figurés triés à la pince montre que ces restes ont une composition spécifique, certains pouvant être considérés comme des sites biologiquement actifs. La composition moyenne du sédiment en acides aminés est représentée essentiellement par les fractions argileuses.

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INTRODUCTION

The organic content of surface sediments in the Pacific manganese nodule belt (Müller and Mangini, 1980; Piper, 1988), and more generally in abyssal areas, is known to be especially low aerobic decomposition (Bender and Heggie, 1984) and extremely low sedimentation rates being responsible for the poor conservation of organic matter. The apparent efficiency of oxic sedimentary environments in the degradation of organic matter would seem to depend mostly on benthic activity (bioturbation, macrobenthos feeding) rather than on intrinsically different kinetics of organic matter decay between oxic and anoxic sediments (Müller and Mangini, 1980; Reimers and Suess, 1983; Pelet, 1984; Westrich and Berner, 1984; Middlenburg, 1989). However, the actual roles of micro and macrobenthos in organic matter decomposition are not clearly established (Jannasch and Wirsen, 1973; Cahet and Sibuet, 1986; Khripounoff and Rowe, 1985), and the relative importance of the processes occurring at the sediment-water interface and in the superficial sediments is still questioned (Emerson *et al.*, 1985; Reimers and Smith, 1986; Martin and Bender, 1988).

Conversely, organic matter accumulation is reserved to continental shelves and oceanic areas of high productivity (berner, 1982), generally in anoxic sediments (Demaison and Moore, 1980), despite the fact that no difference between organic matter burial efficiency in present oxic and anoxic environments (other than relative to sedimentation rates) has been suggested (Henrisch and Reeburgh, 1987).

The purpose of the present study was to seek figured organic debris (palynofacies) preserved in oxic pelagic sediments (Equatorial North Pacific, Nixo area) for a comparison with more organic pelagic sediments having rhytmically fluctuating organic carbon contents (Oman Sea, Ocean Drilling program, Leg 117). Additionally, the organic content (C, N, amino acids) of selected coarse components and bulk sediments from the Nixo area were examined in an attempt to localize specific organic remains or sites of biological activity in the sediment.

MATERIAL AND METHODS

Sampling

Sediments were cored during the NIXO 47 cruise of R/V *Jean Charcot*. Two geographical areas, the "Gouttière" area and the "Seamount" area, were considered. They are respectively centred at 14°04'N, 130°54'W and 14°35'N, 130°40'W (Le Suavé *et al.*, 1987).

Sampling was made with box-corers (AET-TAAF). Eight cores from the "Gouttière" area and three from the "Seamount" area were studied (Tab. 1). Surface layers of the cores were collected on shipboard and then frozen. Cores (T 47004, T 47012 and T 47024) were stored at 2°C until further sumpling of the top 50 cm was made.

Marine anoxic sediments were recovered on Leg 117 of the Ocean Drilling Program in quaternary series drilled at the Oman Margin (Tab. 1). Petrographical and geochemical investigations are detailed elsewhere (Bertrand *et al.*, in press).

Microscopy

The description of organic matter is based on the study of chemically-isolated organic matter (palynofacies) and organic figured components (isolated by handpicking) by means of light microscopy and SEM. Palynofacies study involves description of the aspects of organic components of a rock, using transmitted light microscopy and the evaluation of their relative proportions (Combaz, 1964). In order to eliminate mineral fractions and hydrolyzable organic matter (humic substances), several chemical attacks are conducted on the bulk sample leading to the kerogen. For oxic sediments which do not contain more than 0.5 % TOC, quantities ranging from 300 to 500 mg are required. The chemical treatment is adapted from that described by Durand and Nicaise (1980). Characterization of kerogen is made on the basis of Combaz (1980). The kerogen preparations serve also for SEM observations.

The coarse fractions were obtained by wet-sieving the sediments (125 and 250µm) in bi-distilled water. After description in light microscopy, organic components, radiolarian skeletons and Mn micronodules were handpicked for amino-acids analyses. In contrast with the palynofacies preparation, mechanical separation preseves hydrolyzable figured organic components. Unstable aggregates (Duchaufour *et al.*, 1984) were not considered.

Chemical analysis

ORGANIC CARBON AND TOTAL NITROGEN

Total organic carbon (TOC) was evaluated by the combustion method with Carmhograph 8 (Wösthoff) equipment. Samples were decarbonated with 2N HC1 and dried prior to calcination. Total carbon and nitrogen were analyzed using a CHN Carlo Erba analyzer.

AMINO ACIDS

Hydrolyzable amino acid compositions of bulk sediments were analyzed following previous procedure (Hare, 1973). Samples were placed in screwcap vials flushed with nitrogen and hydrolyzed with 5.6 N HC1 at 110°C for 20 hours. Metals (mostly iron) were eliminated as the hydroxides (NaOH) by centrifugation. After supernatent liquid was neutralized by HC1 and rotary-evaporated, NaC1 was discarded by insolubilization in concentrated HC1. The recovery of internal standard (norleucine) was mostly gretaer than 90 %. Mn micronodules were treated with a protein hydrolyzing specific technique, using oxalic acid (Iachan *et al.*, 1961) recently used for studying Mn oxides (Lallier-Vergès and Albéric, 1989). The recovery of amino

Table 1
Location of NIXO 47 studied sediments, water content (wet weight %), coarse fraction (dry weight %) and total organic carbon content (TOC ± 0.05)
Situation géographique et profondeur d'eau des sites de prélèvement de sédiments de NIXO 47, teneur en eau (par rapport au poids humide), pourcentage des fractions grossières (par rapport au poids sec) et carbone organique total (TOC ± 0,05 %).

CORE	°LAT N	oLONG W	WATER-DEPTH (m)	% WATER CONTENT	% > 250 µm	% > 125 µm	% TOC
"Gouttière" Area							
T47004	14°06.59	130°53.95	4 990	66.86	0.20	0.44	0.39
T 47007	14°06.89	130°53.75	4 995	71.35	0.09	0.52	0.35
T 47011	14°07.35	130°53.62	4 995	72.92	0.18	0.49	0.64
T 47012	14°03.55	130°56.62	4 990	69.25	0.14	0.74	0.57
T 47014	14°02.99	130°56.94	5 010	75.09	0.13	0.62	0.36
T 47016	14°04.10	130°56.26	5 000	75.57	0.10	1.54	0.66
T 47018	14°02.90	130°57.10	5 050	73.66	0.00	0.71	0.33
T47021	14°04.72	130°55.89	5 010	76.21	0.26	0.74	
"Seamount" Area							
T 47024	14°46.17	130°47.67	4910	71.92	0.13	0.49	0.47
T 47029	14°39.04	130°41.90	5 055	65.80	0.56	0.56	0.43
T 47031	14°40.28	130°40.83	5 055				
T 47032	14°35.49	130°41.87	5 120	69.04	0.26	0.61	0.58

Table 2
Leg 117 studied sediments (depth below the seafloor in metres, TOC in %).
Sédiments étudiés au cours du leg 117 (profondeur en mètres, carbone organique total en %).

