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Sources and fate of organic matter in ocean sediments

Organic matter
Sediments
Humic acids
Deep ocean

Matière organique
Sédiments
Acides humiques
Océan profond

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ABSTRACT

The three main sources of organic matter in oceanic basins are marine plankton, terrestrial higher plants and undifferentiated residual organic matter which has been highly degraded in subaerial environments.

The time and areal distribution of marine organic matter is mainly controlled by the conditions of preservation. In deep oceans accumulation occurs mainly in confined anoxic basins, and also in open ocean, where local conditions generate a surplus of supply over bacterial degradation.

Moderately degraded terrestrial organic matter is derived from land plants and carried away by rivers and currents. It is mainly deposited in sediments of the river fans.

Residual organic matter has been highly degraded in subaerial conditions prior to transportation, and may consist of contemporaneous and/or recycled material. It cannot be degraded any more and may be spread over wide areas, regardless of the local environments.

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RÉSUMÉ

Origine et destin de la matière organique dans les sédiments océaniques

Les trois sources principales de matière organique dans les bassins océaniques sont le plancton marin, les végétaux supérieurs terrestres et la matière organique résiduelle qui a subi une profonde dégradation dans des environnements subaériens.

La répartition de la matière organique marine dans l'espace et dans le temps est surtout contrôlée par les conditions de préservation. Dans les océans profonds, elle s'accumule principalement dans des bassins confinés et anoxiques, ainsi qu'en milieu ouvert, quand les conditions locales amènent un surplus de productivité par rapport à la dégradation bactérienne.

La matière organique terrestre modérément dégradée dérive des végétaux supérieurs ; elle est transportée par les rivières et les courants. Elle se dépose surtout dans les cônes deltaïques des rivières.

La matière organique résiduelle a été profondément dégradée dans des conditions subaériennes avant d'être transportée ; elle peut comprendre du matériel contemporain aussi bien que du matériel recyclé. Cette matière organique n'est plus dégradable et elle peut se déposer sur de vastes zones, quel que soit l'environnement local de dépôt.

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INTRODUCTION

The nature and origin of the organic matter deposited in oceanic basins has been investigated in recent and ancient sediments. Four cruises (Fig. 1 : Orgon 1, 2, 3 and 4) have allowed us to core and study the organic content of deep ocean sediments of Pleistocene to Holocene age, with water depths reaching down to 4,000 m. Furthermore, ancient sediments of Cretaceous age, deposited in the Atlantic oceanic basins, and cored by the DSDP/IPOD program, have been studied systematically for their organic geochemistry.

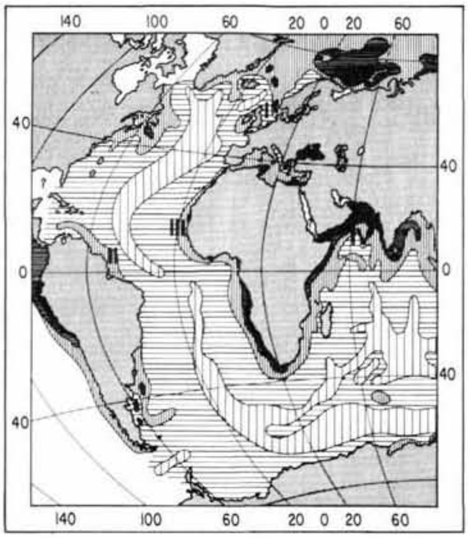

Figure 1

Content of organic matter in marine surface sediments, and location of the Orgon 1, 2, 3 and 4 cruises (adapted from Romankevic, 1977).

Teneur en matière organique des sédiments marins et position des campagnes Orgon 1, 2, 3 et 4 (adapté de Romankevic, 1977).

Table

Elementary analysis of the humic acid and insoluble residue fractions of terrestrial and marine organic matter in young oceanic sediments (Orgon cruises). All ratios are atomic ratios.

Analyse élémentaire des acides humiques et des résidus insolubles de matière organique d'origine terrestre ou marine, dans des sédiments océaniques récents (campagnes Orgon). Données exprimées en rapports atomiques.

