Geomaterials (Sedimentology)

Does a strong pycnocline impact organic-matter preservation and accumulation in an anoxic setting? The case of the Orca Basin, Gulf of Mexico

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Abstract

The Orca Basin (an intraslope depression located in the Gulf of Mexico) collects sedimentary particles of terrestrial origin (clastic and organic particles mainly supplied by the Mississippi River) and of marine origin (biogenic productivity). The basin is partly filled with dense brines leached from salt diapirs cropping out on the sea floor, and is permanently stratified. A strong pycnocline induces anoxic bottom conditions, expectedly favorable to organic matter (OM) preservation. Here, we report on OM in the upper 750 cm below sea floor of Core MD02-2552 (Holocene). The organic content is dominated by marine-derived amorphous OM. The organic assemblage is unexpectedly degraded to some extent, which may be accounted for by a relatively long residence time of organic particles at the halocline-pycnocline at ∼2240 m. Thus the organic particles are temporarily trapped and kept in contact with the dissolved oxygen-rich overlying water mass. Lastly, the land-derived organic fraction shows co-variations with the land-derived clay mineral supply. *To cite this article: N. Tribovillard et al., C. R. Geoscience 341 (2009).*

Résumé

Une pycnocline concentrée a-t-elle un impact sur la préservation de la matière organique et sur son accumulation dans un dépôt anoxique ? Le bassin d'Orca, petite dépression située dans le Golfe du Mexique, reçoit des particules sédimentaires d'origine continentale (clastiques et organiques), véhiculées par le Mississippi principalement, et d'origine marine (productivité). Le bassin est partiellement rempli par des saumures issues du lessivage de diapirs salifères affleurant dans les fonds marins. La colonne d'eau y est très fortement stratifiée et le corps d'eau situé sous la halocline-pycnocline est totalement anoxique. Cette anoxie est *a priori* favorable à la préservation de la matière organique (MO). Nous étudions ici le contenu organique des premiers 750 cm de la carotte MD02-2552 déposés au cours de l'Holocène. Le contenu organique est dominé par la MO amorphe d'origine marine. L'état de préservation de la MO est étonnamment mauvais, compte tenu du contexte de dépôt. Cela est dû au fait que la MO est retenue durablement à l'interface de densité à ∼2240 m de profondeur, ce qui permet un long séjour dans des conditions encore

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relativement riches en oxygène dissous. Enfin, les particules organiques terrigènes montrent une distribution relativement bien corrélée à celle des minéraux argileux. ***Pour citer cet article : N. Tribovillard et al., C. R. Geoscience 341 (2009).***
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1. Introduction

Organic matter (OM) storage in marine sediments is an important step of the carbon cycle on geological time scales. Usually, the main factors conditioning OM accumulation concern the origin of organic products, and their conditions of productivity, transfer to the sediments and diagenesis (see extensive reviews in [16,25,26], and references therein). In this paper, we report on the sources, quantity and preservation state of OM of recent, mostly Holocene, sediments of the Orca Basin (Fig. 1A et B). Located within the Gulf of Mexico, the Orca Basin is a small depression characterized by the presence of very dense bottom brines, separated from the above water mass by a marked pycnocline or halocline (Fig. 1C). The stratified bottom water mass causes the development of anoxic bottom conditions that can potentially favor organic-matter preservation. Our aims are to discriminate land-derived and autochthonous fractions of the sedimentary OM and to account for the preservation state of OM that results from two antagonist factors: the anoxic bottom waters must favor OM preservation but the extreme density contrast separating bottom brines from the overlying oxygenated water mass forces OM to lie durably at the pycnocline where it may undergo extensive degradation.

2. The Orca Basin, a short description

The Orca Basin is characterized by strong water-column stratification (Fig. 1C) [17,24]. The 400-km^2 elbow-shaped depression results from regional salt tectonics along the Louisiana continental slope. The basin water depths range from about 1800 to 2400 m in the deepest parts (Fig. 1B). The bottom 200 m of the Orca Basin are permanently anoxic [7,18,27] and salinity is kept above 260 g/l due to the dissolution of shallow subsurface salt diapirs [19], whereas the overlying seawater has a salinity of 35 g/l. The resulting density contrast at the seawater-brine interface induces a strong stratification of the water column ([24] and references therein). A considerable part of the particulate flux settling into the basin is trapped at

the pycnocline region (2200–2250 m; [17]) and the retained particules consist of up to 60% OM [22,27]. Wong et al. [29] and Sheu [17] reported that the settling OM is trapped at the stable pycnocline long enough to undergo a detectable degradation that is reflected by the strong release of biogenic iodine at the density interface. Addy and Behrens [1] dated the beginning of anoxia around 8000 years BP but Presley and Stearns [11] proposed that anoxia have existed for at least 50,000 years.