Hole, Core, Sect., Interval (cm)	Depth m	TOC	Lithology
723A-36X-4, 45-47	331.25	4.69	Calcareous clayey silt
724A-1H-2, 122-124	2.72	0.64	Calcareous clayey silt
724-4H, 71-73	27.61	2.21	Calcareous clayey silt
724A-4H-3, 71-73	29.11	0.44	Calcareous clayey silt
726A-4H-5, 20-22	31.60	0.34	Foram. bearing nannofossil ooze
726A-5H-1, 86-88	35.76	2.90	Calcareous clayey silt
728A-16X-2, 30-32	145.30	2.77	Marly nannofossil ooze
728A-27X-4, 67-69	254.97	0.83	Marly nannofossil ooze
729A-4R-5, 0-2	28.30	0.91	Nanno, bearing marly limestone
729A-4R-5, 85-87	29.15	0.04	Nannofossil bearing limestone
730A-26X-2, 40-42	241.50	0.31	Marly nannofossil chalk
730A-26X-5, 40-42	246.00	0.94	Calcareous clayey silt
730A-5H-4, 109-111	42.39	3.09	Diatomaceous silty clay
730A-5H-6, 109-111	45.39	1.32	Diatomaceous marly nanno. ooze
730A-7X-2, 130-132	58.60	4.58	Diatomaceous silty clay

acids is better with the procedure, because HC1 hydrolysis destroys amino acids in the presence of Mn-oxides. Demineralization steps were omitted for other coarse components. Amino acid analysis was carried out on a Beckman 118 BL autoanalyzer.

BULK SEDIMENT OUTLINES

Chemical characterization

General sediment lithofacies are brown radiolaria-bearing to radiolaria-rich argillaceous muds (for more details concerning sedimentary features of Nixo sediments, see Ricou, 1990). Organic carbon in top sediments of the Nixo area ranges from 0.3 to 0.7 % (Tab. 1) and decreases to 0.2 % at 40 cm depth (Tab. 2). These results are typical for recent deep-sea deposits of similar environment (Whelan, 1977; Müller, 1977; Müller and Mangini, 1980; Khripounoff and Row, 1985; Piper, 1988). The C/N ratio is low (about 6 at the water-sediment interface) and decreases with depth (Fig. 1). This particularity of distant offshore deep-sea sediments (Müller, 1977) distinguishes them from other marine sediments (Jocteur-Monrozier and Jeanson, 1979) where C/N ratios generally increase with depth in cores in response to a greater lability of organic nitrogen compounds. C/N decrease in superficial deep-sea sediments is probably dependent on associations of ammonia and some organic nitrogen with clays (Müller, 1977) and may extend during further diagenesis (Waples and Sloan, 1980). There are indications that the phenomenon does no depend on a strict conservation of amino acids (Whelan, 1977) or aliphatic amines (Lee and Olson, 1984). Sediment tops (T 47004, T 47012 and T 47024) have total amino acid contents from 9 to 14 micromoles (Tab. 3). These values are also characteristic of deep-sea deposits (Degens *et al.*, 1964; Degens, 1970, Schroeder and Bada, 1976; Albéric and Khripounoff, 1984, Steinberg *et al.*, 1987). Superficial sediments with lower values (0.2 micromoles/g) have been reported by Whelan (1977). In the three top samples studied, amino acid-C comprises

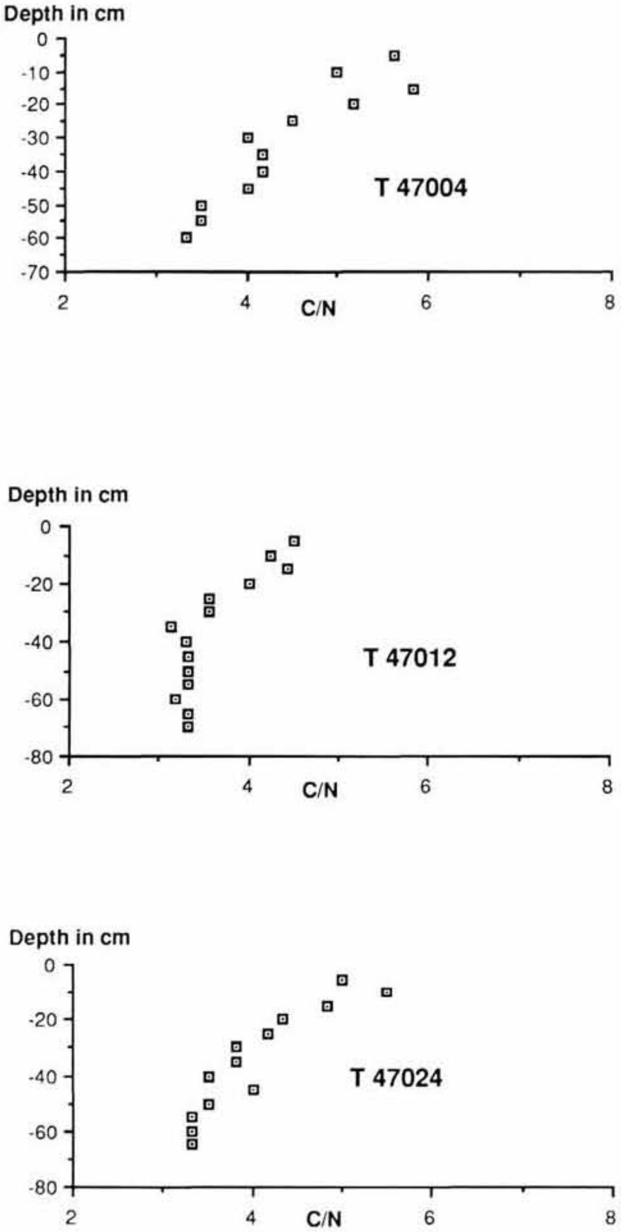


Figure 1

C/N profiles in T 47004, T 47012 and T 47024 cores.
Profils du rapport C/N le long des carottes T 47004, T 47012 et T 47024.

Table 3
Total organic carbon (TOC) and total nitrogen (TN) contents in T 47004, T 47012 and T 47024 cores. Depths in cm.
Teneurs en carbone organique total et azote total le long des carottes T 47004, T 47012 et T 47024. Profondeurs en cm.