Cruise/ core/ sample	Water depth (m)	Depth in the core	Geologic age	Origin of organic matter	Pre-sedimentary degradation level	Hydrolyzable fraction (% of the total organic carbon)	Fulvic acids (% of total organic carbon)
1 KL 8-3	440	1 m	Pleistocene (Riss)	C	low	—	7
1 KL 14-3	1 500	1,5 m	Pleistocene (Würm)			—	4
1 KL 14-17	1 500	8,5 m				—	6
2 KL 15-6	1 930	2,5 m	Pleistocene (Würm)	C	low	41	17
2 KL 17-4	1 740	1,5 m				37	18
2 KL 4-3	3 750	1 m	Pleistocene (Würm)	C	high	60	16
2 KL 6-7	4 900	3 m				51	29
3 KL 6-4	4 450	1,5 m	Pleistocene (Würm)	C	high	30	6
3 KL 16-1	3 050	0 m	Holocene	M	high	62	15
3 KL 10-1	3 750	0 m	Holocene			79	19
4 KL 4-1	4 730	0 m	Holocene	M	moderate	43	13
4 KL 5-1	4 010	0 m	Holocene			46	9
2 KL 1-5	1 730	2 m	Holocene	M	low	31	6
3 KL 14-3	1 900	1 m	Top of Pleistocene	M	low	44	8
4 KL 1-1	1 070	0 m	Holocene	M	low	44	10
4 KL 9-1	830	0 m	Holocene			24	7

C = Continental.
M = Marine.

ORGANIC MATTER IN YOUNG OCEANIC SEDIMENTS

Organic matter observed in Pleistocene to Holocene sediments of the Orgon project belongs to the early stage of diagenesis (defined according to Tissot, Welte, 1978 and Pelet, 1980) as it is young and has never been buried more than 1 to 10 m. Detailed results are reported elsewhere (Comité d'Etudes Géochimiques Marines, 1977 ; 1978 ; 1979 ; in press).

In present day or very recent sediments, the origin of sedimentary organic matter can be inferred from geography : in any area the possible sources of organic matter are known, or can be known. This approach has been systematically used in Orgon cruises. The optical examination of the samples, which has been also systematically done, is considered as a confirmation, and not as a primary data source. The chemical composition of organic matter is not considered as a relevant information for the determination of organic matter origin at the beginning of Orgon studies — but an evidence for a link between these two parameters can be an output of the study.

Terrestrial organic matter is abundantly present in the Pleistocene sediments of the Amazon river deep-sea fan, from the rim of the continental slope down to the Demerara abyssal plain (Orgon 2) and in the Holocene/Pleistocene sediments of the Norwegian sea (Orgon 1). Marine organic matter, derived essentially from phytoplankton, is present in the open sea environments of Arabian and Oman Sea (Orgon 4) and, with a slight continental admixture, in the Atlantic Ocean offshore Mauretania (Orgon 3). In these two latter cases, a very high productivity of the plankton, due to upwelling conditions, results in a surplus of organic matter as compared to the abundance of oxygen in waters, and in an enhanced preservation. In the barred and anoxic Cariaco Trench, this marine organic matter contains a significant proportion of bacterially derived organic matter, and also continental material admixture.

At this stage of sediment evolution, humic acids and insoluble (stable) residue are the most representative fractions of organic matter. Geographic, geological and chemical data are given in the Table for those samples where all, or nearly all, the pertinent data are available at the same time. But the conclusions which follow are based on the examination of all the 213 Orgon samples where only partial data are available. The humic acid fraction shows the following characters. On the shelf and the upper part of the slope, where the organic material has only suffered a slight degradation, the terrestrial input shows lower H/C and N/C