The Orca Basin collects an important land-derived fraction consisting of terrigenous clastic and OM from the Mississippi River. The Mississippi River is by far the largest sediment source to the Gulf of Mexico. The tributary contributing most to overall runoff is the Ohio River, reflecting the higher precipitation in the eastern part of the Mississippi catchments. Most of the sediment load, however, is derived from the Missouri River catchments [20].

3. Material and methods

We sampled core MD02-2552 collected during the 2002 cruise of the R/V *Marion-Dufresne*. The core location is: latitude 26°56.80 N, longitude 91°20.72 W, maximum water depth 2240 m. The sediments consist entirely of black microlaminated (mm- to cm-scale) mud (silty clay). Seventy-five sediment samples were taken every 10 cm through the upper 7.5 m of the core. Only one age datum is available for the studied interval: the sample at 540 cm below sea floor (cmbsf) is dated by ^{14}C at 9838 yr cal BP [20]. The next available ^{14}C age datum downcore is at 790 cmbsf and is 13,500 yr cal BP. If we extrapolate an age for the base of the sampled interval, the deepest sample would be dated of 12,700 yr cal BP [24].

Usual Rock-Eval pyrolysis parameters, namely, total organic carbon content (TOC, wt %), Tmax (°C), and Hydrogen Index (HI, in mg hydrocarbon per g TOC) were determined with a Delsi Oil Show Analyser (Rock Eval II). The pyrolyse cycle was adapted to recent sediments (see [6] for procedural details and [5] for Rock Eval use for Holocene sediments). The trace-metal and carbonate contents, Rock-Eval and grain-size
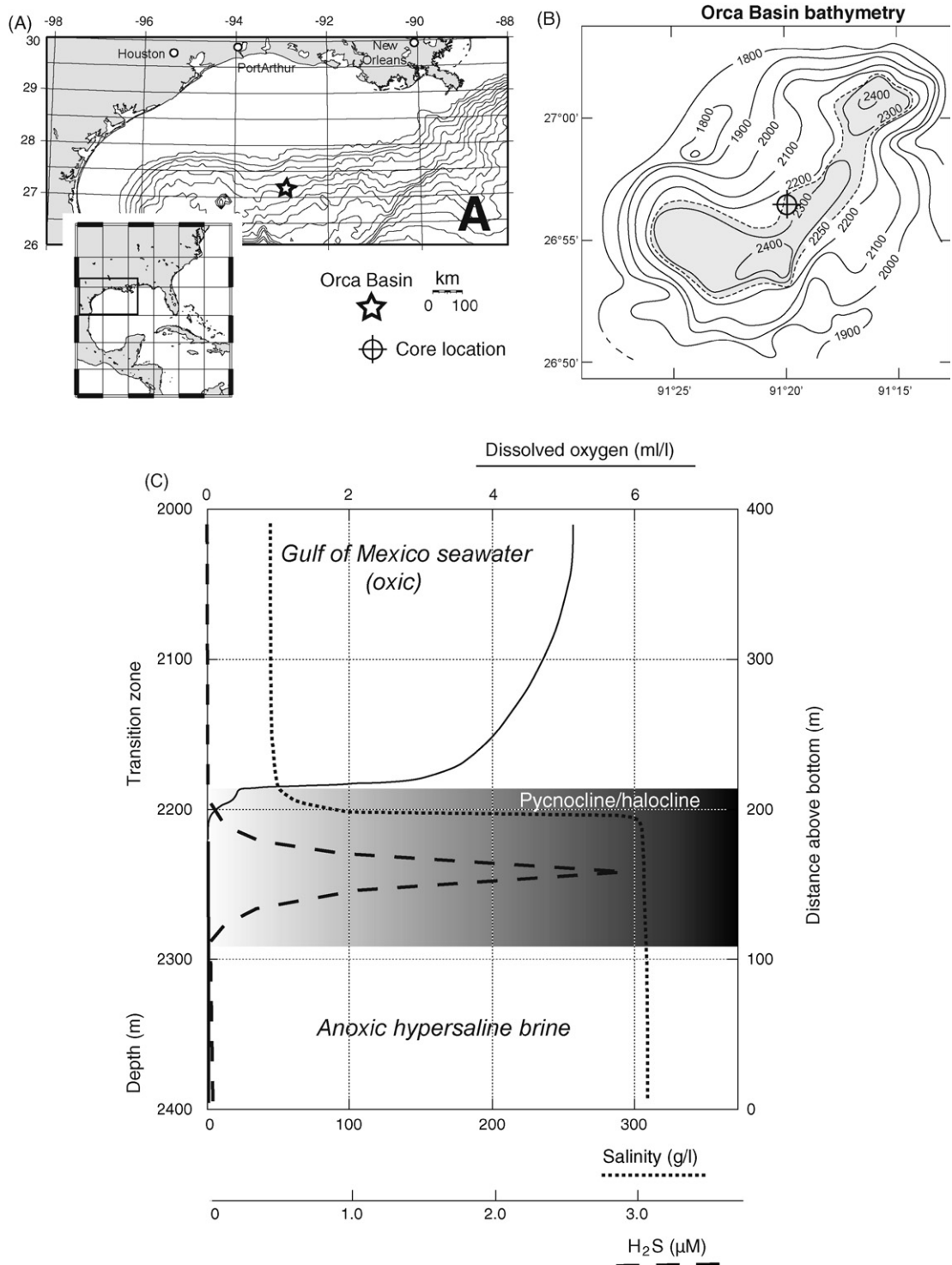
Fig. 1. Location (A) and bathymetry (B) of the Orca Basin in the Gulf of Mexico. The general maps were drawn using the online map creation device at the following website: http://www.aquarius.ifm-geomar.de/. The bathymetry map is redrawn from [24]. Contours in meters. C. Depth profiles of dissolved oxygen, dissolved H₂S and conductive salinity in the Orca Basin (redrawn from [15,18]).