SAMPLE T 47004	% TOC	% TN	SAMPLE T 47012	% TOC	% N	SAMPLE T 47024	% TOC	% TN
5-7	0.45	0.08	5-7	0.36	0.08	5-7	0.35	0.07
10-12	0.35	0.07	10-12	0.34	0.08	10-12	0.33	0.06
15-17	0.35	0.06	15-17	0.31	0.07	15-17	0.29	0.06
20-22	0.31	0.06	20-22	0.28	0;07	20-22	0.26	0.06
25-27	0.27	0.06	25-27	0.25	0.07	25-27	0.25	0.06
30-32	0.24	0.06	30-32	0.25	0.07	30-32	0.23	0.06
35-37	0.25	0.06	35-37	0.22	0.07	35-37	0.23	0.06
40-42	0.25	0.06	40-42	0.23	0.07	40-42	0.21	0.06
45-47	0.24	0.06	45-47	0.20	0.06	45-47	0.24	0.06
50-52	0.21	0,06	50-52	0.20	0.06	50-52	0.21	0.06
55-57	0.21	0,06	55-57	0.20	0.06	55-57	0.20	0.06
60-62	0.20	0,06	60-62	0.19	0.06	60-62	0.20	0.06
			65-67	0.20	0.06	65-67	0.20	0.06
			70-72	0.20	0.06			

about 12-15 % of total organic carbon and amino acid-N, 19-25 % of total nitrogen. Ammonium-N (contained in 5,6 N HCl hydrolysates) corresponds to about 12-15 % of total nitrogen. Although amino acid contents decrease with depth (5 micromoles/g at 40 cm), the proportion of amino-C remains mostly constant, indicating no preferential loss of amino acids versus whole organic matter (TOC). On the contrary, amino-N percentage diminution with depth (12 % at 40 centimetres) indicates the occurrence of some more resistant organic nitrogen fractions (neither ammoniac, nor amino acids), responsible for the decrease of C/N ratios.

The studied sediments contain appreciable proportions of non-proteic amino acids (β-alanine and γ-aminobutyric acid) (Fig. 2a). These compounds (in very small quantities in planktonic organic matter and settling marine particles) are relatively abundant in superficial deep-sea sediments, where they appear to be with clays (Degens, 1965; Schrœder, 1975; Whelan, 1977). Present in deep-sea sediments as NaOH non-extractible compounds (Albéric and Khripounoff, 1984), these amino acids may be considered as residual with reference to their relative increase during the transit of organic matter in the digestive tract of deposit-feeding invertebrates. During burial, following the diminution of total amino acid contents, these two compounds may become the major amino acids of sediments (Schrœder and Bada, 1976; Whelan, 1977). At a depth of 40 cm in the T 47012 core, they account for about 40 % of total amino acids (Fig. 2b). However, their contribution to the preserved total nitrogen is very low.

As observed for these sediments and in previous studies, the sedimentation of deep-sea clays in an oxic environment is characterized by an early relative enrichment in β-alanine and γ-aminobutyric acid, which is not observed in shallower sediments (Terashima, 1979; Rosenfeld, 1979) or in deep-sea sediments richer in organic carbon (Henrichs *et al.*, 1984). However, deep burial (> 100 m) in anaerobic conditions seems to lead to an equal relative increase of non-proteic amino acids in the sediments (Hare, 1973; Schœder and Bada, 1976).

Palynofacies composition

OPTICAL AND ELECTRON MICROSCOPY OBSERVATION

The very weak amount of extracted organic matter in the water-sediment interface samples has three major types of component: planktonic organisms and algae; benthic organisms; and material of terrestrial origin (lignaceous debris, spores and pollens).

Organic debris exhibiting membrane shapes (Pl. 1C) have been classified with algae. Their morphology recalls the

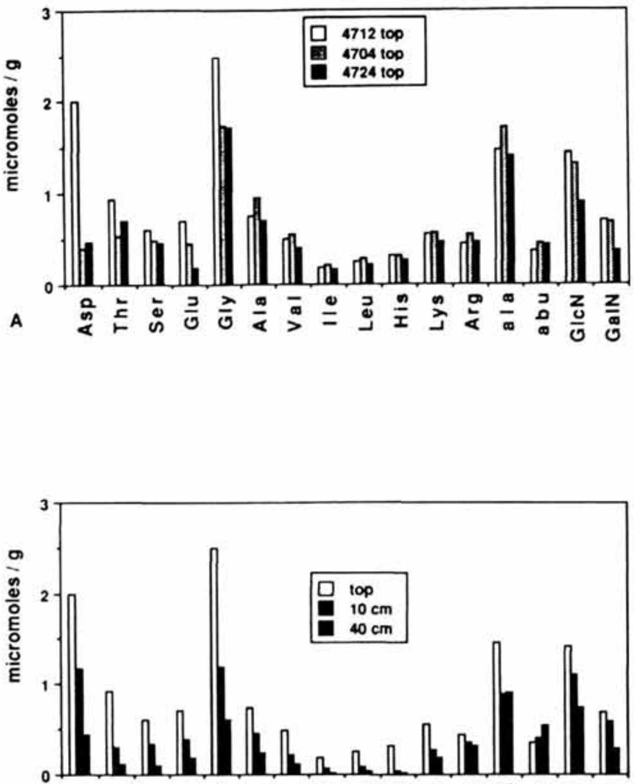
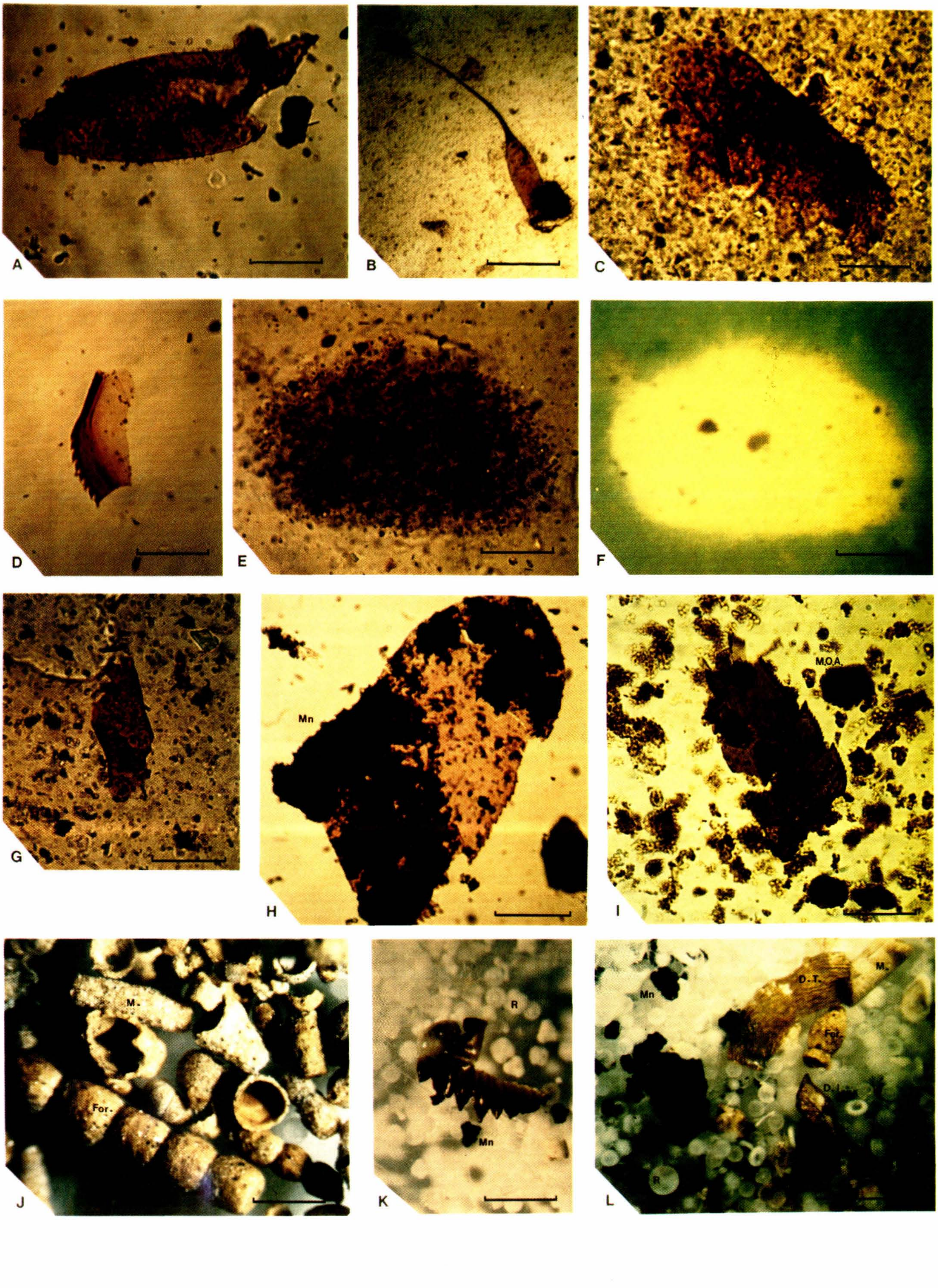