Humic acids					Stable residue						
% of total organic carbon	Elemental composition				% of total organic carbon	Elemental composition				Core location	Comments
	H/C	O/C	N/C	S/C		H/C	O/C	N/C	S/C		
21	0,90	0,37	0,04	—	—	1,01	0,25	0,03	—	Norwegian	Cold
31	1,11	0,48	0,07	0,02	—	—	—	—	—		
26	1,01	0,43	0,06	0,01	—	—	—	—	—	Sea	Climate
18	1,08	0,51	0,06	0,01	—	—	—	—	—	Amazon	
15	1,06	0,53	0,05	0,01	32	0,87	0,29	0,02		Core	
18	1,28	0,51	0,07	0,01	50	0,98	0,22	0,03	—	Demerara	
17	1,31	0,53	0,07	0,01	30	0,72	0,22	0,02	—	Abyssal Plain	
23	1,36	0,54	0,07	0,03	48	1,04	0,30	0,06	0,03	Cape Verde Abyssal Plain	Some admixture of marine OM
12	1,21	0,48	0,08	0,01	26	0,90	0,32	0,03	0,02	Cape Verde Rise	Some admixture
23	1,18	0,47	0,08	0,01	7	1,14	0,31	0,05	0,01	Mauretania Abyssal Plain	of Continental OM
33	1,38	0,47	0,09	0,01	29	1,15	0,26	0,05	0,01	Alula Fartak trend	
4	1,32	0,53	0,10	0,01	41	1,15	0,27	0,06	0,01	Arabian Sea	
15	1,31	0,44	0,09	0,02	42	1,17	0,32	0,06	—	Cariaco Trench	Some admixture of continental OM
17	1,34	0,42	0,08	0,02	36	1,20	0,28	0,06	0,02	Offshore Mauretania	Some admixture of continental OM
27	1,33	0,45	0,09	0,01	33	1,18	0,29	0,06	0,01	Arabian sea	
11	1,29	0,46	0,10	0,01	58	1,16	0,23	0,05	0,01	Continental Slope	

ratios, and a higher O/C ratio than the marine input (phyto- and zoo-plankton).

Significant changes can be observed with increasing degradation. When the sediments are progressively retransported, mainly by sliding, along the continental slope towards the abyssal plain off Mauretania, the marine organic matter is degraded (oxidized) by biochemical, and also possibly inorganic, reactions. The H/C ratio is lowered, and also the N/C ratio suggesting a loss of ammonia, whereas the O/C ratio increases. This view is supported by an increase of the fulvic acids and also of the hydrolyzable organic fraction.

The terrestrial organic matter presented in the Table did not suffer a significant degradation in subaerial conditions (this case will be dealt with later on). In the Amazon fan, the terrestrial organic matter shows a significant trend from the shelf, along the continental slope down to the abyssal plain. The increasing degradation of the organic matter is probably related to the fact that the far reaching fraction has been transported in a soluble, colloidal form, or as an organic-mineral complex. The H/C ratio is increased, whereas the O/C ratio remains essentially unchanged and the N/C ratio increases, suggesting a loss of carbon dioxide. This alteration results in an elementary composition close to that of the degraded marine material.

The insoluble residue shows similar trends, at least for marine organic matter. This must always be the case for marine planktonic organic matter, where humic acid and insoluble residue have the same origin. But for terrestrial organic matter, the insoluble residue may in some cases contain ancient reworked material, or material profoundly degraded in subaerial conditions which can obscure the relations clearly shown by the humic fraction, always young at the geological scale.

Infrared spectroscopy of the humic acids (Fig. 2) shows the same pattern. Degradation of the marine organic matter is marked by a decrease of the peptidic and of the aliphatic bands. Degradation of the terrestrial material is marked by a decrease of the polysaccharids and an increase of the aliphatic bands. Thus, the most altered marine and terrestrial inputs progressively reach a more comparable composition.

Optical examination of the organic matter (OM) by transmitted light (Fig. 3 to 7), which deals with a fraction close to the insoluble residue, shows the same trends for the marine samples : the less degraded sample (KL15, Fig. 3) shows essentially big flakes of amorphous OM of light colour (which darkens with the thickness of the flakes), whereas the more degraded sample (KL10, Fig. 4) shows, among smaller and darker amorphous OM flakes, a more important number of dark particles. It is more difficult to conclude from the simple examination of the terrestrial samples. Note that the size of the flakes is a preparative artefact, whose meaning is unknown to date (Fig. 5 and 6). For the sake of comparison is also given a view of OM of mixed origin deposited in an euxinic environment (Cariaco trench) : the flakes of amorphous OM appear as smaller and thinner than for the marine/open sea samples (Fig. 7).