Fig. 1. Localisation (A) et bathymétrie (B) du Bassin d'Orca dans le Golfe du Mexique. Les cartes ont été dessinées grâce au site : http://www.aquarius.ifm-geomar.de/. La bathymétrie est redessinée d'après [24]. Les profondeurs sont en mètres. C. Distribution verticale des teneurs en O₂ et H₂S et de la salinité dans le Bassin d'Orca (d'après [15,18]).

parameters were published in [24]. Standard palyno-
logical techniques [8] were used to prepare total
untreated kerogen slides from the residues of HCl and
HF digestion. The nature of the palynofacies assem-
blages was determined by analyzing 300 points per
slide. Following [25], several particle categories were
discriminated: plankton-derived amorphous organic
matter (AOM), and the so-called ''figured elements''
(i.e., the nature/origin of which can be identified):
phytoclasts, spores and pollen, marine algae, and
zooplankton debris. The phytoclasts were subdivided
into:

- black opaque particles, i.e., biochemically oxidized
  wood debris;
- structured brown phytoclasts, i.e., cortex and sec-
  ondary xylem;
- leaf and membranous tissues, i.e., cuticles and
  epidermal tissues.

The black opaque particles may reflect several
possible origins: combustion residue (i.e., soot and
charcoal), or deeply oxidized phytoclasts created by
repeated cycles of degradation, or a woody particles
altered by thermal maturation (i.e., coalfield material)
and inherited from the geological substratum [16,25].
The phytoclast categories were based primarily on
translucency, particle shape, and the presence or
absence of botanical microstructure. The qualitative
six-point fluorescence scale of Tyson [25] was used to
estimate the level of preservation of OM.

The clay mineral data used here are from [20] and the
composition of clay mineral assemblage was deter-
mined following [3].

4. Results

4.1. Palynofacies

The palynofacies are dominated by a brown-colored
amorphous OM (AOM) that is characterized by a
heterogeneous ''floc'' structure and ''fuzzy'' outlines,
and shows a relatively granular texture (Fig. 2). This
AOM also shows a hardly-detectable fluorescence. In
all the observed slides, AOM represents more than 80%
of the OM visible on slide surface. This kind of brown
AOM is of marine origin, deriving from bacterial, algal
and planktonic sources [13,16,25]. Several studies
indicated that this type of brown AOM is nonsulfurized
whereas organic S-rich OM appears as orange-colored
AOM – not observed here (see descriptions in
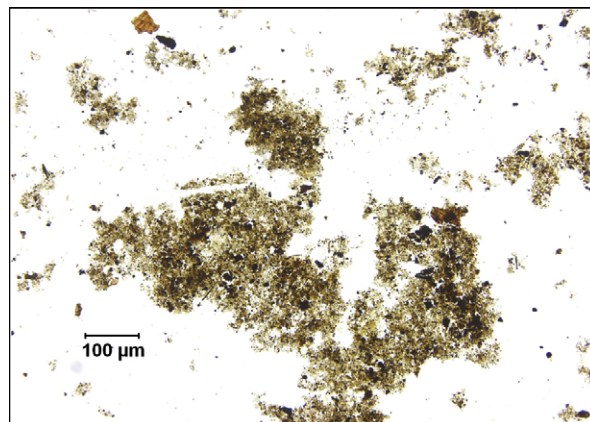[8,9,12,23]). The observed AOM particles show a