Figure 2

Composition of hydrolyzable amino acids in surface sediments (A) and with depth in T 47012 core (B). Aspaspartic acid; Thr – threonine; Ser – serine; Glu – glutamic acid; Gly – glycine; Ala – alanine; Val – valine; Ile – isoleucine; Leu – leucine; His – histidine; Lys – lysine; Arg – Arginine; βala – β-alanine; γ-abu – γ-aminobutyric acid; GlcN – glucosamine; GalN – galactosamine.

Composition en acides aminés des sédiments superficiels (A) et le long de la carotte 47012 (B).


A
B
C
D
E
F
G
Mn
H
M.O.A.
I
M.
For.
J
R
Mn
K
Mn
D.T.
M.
For.
D.T.
R
L

◀ Plate 1

Transmitted light microscopy (A, B, C, D, E, G, H, I); stereo-macroscope (J, K, L)
Microscopie en lumière transmise (A, B, C, D, E, G, H, I); loupe binoculaire (J, K, L).
A – Alveolate plankton, T 47004 sample (scale bar = 100 μm).
Plancton alvéolé, échantillon T 47004 (échelle = 100μm).
B – marine figured undetermined organism, T 47021 sample (scale bar = 25 μm).
Organisme marin figuré indéterminé, échantillon T 47021 (échelle = 25 μm).
C – Membranous fragment (possibly algal), T 47012 sample (scale bar = 100 μm)
Fragment membranaire sans doute algaire, échantillon T 47012 -échelle = 100 μm).
D – Arthropod appendix fragment, T 47018 sample (scale bar = 100 μm).
fragment d'appendice d'arthropode, échantillon T 47018 (échelle = 100 μm).
E – Brown shapeless "amorphous" organic aggregates from T 47011 (scale bar = 100 μm).
Flocons de matière organique "amorphe", échantillon T 47011 (échelle = 100 μm).
F – Same aggregates under UV excitation : fluorescence emission.
Mêmes flocons vus sous excitation UV : teinte de fluorescence.
G – Arthropod epiderm, T 47024 sample (scale bar = 100 μm).
Epiderme d'arthropode, échantillon T 47024 (échelle = 100 μm).
H – Arthropod appendix coated with Mn oxides, T 47018 sample (scale bar = 100 μm).
Appendice d'arthropode encroûté d'oxydes de Mn, échantillon T 47108 (échelle) 100 μm).
I – Arthropod appendix associated with "amorphous" organic matter (Oman Margin), (scale bare = 100 μm).
Appendice d'arthropode associé à de la matière organique "amorphe" (Marge de l'Oman), (scale bar = 100 μm).
J – Benthic foraminifera (For) and "manchons" (M), handpicked in surface sediments (scale bar = 1 mm).
Foraminifères benthiques avec loges (For) et "manchons" (M), prélevés dans les sédiments de surface (échelle = 1 mm).
K – Arthropod debris, radiolaria (R) and concretional Mn micronodules (Mn), T 47024 samples (scale bar = 500 μm).
Débris d'arthropode, radiolaire (R) et micronodules de Mn concrétionnaires (Mn), échantillon T 47024 (échelle = 500 μm).
L – Translucent laminated debris (d.t.), benthic foraminifers (For, M), concretional Mn micronodules (Mn) and radiolaria (R), T 47018 sample (scale bar = 1 mm).
Débris organique laminé translucide (d.t.), foraminifères benthiques (For, M), micronodules de Mn concrétionnaires (Mn) et radiolaires (R), échantillon T 47018 (échelle) 1 mm).