In addition to the marine and terrestrial types of organic matter, more or less altered, another organic fraction has been recognized, mainly in the Norwegian Sea (Orgon 1). Detrital organic matter, which is either recycled from older formations or has suffered a deep oxidation in subaerial conditions (natural fires, macerals of fusinite or inertinite type) : this fraction is called "residual organic matter" in the present paper.

ORGANIC MATTER IN ANCIENT OCEANIC SEDIMENTS

Organic rich shales, mudstones and marls of Cretaceous age, commonly referred to as "black shales" have been found in many location of the Atlantic ocean basins. Geochemical results are reported in the Initial reports of the

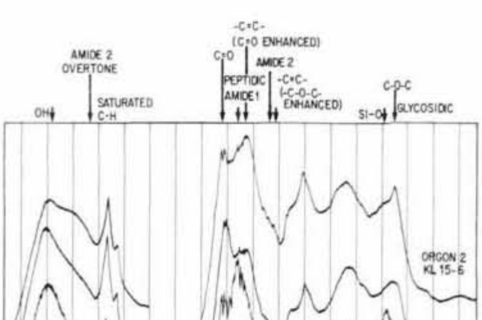

Figure 2

Infrared spectroscopy of some humic acids isolated from marine and terrestrial organic matter deposited in oceanic sediments. Origin of organic matter : Orgon 2 KL 15-6, terrestrial, low degradation ; Orgon 2 KL 6-9, terrestrial, high degradation ; Orgon 3 KL 10-0, marine, high degradation ; Orgon 3 KL 15-0 marine, low degradation.

Spectrométrie infrarouge d'acides humiques provenant de matière organique marine et terrestre déposée dans des sédiments océaniques. Origine de la matière organique : carotte Orgon 2 KL 15-6, terrestre, faible dégradation ; carotte Orgon 2 KL 6-9, terrestre, forte dégradation ; carotte Orgon 3 KL 10-0, marine, forte dégradation ; carotte Orgon 3 KL 15-0, marine, faible dégradation.

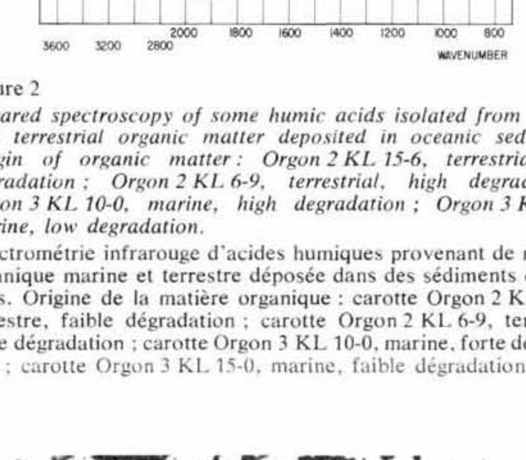

Figure 3

Microscopic view of isolated organic matter from Orgon 3/KL 15-0 sample (Marine OM, Offshore Mauretania).

Vue microscopique de matière organique isolée à partir de la carotte Orgon 3 KL 15-0 (matière organique marine, Mauritanie).

Figure 4
Microscopic view of isolated organic matter from Orgon 3/KL 10-0 sample (Marine OM, Offshore Mauretania).
Vue microscopique de matière organique isolée à partir de la carotte Orgon 3 KL 10-0 (matière organique marine, Mauritanie).

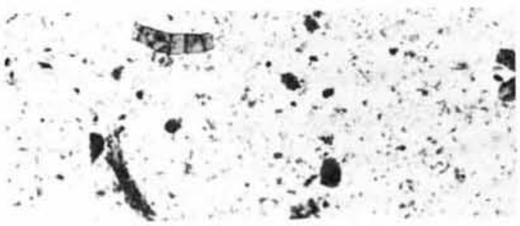

Figure 5
Microscopic view of isolated organic matter from Orgon 2/KL 15-6 sample (terrestrial OM, Amazon fan).
Vue microscopique de matière organique isolée à partir de la carotte Orgon 2 KL 15-6 (matière organique terrestre, cône de l'Amazone).