Fig. 2. Microphotographs showing the amorphous OM that dominates the palynofacies.

Fig. 2. Microphotographies illustrant la matière organique amorphe rencontrée dans les sédiments étudiés.

relatively small surface area and a sort of brittle aspect,
relative to what is commonly observed on this type of
AOM.

In addition to AOM, figured organic elements are
observed. To determine the respective proportions of
phytoclasts and palynomorphs in the study units, we
used a particle-counting procedure that ignored AOM.
The stratigraphic distribution of the figured components
of the palynofacies is illustrated in Fig. 3. The figured
elements are dominated by brown phytoclasts, opaque
debris, and marine algae, ranked in order of decreasing
abundance. Present in small quantities are zoomorph
remains, leaf and membranous tissues, as well as spores
and pollen grains. From the base of the core to
200 cmbsf, the abundance of opaque debris decreases
progressively (with some minor increases however at ca
270 and 230 cmbsf); the abundance of marine algae
remains rather constant (10–20% of the non-amorphous
fraction). A peculiar level is observed at 200 cmbsf
marked by a minimum in the abundance of opaque
debris and a sharp decrease in the abundance of marine
algae. Above 200 cmbsf, the abundance of opaque
debris increases progressively, while the abundance of
marine algae remains low (< 10%). The 200-cmbsf
level is also characterized by a peak in zoomorph
remains.

The interval between 280 and 380 cmbsf corre-
sponds to a transition zone within which the abundance
of brown phytoclasts decreases substantially, from
concentrations of 45 to 65% below 380 cmbsf to
concentrations mainly comprised between 30 and 50%
above 280 cmbsf. The horizon at about 340 cmbsf
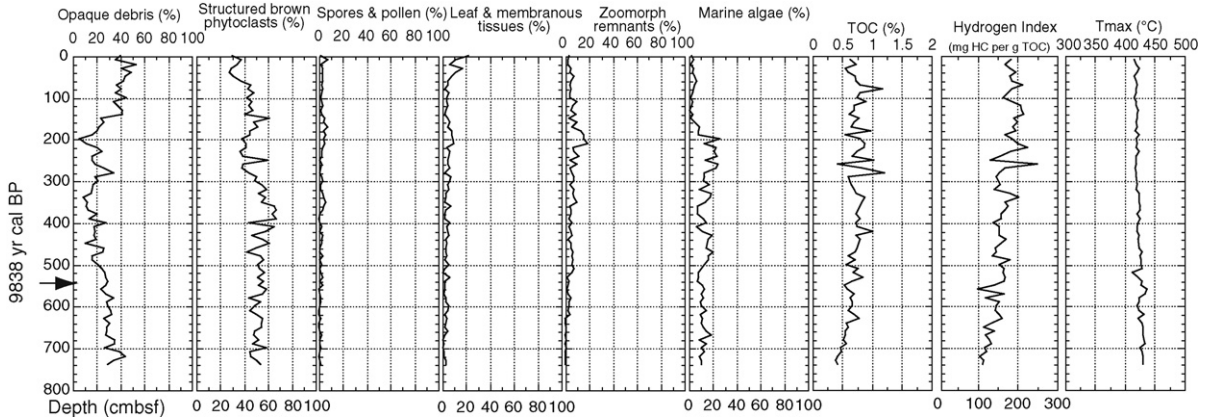corresponds to the end of a steadily-decreasing vertical

Fig. 3. Stratigraphic distribution of the various types of figured elements of the palynofacies, of three classical Rock Eval pyrolysis parameters (total organic carbon or TOC; Hydrogen Index; Tmax).

Fig. 3. Distribution verticale des différents types d'éléments figurés observés dans les palynofaciès et des paramètres classiques de la pyrolyse Rock Eval (carbone organique total ou TOC, indice d'hydrogène ou HI, Tmax).

trend in opaque debris, and the beginning of an increasing-upward sequence (which shows some initial instabilities). The distributions of the other types of figured elements show no relationship with the on going of this horizon.