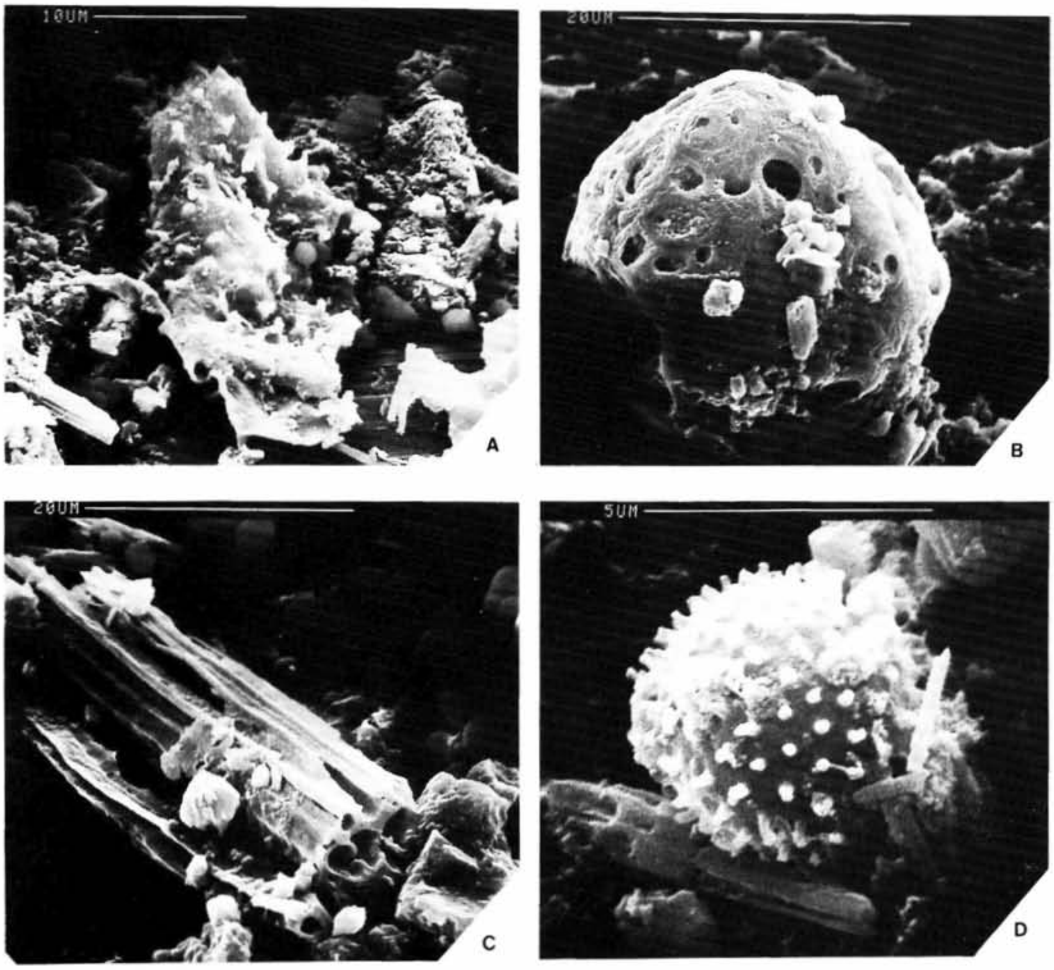


Plate 2

SEM observations
Observations au MEB.
A – Epiderm arthropod fragment
Fragment d'épiderme d'arthropode.
B – Carbonaceous spherule
Sphérule carboné.
C – Lignaceous debris
Débris ligneux.
D – Spore.

organic structures obtained by Janin and Bignot (1983) after Mn nodule dissolution. Alveolate plankton without any mineralized skeleton (Pl. 1A) often occurs. Undetermined organoclasts (Pl. 1B) with a bottle-shaped morphology have often been found. In some samples, orange-brown shapeless organic matter aggregates associated with mineral groudmass have been observed (Pl. 1E).

Epiderm and appendix fragments of arthropods (Combaz, 1980) are the best preserved fragments (Pl. 1D, 1G, 2A). They are often covered with Mn oxides (Pl. 1H).

Carbonaceous spherules have been observed by SEM (Pl. 2B). They could be soot or forms of industrial pollution (Jedwab, 1971). Lignaceous debris (Pl. 2C), spores and pollens (Pl. 2D), representing the organo-detrital fraction, are present in all the sediments. Lignaceous debris are altered but still translucent in light microscopy. These terrestrial components are air-oxidized debris (Huc, 1978).

Due to the small number of "Seamount" area samples, it is difficult to establish reliable comparisons between areas. However, figured organic matter seems more abundant in the "Gouttière area" than in the "Seamount" area. The upper part of T 47031 core, located on the seamount, which is enriched in volcanic components, is devoid of kerogen.

Organic debris in T 47004, T 47012 and T 47024 cores shown a strong diminution with depth and disappear at about 30 cm. Thus, figured organic matter, although refractory to superficial alteration processes, appears still metabolizable beneath the water-sediment interface, if we consider the organic matter input to be constant.

UV EXCITATION OBSERVATION

Excitation by an incident UV beam (365 nm) permits the characterization of organic matter by its own fluorescence emission, and the evaluation of its evolution state during diagenesis. The previously described shapeless aggregates exhibit a fluorescence emission (Pl. 1F) similar to that of some immature algal particles. This fluorescence emission undergoes a negative alteration after a few minutes of continuous UV excitation. This phenomenon could be related to the presence of hydrocarbons inside these aggregates (Martinez *et al.*, 1987); in that case, their occurrence would remain to be explained. The other observed marine organic debris do not present any fluorescence emission.

Comparison with Oman margin anoxic sediments

In Oman margin anoxic sediments, the main component is optically amorphous organic matter (up to 95 % of kerogen) (Pl.1I), consisting of orange-brown coloured aggregates (Bertrand *et al.*, in press). Surface sediments from the Oman Margin (Caratini *et al.*, 1981) also present the same charateristics (97 % of amorphous organic matter). When studied by TEM, amorphous organic matter often exhibits a membrane-shaped structure (Raynaud *et al.*, 1988) and would mainly result from the degradation of phytoplankton. The aspect of the amorphous organic matter from Oman Margin sediments, using transmitted light microscopy, is similar to that of aggregates described in NIXO oxic sediments.

Figured organic debris from Oman Margin sediments are mainly of marine origin. They constitute the main part of organic matter when the TOC contents is low (0.5 – 0.2 %). Their components are similar to those from NIXO sediments : refractory parts from pelagic and benthic organisms (Pl. 1I). These results suggest that this residual figured organic matter is weakly affected by oxidation processes.

Discussion

The main difference in respect of kerogen composition between anoxic and oxic studied sediments, relates to the proportion of the "amorphous" organic matter.

Caratini *et* al. (1983) have shown along a transect running offshore from the Mauritanian coast that the quantity of "amorphous" organic matter decreases in relation to figured organic matter when descending the continental slope. This result may reflect the limited influence of coastal upwelling and consequently the boundaries of high phytoplanktonic development, but it may also reveal the increasing alteration degree of the deposited organic matter due to oxygenated bottom waters.

In oxic deposits (equatorial North Pacific), the isolated organic matter presents sparse "amorphous" organic matter showing that through the trophic chain (pellets), a little part of phytoplanktonic matter may attain deep-sea sediments.

Oceanic upwelling domains (equatorial Pacific) do not yield such a massive phytoplanktonic production as coastal upwelling regimes (Degens *et al.*, 1976). The lack of detrital sedimentation promotes a very low sedimentation rate and a long period of contact with cold O2-enriched bottom waters; degradation processes due to biological and microbial activity may occur, and reactive organic matter is consumed.

COARSE FRACTION BIOGENIC COMPONENTS

The proportions of the coarse fractions are given in Table 1. Data were recalculated for sediment dry weight. When clay aggregates are eliminated, the coarse fractions generally represent less than 1 % of total sediment weight. Coarse fractions are more abundant in sediments with a high volcanic contribution (T 47031) because they are principally composed of volcaniclastic debris.