Figure 6
Microscopic view of isolated organic matter from Orgon 2/KL 6-9 sample (terrestrial OM, Amazon fan).
Vue microscopique de matière organique isolée à partir de la carotte Orgon 2 KL 6-9 (matière organique terrestre, cône de l'Amazone).

DSDP project, legs 11, 36, 40, 41, 43, 44, 47, 48, 50, 51 to 53. The sediments have never been buried more than 1,000-1,500 m. Thus they are still in the early stage of thermal evolution called diagenesis (Tissot, Welte, 1978 ; Pelet, 1980) and they have not yet reached the stage of hydrocarbon generation (catagenesis).

Over the diagenesis stage, the main and most significant fraction of organic matter in ancient sediments is the kerogen, which amounts to 95-99 % of the total organic material. Studies carried on kerogen of the Cretaceous

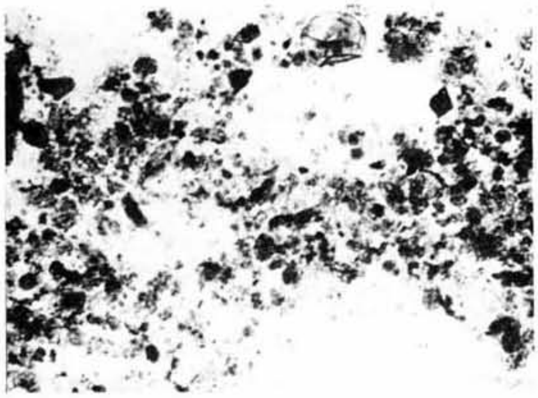

Figure 7
Microscopic view of isolated organic matter from Orgon 2/KS 1-1 sample (Marine OM, Cariaco Trench).
Vue microscopique de matière organique isolée à partir de la carotte Orgon 2 KS 1-1 (matière organique marine, fosse de Cariaco).

black shales are reported in Tissot *et al.* (1979) and Tissot *et al.* (in press). Elemental analysis, infrared spectroscopy and optical examination by transmitted light were in particular performed on the isolated insoluble fraction of kerogen (hereafter referred to as kerogen, since it amounts to more than 9/10 of the total kerogen).

The elemental analysis of some kerogens originating from North and South Atlantic are plotted in Figure 8 by using the atomic H/C and O/C ratios. The main types of kerogen can be examplified by the four pairs of samples noted A_1 and A_2, B_1 and B_2, C_1 and C_2, D_1 and D_2, respectively :
a) marine organic matter, deposited and preserved in a reducing environment corresponds to samples A_1 and A_2. The high H/C ratio and the relatively low O/C ratio are rather characteristic and comparable to values observed in shallow immature source rocks with a high potential for oil generation. Optical examination shows mainly an amorphous organic material, commonly referred to as "sapropelic". This type of kerogen has been named "type II" in kerogen studies of source rocks (Tissot *et al.*, 1974) ;

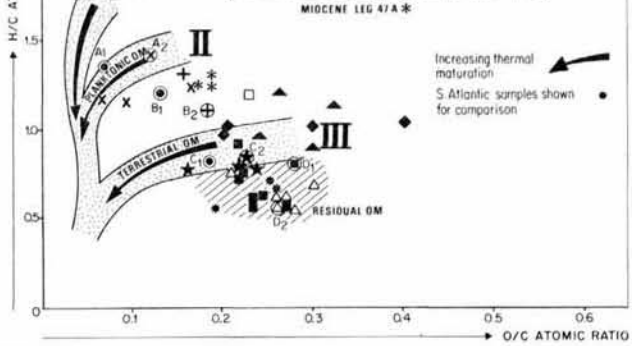

Figure 8
Elementary composition of kerogens isolated from the Cretaceous black shales of the Atlantic (Tissot et al., *1979).*
Composition élémentaire de divers kérogènes provenant des argiles noires du Crétacé de l'Atlantique (Tissot *et al.*, 1979).