4.2. Rock Eval parameters

In general, the three parameters, namely, TOC; HI and Tmax, show little variation (Fig. 3). A slight increase in TOC and HI is observed from the base of the
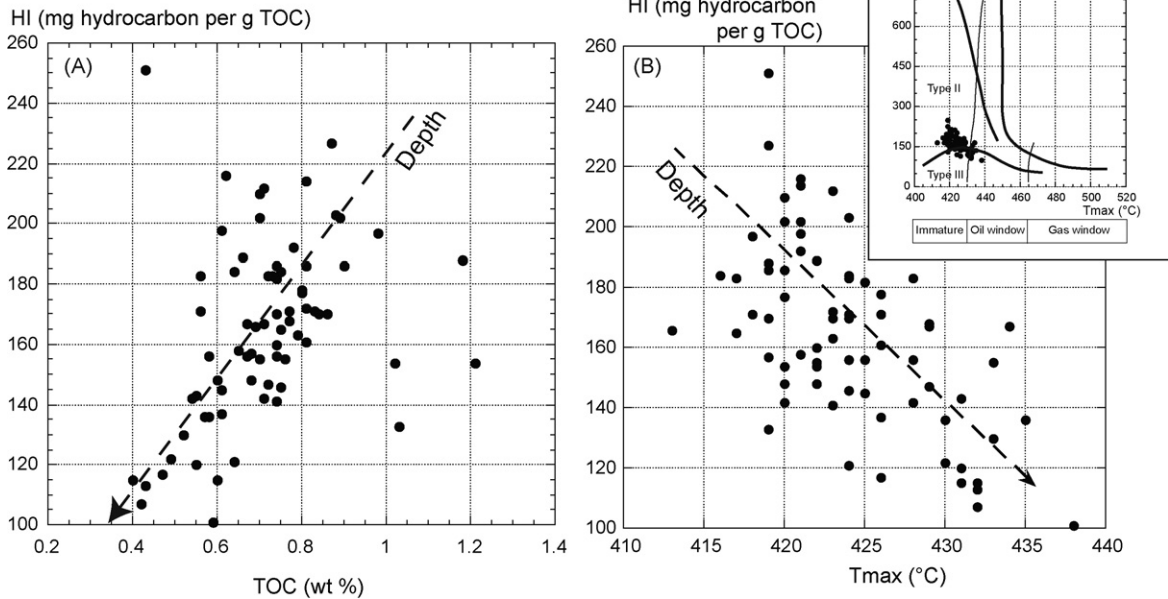

Fig. 4. Rock Eval pyrolysis parameters. A. TOC vs Hydrogen Index (HI). B. Tmax vs HI crossplot illustrating the origin and maturation state of the samples. The arrows on A and B show the general tendency with sample depth below sea floor.

Fig. 4. Paramètres de la pyrolyse Rock Eval. A. Diagramme TOC vs HI. B. Diagramme Tmax vs HI permettant d'illustrer la nature et le degré de maturation de la matière organique. Les flèches en A et B illustrent la tendance générale de l'évolution des paramètres avec la profondeur des échantillons.

section upward, followed by a small decrease at the top (Fig. 3). Tmax values show a smooth distribution with a faint general decrease upward (Fig. 3). As indicated by a Tmax vs HI diagram (Fig. 4), the studied core contains an immature mixture of type-II and type-III OM, i.e., of marine and terrestrial OM. A rough tendency may be observed between TOC and HI (Fig. 4), and the four samples that are the richest in OM (TOC > 1%) do not show the highest HI values. A rather poor correlation is suggested in a Tmax vs HI crossplot (Fig. 4) in which the highest Tmax values are associated with the lowest HI value. Noticeably, no relationship can be observed between Rock Eval parameters and the palynofacies constituents.