Description of the different components

All the coarse fractions of surface sediment samples frozen on shipboard contain organic debris. In the > 250 µm fractions, there are mainly benthic animal fragments (Pl. 1K) and vegetal debris. In the > 125 µm fractions, they correspond to pelagic remains and brown translucent organic debris with a slightly laminated structure (Pl. 1L) which were not observed in chemically isolated organic matter (see above).

The presence of benthic foraminifera (up to 30 % of the coarse fraction in the T 47011 > 250 µm sample) is a constant parameter of these sediments (Pl. 1J). One type has a test composed of orange coarse-grained silicate minerals with a cellular shape. Other types (called "manchons") with a tubular structure have tests made of a pale-grey fine-grained siliceous cement.

The proportions of Radiolaria are high, mainly in the > 125 µm fractions (70-95 %). Their shells are well-preserved, except in the T 47029 core.

Mn micronodules, quantities of which range from 5 to 30 % of coarse fractions, are mainly concretional micronodules with a botryoidal morphology (Pl. 1L). They result from the accretion of Mn oxides within the sediment; an appreciable amount of clays being trapped during their growth (Lallier-Vergès, 1986). However, about 20 % of Mn micronodules are radiolarian tests replaced by Mn oxides.

The coarse fractions of surface sediments from T 47029 and 47032 cores differ from the others in that then contain very few figured organic remains. Coarse fractions of T 47029 are typical of low sedimentation rate sediments as "red clays" : numerous ferromanganese nodule fragments, indurated sediment debris, palagonite, fish-teeth, concretional Mn micronodules, altered and preserved radiolaria, and benthic foraminifers. The T 47032 core mainly presents Mn oxide dendrites growing inside indurated sediment.

Amino acids in coarse fraction components

Coarse fractions account for less than 1 % of total sediment weight, so their contribution to the whole amino acid composition of the sediment would be significant only for nearly pure proteinic substances. Radiolarian shells, Mn micronodules and lignaceous debris bear less amino acids than the bulk sediment. On the other hand, benthic foraminifera (Pl. 1J) and laminated translucent fragments (Pl. 1L) are greatly enriched in amino acids (Tab. 4).

The amino acid abundance of benthic foraminifera probably results from their recent existence in the sediment and one may consider that they still belong to the biological fraction of the sediment. The occurrence of taurine (Fig. 3) in these samples clearly shows that they do not consist of altered shells but of recent remains of living organisms.

The translucent fragments are particularly rich in amino acids (480 micromoles/g). Their nature is probably totally organic. Amino acids and amino sugars account for not more than 6 % weight of the sample. About 8 % of total amino acids are represented by an undetermined component (n.d., Fig. 3) which has already been observed, in low quantities, in sediment-trap particles (previous studies). This latter has never been described in sediments. Its elution position (between phenylalanine and β-alanine) could correspond to that of certain hexosamines, such as glucosaminitol (Cheng and Boat, 1978). However, the hydrolysis conditions are not likely to produce such compounds. Apart from glucosamine (11 %) and the undetermined component, glycine (45 %) and histidine (8 %) are the most characteristic amino compound of these particles (Fig. 3).

Radiolaria skeletons are approximately four times lower in amino acids than the sediment (Tab. 4). Measured value (about 3 micromoles/g) is higher than mean value reported for recent species (about 1.5 micromoles/g; King, 1974), although individual amino acid compositions are similar.

Table 4

Total amino acid and NH_4 + contents (micromoles/g) of sediment and coarse fraction components. Amino-N/TN, NH_4 + N/TN and amino-C/TOC % in sediments.

Composition en acides aminés totaux et NH_4 + (micromoles/g) des sédiments et constituants des fractions grossières. Rapports (%) N-aminé/TN, N-NH_4 +/TN and C-aminé/TOC dans les sédiments.

SAMPLE	TOTAL AMINO ACIDS µmol/g	NH4+ µmol/g	AMINO n %	NH4+ -N %	AMINO C %
BULK SEDIMENT					
T 47004 top	10	9	22	13	11
T 47024 top	9	9	19	15	10
T 47012 top	14	8	25	12	15
T 47012 10 cm	8	7	17	12	12
T 47012 40 cm	5	5	12	10	11
COARSE FRACTIONS					
radiolaria	2.7				
Mn micronodules	1.9				
lignous debris	tr.				
translucent fragments	485				
benthic foraminifers with cells	28				
benthic foraminifers : "manchons"	14				

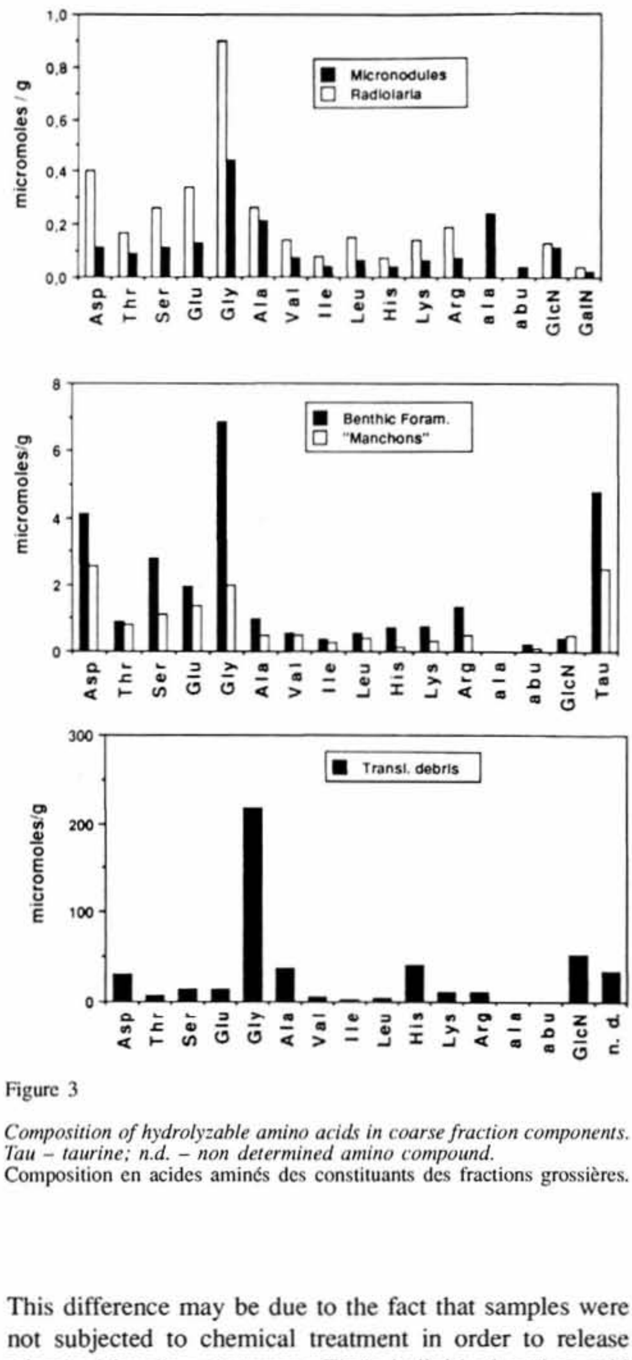


Figure 3

Composition of hydrolyzable amino acids in coarse fraction components. Tau – taurine; n.d. – non determined amino compound.
Composition en acides aminés des constituants des fractions grossières.