b) terrestrial organic matter, moderately degraded, corresponds to samples C_1 and C_2. They are hydrogen poor ($H/C < 1$) and oxygen rich : the O/C ratios ca. 0.2 to 0.3 are relatively high for ancient sediments. Comparable values are observed in shallow immature source rocks of comparable terrestrial origin, and in brown coals. Optical examination has confirmed the important proportion of plant debris. However, the occurrence of coaly fragments with high reflectivity (23 % of inertinite in C_1) suggests a contribution of recycled material. This type of kerogen has been named "type III" in kerogen studies of source rocks (Tissot *et al.*, 1974) ;

c) some kerogens show an intermediate composition such as B_1 and B_2, with a high H/C ratio, associated with a relatively high O/C ratio. In some cases, optical examination clearly shows an admixture of different sources : amorphous material, possibly of marine origin, plant fragments moderately degraded, and/or coaly debris. However, other cases, where optical examination does not show such an admixture, could be interpreted as resulting from alteration of either marine, or terrestrial material, comparable to the situations observed in Orgon cruises ;

d) finally, some kerogens are mainly or wholly comprised of "residual" organic matter, either recycled or deeply oxidized in subaerial conditions. Their hydrogen content is low to very low, whereas the O/C ratio is abnormally high, as compared to the H/C ratio. Optical examination confirms the high proportion of dark, coaly debris (inertinite, high reflectance vitrinite) : samples D_1 and D_2.

Infrared spectroscopy (Fig. 9) confirms the view on the relative composition of the four groups of kerogen. Marine organic matter preserved in a reducing environment (A_1) shows an abundance of aliphatic structures, whereas polyaromatic nuclei and oxygenated functional groups are only subordinate. Terrestrial organic matter, moderately degraded (C_1) shows a reverse situation, whilst the admixture of marine and terrestrial material (B_1) offers an intermediate composition. Finally, the "residual" organic matter (D_2) has practically no more aliphatic bands, whereas aromatic nuclei and oxygenated functional groups are abundant.

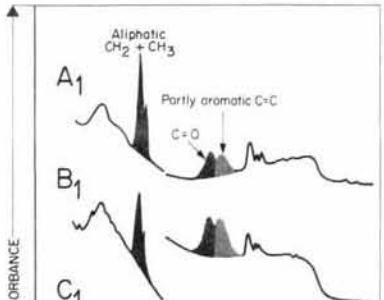

Figure 9

Infrared spectroscopy of four typical kerogens isolated from the Cretaceous black shales of the Atlantic (Tissot et al., *1979).*

Spectroscopie infrarouge de quatre kérogènes typiques provenant des argiles noires du Crétacé de l'Atlantique (Tissot *et al.*, 1979). *1979).*

To summarize these observations, we can consider that three types of organic matter can be clearly recognized in ancient sediments by physico-chemical and optical studies of their kerogen :

— marine, planktonic organic matter preserved in a reducing environment (type II) ;

— terrestrial organic matter, moderately degraded (type III) ;

— residual organic matter, which has been recycled and/or oxidized in subaerial environments.

In addition to that, some organic matter with an intermediate composition between those of marine and terrestrial types can be either a true admixture of both facies, or the result of a degradation (of marine or terrestrial material) which is finally deposited in deep locations of the abyssal plain or continental rise.

PRINCIPAL ENVIRONMENTS OF ORGANIC MATTER DEPOSITION IN OCEAN SEDIMENTS

The observed distribution of the organic matter in ocean sediments of the Orgon and DSDP/IPOD projects can be interpreted in terms of depositional environments (Tissot *et al.*, 1979 ; Pelet, 1980 ; Tissot *et al.*, in press) : Figure 10.

The typical habitat for accumulation of the marine organic matter in ocean sediments is a sea where the primary production of phytoplankton is abundant ; this situation is usually found along continental margins, and especially in areas of upwelling, such as West Africa and Oman sea. A substantial fraction of the organic matter is preserved in confined or barred basins where a stratified water column has restricted free oxygen to the surface layer, and also in open conditions where local seasonal conditions generate a surplus of organic productivity as compared to the available oxygen for heterotrophic fauna and aerobic microbes. The resulting sediments are usually organic rich (1 to 30 % by weight) and the kerogen belongs to type II. Its potential for subsequent oil generation is high.