This difference may be due to the fact that samples were not subjected to chemical treatment in order to release adsorbed humic substances. Their individual amino acid composition underlines the lack of non-proteic amino-acids.

The Mn micronodules have a proteic amino acid composition very similar to that of radiolaria and sediments (Fig. 3), although their contents is much lower (about the half relatively to radiolaria). The occurrence of β-alanine and γ-aminobutyric acid, in the same proportions as in the sediment, reveals the incorporation of clays in the micronodules during their accretion. No biochemical activity (present or ancient) has been detected in Mn micronodules, through amino acids analysis. This observation is similar to those made for Mn-oxide mineralized biological rests (Lallier-Vergès and Albéric, 1989) or for organic pigments in Mn nodules (Glasby and Hodgson, 1971).

The study of the amino acid composition of coarse organic fractions revealed new components and showed that the figured fragments only constitute a minor part of the total amino acid content of the sediment, the major part being associated with finer fractions.

CONCLUSION

Low TOC, C/N decrease with depth in the core, enrichment in β-alanine and γ-aminobutyric acid in Nixo deep-Pacific sediments indicate typical oxic sedimentation. The optical study of chemically isolated organic matter from these surface sediments revealed the dominance of the figured organic matter which is composed of very resistant components, such as vegetal debris, external parts of planktonic and benthic organisms and sparse aggregates of "amorphous" organic matter. Conversely, the chemically extracted organic matter of TOC-rich anoxic deposits (Oman Margin) is mainly composed of "amorphous" organic matter and rare benthic fragments. This "amorphous" organic matter, considered to result from the decomposition of phytoplankton, is indicative of both high phytoplanctonic productivity and good conditions of preservation of reactive organic matter.

Figured organic matter (benthic and resistant pelagic remains and altered vegetal debris) associated with the occurrence of radiolarian tests and zooplankton pellets would correspond to less productivity and low phyto/zooplankton ratio. These organic input characteristics associated to a very low detrital sedimentation rate appear to be responsible for oxic sedimentation.

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REFERENCES

Albéric P., A. Khripounoff (1984). Relations entre les compositions en acides aminés des particules en voie de sédimentation, du contenu intestinal des holothuries abyssales et du sédiment environnant, *Mar. Chem.*, **14,** 379-394.

Bender M.L., D.T. Heggie (1984). Fate of carbon reaching the deep sea floor : a status report, *Geochim. Cosmochim. Acta,* **48,** 977-986.

Berner R.A. (1982). Burial of organic carbon and pyrite sulfur in the modern ocean : Its geochemical and environmental significance, *Am. J. Sci.,* **282,** 451-473.

Bertrand P., E. Lallier-Vergès, H. Grall (1990). Organic Petrology of Quaternary and Neogene Sediments from North Indian Ocean (Ocean Drilling Program, LEG 117). I : Amount, type and preservation of organic matter, *ODP Proceedings Part B,* in press.

Cahet G., M. Sibuet (1986). Activité biologique en domaine profond : transformations biochimiques *in situ* de composés organiques marqués au carbone-14 à l'interface eau-sédiment par 2 000 m de profondeur dans le golfe de Gascogne. *Mar. Biol.,* **90,** 307-315.

Caratini C., J. Bellet, C. Tissot (1981). Etude microscopique de la matière organique : palynologie et palynofaciès, *Géochimie organique des sédiments marins profonds, orgon IV, golfe d'Aden, mer d'Oman,* edited by CNRS, Paris 255-307.

Caratini C., J. Bellet, C. Tissot (1983). Les palynofaciès : représentation graphique, intérêt de leur étude pour les reconstitutions paléogéographiques, *Géochimie organique des sédiments marins;* d'Orgon à Messidor, edited by CNRS, Paris, 327-352.

Cheng P.W., T.F. Boat (1978). An improved method for the determination of galactosaminitol, glucosamine and galactosamine on an amino acid analyzer, *Anal. Biochem.,* **85,** 276-282.

Combaz A. (1964). Les palynofaciès, *Rev. Micropal.,* **7,** 205-218.

Combaz A. (1980). Les kérogènes vus au microscope, in : *Kerogen,* edited by B. Durand, Editions Technip, Paris, 56-88.

Degens E.T. (1965). *Geochemistry of sediments.* Prentice Hall, Englewood Cliffs, New York, 342 pp.

Degens E.T. (1970). Molecular nature of nitrogenous compounds in sea water and recent sediments, in : *Symposium on organic matter in natural waters,* edited by D.W. Hood, University of Alaska Press, College, 77-106.

Degens E.T., J.H. Reuter, and K.N.F. Shaw (1964). Biochemical compounds in offshore california sediments and sea waters. *Geochim. Cosmochim. Acta,* **28,** 45-66.

Degens E.T., K. Mopper (1976). Factors controlling the distribution and early diagenisis of organic material in marine sediments, in : *Chemical Oceanography.* 2nd. ed., edited J.P. Riley and R. Chester. Academic Press, London, **6,** 60-114.

Demaison G.J., G.T. Moore (1980). Anoxic environment and oil source bed genesis, *Bull. Am. Assn. Pet. Geol.,* **64,** 1179-1209.

Duchaufour H., L. Jocteur Monrozier, R. Pelet (1984). Optical and geochemical studies of granulometric fractions from recent marine sediments, *Org. Geochem.,* **6,** 305-315.

Durand B., G. Nicaise (1980). Procedures for kerogen isolation, in : *Kerogen,* edited by B. Durand, Editions Technip, Paris, 56-88.

Emerson S., K. Fischer, C. Reimers, D. Heggie (1985). Organic carbon dynamics and preservation in deep-sea sediments, *Deep-Sea Res.,* **32,** 1-21.

Glasby G.P., G.W. Hodgson (1971). The distribution of organic pigments in marine manganese nodules from the Northwest Indian Ocean, *Geochim. Cosmochim. Acta,* **35,** 845-851.

Hare P.E. (1973). Amino acids, amino sugars and ammonia in sediments from the Cariaco Trench, *Init. Rep. D.S.D.P.,* **20,** edited by B.C. Heezen, I.D. Macgregor *et al.,* 941-942.