Marine organic matter may also be retransported, mainly by sliding on the continental slope, down to the continental rise and abyssal plain. Under such circumstances, the organic matter is degraded (oxidation, loss of ammonia) by biochemical action (benthos), and possibly also by inorganic reactions. The resulting sediments contain a lower proportion of organic matter than on the continental slope and the kerogen shows an intermediate composition between types II and III. Its potential for subsequent oil generation is only moderate.

The typical habitat for accumulation of moderately degraded terrestrial organic matter in ocean sediments is a large river fan, such as the Amazon fan. The terrestrial, mainly particulate, organic input is carried by rivers and currents onto the continental shelf and slope. The association with detrital mineral particles helps to minimize the degradation in oceanic environment by shortening the transit time in oxygenated waters and insuring a quick burial. The resulting sediments are moderately rich (ca. 1 %, by weight) and the kerogen belongs to type III. Its potential for subsequent oil

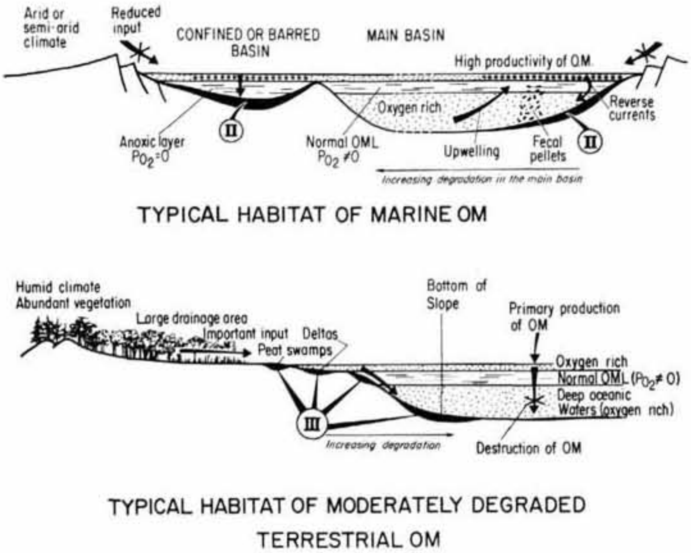

Figure 10

Principal environments of deposition of the organic matter in ocean sediments (modified after Tissot et al., *1979).*

Principaux environnements de dépôt de la matière organique dans les sédiments océaniques (Tissot *et al.*, 1979, modifié).

generation is relatively low, as compared to the kerogen type II.

Terrestrially derived organic matter may also be carried further away from the coast line, and be deposited in sediments of the continental rise or abyssal plain, such as the Demerara plain, which terminates the Amazon fan. There, the organic material is mainly transported in a soluble or colloidal form, or as an organometallic complex. Under such circumstances more alteration of the original material is observed, including possibly a loss of carbon dioxide. The resulting sediment contains a low proportion of organic matter and the kerogen shows an intermediate composition between types II et III. However, the potential for subsequent oil generation is low, mainly due to the low abundance of organic matter.

Residual organic matter has already been deeply degraded in subaerial conditions (recycled and/or oxidized) and cannot be degraded any more. Thus, the residual organic matter is no more sensitive to the specific conditions of deposition and can be found in any location, from the shelf to the abyssal plain. Furthermore, it can either be the only organic constituent of some deep oceanic sediments, or be found in association with any of the previous kerogen types. It has not petroleum potential by itself.

CONCLUSIONS

Three main types of organic matter have been distinguished in ocean sediments. Their source and fate during transport and sedimentation have been discussed. Basically they correspond to marine planktonic material deposited in a reducing environment, terrestrial moderately degraded material, and residual organic matter which has been recycled and/or oxidized in subaerial environments.

In addition to that, degraded marine or terrestrial material, which are transported onto the continental rise and abyssal plain, progressively acquire a comparable intermediate composition, as a result of two different alteration processes. Although they may be widespread, their abundance in sediment remains usually low.

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