Henrichs S.M., W.S. Reeburgh (1987). Anaerobic mineralization of marine sediment organic matter : Rates and the role of anaerobic processes in the oceanic carbon economy, *Geomicrobiol. J.,* **5,** 191-237.

Henrichs S.M., J.W. Farrington, C. Lee (1984). Peru upwelling region sediments near 15°S. Dissolved free and total hydrolyzable amino acids, *Limnol. Oceanogr.,* **29,** 20-34.

Huc A. (1988). Sedimentology of organic matter, in : *Humic Substances and their Environment,* edited by F.H. Frimmel and R.F. Christman, 215-243.

Iachan A., L.V. Disitzer and J.C. Perrone (1961). A new method for protein hydrolysis with crystallized oxalic acid, *An. Acad. bras. Cienc.,* **33,** 169-172.

Janin M.C., G. Bignot (1983). Microfossiles thallophytiques des concrétions polymétalliques laminées, *Micropaléontologie,* **25,** 4, 251-264.

Jannasch H.W., C.O. Wirsen (1973). Deep-sea microorganisms : *in situ* response to nutrient enrichment, *Science,* **180,** 641-643.

Jedwab J. (1971). Particules de matière carbonée dans les nodules de manganèse des grands fonds océaniques, *C. R. Acad. Sc. Paris,* **272,** 1968-1971.

Jocteur-Monrozier L., P. Jeanson (1979). L'azote organique et ammoniacal, combinaisons et stabilité chimique, in : *Géochimie organique des sédiments marins profonds, Orgon III,* edited by C.N.R.S., Paris, 405-422.

Khripounoff A., G.T. Rowe (1985). Les apports organiques et leur transformation en milieu abyssal à l'interface eau-sédiment dans l'Océan Atlantique tropical, *Oceanologica. Acta,* **8,** 293-301.

King K., jr (1974). Preserved amino acids from silicified protein in fossil Radiolaria, *Nature,* **252,** 690-692.

Lallier-Vergès E. (1986). Micronodules de manganèse et sédiments pélagiques dans l'Océan Pacifique; Caractérisation formation, diagenèse, *Doc. Bur. Rech. Géol. Min.,* France, **119,** 478 pp.

Lallier-Vergès E., P. Albéric (1989). Burrowing : a major process in the Mn-Ni enrichment of red clays, *Mar. Geol.,* **86,** 75-79.

Le Suavé R., M. Voisset, J.F. Bourillet, P. Cochonat, J. Guillaume, E. Le Drezen, Y. Morel, G. Ollier, S. Rey, S. Ricou and P. Saget (1987). Mise en évidence de phénomènes tectoniques et érosifs récents en domaine intraplaque profond, à l'aide du S.A.R. Example du Pacifique nord équatorial, *C. R. Acad. Sci., Paris,* Série II, **305,** 1211-1216.

Lee C., B. Olson (1984). Dissolved, exchangeable and bound aliphatic amines in marine sediments : initial results, *Org. Geochem.,* **6,** 259-263.

Martin W.R., M.L. Bender (1988). The variability of benthic fluxes and sedimentary reminalization rates in response to seasonally variable organic carbon rain rates in the deep sea : a modeling study, *Am. J. Sci.,* **288,** 561-574.

Martinez L., B. Pradier, P. Bertrand (1987). La microspectrofluorimétrie en pétrologie organique. Méthodologie et application à l'étude de la maturation des algues fossiles du Toarcien du bassin de Paris, *C. R. Acad. Sci., Paris, Série III,* **304,** 441-446.

Middleburg J.J. (1989). A simple rate model for organic matter decomposition in marine sediments, *Geochim. Cosmochim. Acta,* **53,** 1577-1581.

Müller P.J., A. Mangini (1980). Organic carbon decomposition rates in sediments of the pacific manganese nodule belt dated by 230Th and 231Pa, *Earth Planet. Sci. Lett.,* **51,** 94-114.

Müller P.J. (1977). C/N ratios in Pacific deep-sea sediments : effect of inorganic ammonium and organic nitrogen compounds sorbed by clays, *Geochim. Cosmochim. Acta.,* **41,** 765-776.

Pelet R. (1984). A model for the biological degradation of recent sedimentary organic matter, *Org. Geochem.,* **6,** 317-325.

Piper D.Z. (1988). The metal oxides fraction of pelagic sediment in the equatorial North Pacific Ocean : A source of metals in ferromanganese nodules. *Geochim. Cosmochim. Acta.* **52,** 2127-2145.

Raynaud J.F., B. Lugardon, G. Lacrampe-Couloume (1988). Observations de membranes fossiles dans la matière organique «amorphe» de roches mères du pétrole, *C. R. Acad. Sci., Paris, Sér. II,* **397,** 1703-1709.

Reimers C.E., K.L. Smith Jr (1986). Reconciling measured and predidcted fluxes of oxygen across the deep sea sediment-water interface, *Limnol. Oceanogr.,* **31,** 305-318.

Reimers C.E., E. Suess (1983). The partitioning of organic carbon fluxes and sedimentary organic matter decomposition rates in the ocean, *Mar. Chem.,* **13,** 141-168.

Ricou S. (1990). La dynamique sédimentaire en milieu intraplaque océanique dans les zones riches en nodules polymétalliques (Zones Clarion-Clipperton, Pacifique nord-Est). *Thèse de Doctorat, Université, Université Louis Pasteur, Strasbourg, France,* 184 pp.

Rosenfeld J.K. (1979). Amino acid diagenesis and adsorption in nearshore anoxic sediments, *Limnol. Oceanogr.,* **24,** 1014-1021.

Schrœder R.A. (1975). Absence of β-alanine and γ-aminobutyric acid in cleaned foraminiferal shells : implications for use as a chemical criterion to indicate removal of non-indigenous amino acid contaminants, *Earth. Planet. Sci. Lett.,* **25,** 274-278.

Schrœder R.A., J.L. Bada (1976). A review of the geochemical applications of the amino acid recemization reaction, *Earth Sci. Rev.,* **12,** 347-391.

Steinberg S.M., M.J. Venkatesan, I.R. Kaplan (1987). Organic geochemistry of sediments from the continental margin off southern New England, USA, PART I. Amino acids, carbohydrates and lignin, *Mar. Chem.,* **21,** 249-265.

Terashima M. (1979). The distribution of amino acids in submarine sediments from the eastern part of the East China Sea, *Chem. Geol.,* **25,** 135-154.

Waples D.W., J.R. Sloan (1980). Carbon and nitrogen in deep-sea sediments, *Geochim. Cosmochim. Acta,* **44,** 1463-1470.

Westrich J.T., R.A. Berner (1984). The role of sedimentary organic matter in bacterial sulfate reduction : The G model tested, *Limnol. Oceanogr.,* **29,** 236-249.

Whelan J.K. (1977). Amino acids in a surface sediment core of the Atlantic plain. *Geochim. Cosmochim. Acta,* **41,** 803-810.