4.3. Comparison with the clay-mineral content

The vertical distribution of the land-derived organic figured elements can be compared to that of the clay minerals, which are delivered to the Orca Basin mostly by the Mississippi River. The clay-mineral data reported here are from Sionneau et al. [20 and references therein]. The most salient feature observed is the rather good covariation between the concentrations of opaque debris and the ratio of chlorite to kaolinite (Fig. 5A). For both parameters, a decreasing trend is observed from the base of the section to 350 cmbsf, then an interval of strong covariation is observed from 350 cmbsf to 200 cmbsf. The correlation between opaque debris and the chlorite/kaolinite ratio is less strong for the upper 200 cm of the core, despite a general upward increase in both parameters. However, for the upper 200 cm, a peak-to-peak correspondence is observed between the chlorite/kaolinite ratio and the sum of the abundances of all terrigenous figured elements (Fig. 5B). No other significant relationship was observed between clay minerals and palynofacies constituents (brown phytoclasts, sporomorphs, and marine palynomorphs).
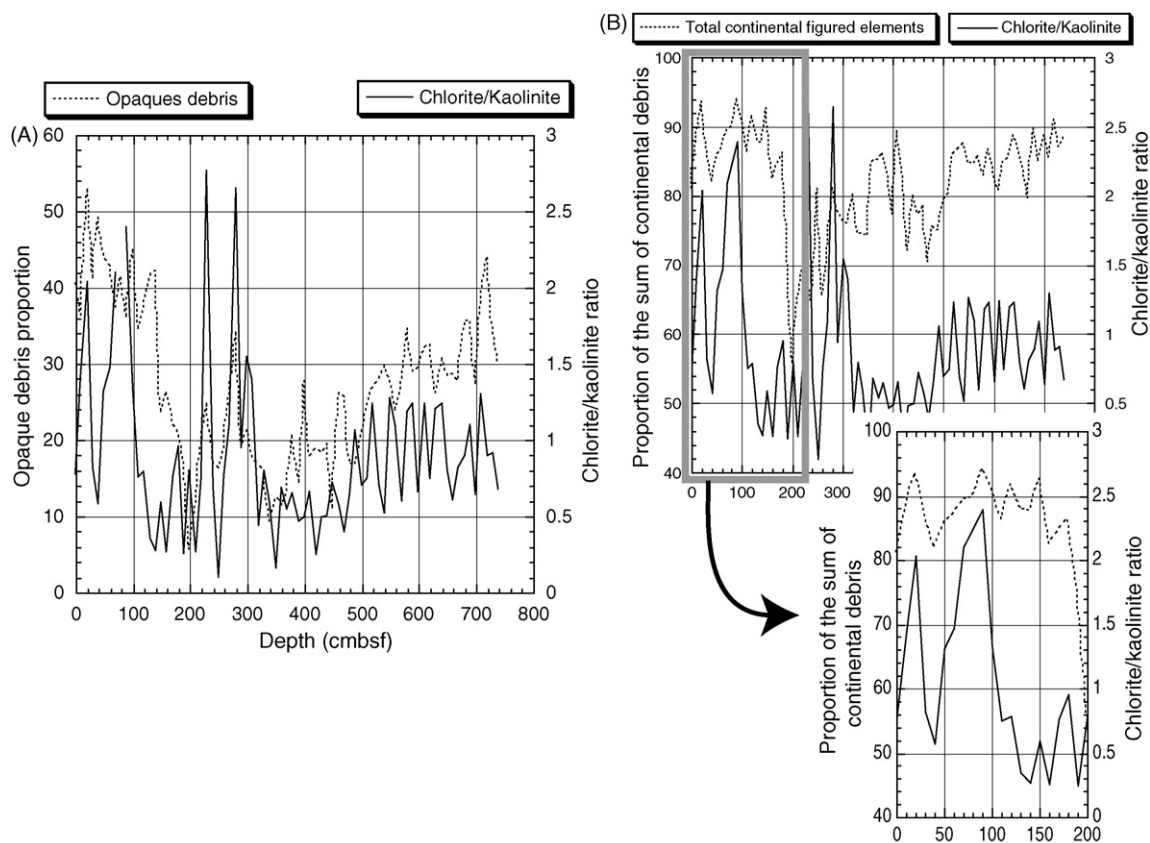

Fig. 5. Stratigraphic distribution of the values of the chlorite/kaolinite ratio, compared to that of opaque organic debris (A) and the sum of the terrigenous figured elements (B).

Fig. 5. Distribution stratigraphique des valeurs du rapport chlorite/keolinite, comparé à celui des débris organiques opaques (A) ou de la somme des débris organiques continentaux (B).

5. Interpretations

5.1. OM preservation

The whole data set shows moderate HI values (100–200 mg hydrocarbon per g TOC) for a recent organic content overwhelmed by marine-origin AOM, whereas higher values would have been expected for Holocene deposited under anoxic conditions [5]. This observation indicates that OM could be relatively degraded all along the studied part of the core. The quasi-absence of fluorescence of the AOM confirms this interpretation.

The stratigraphic distribution of the Rock Eval parameters is not impacted by the variations in the abundance of the various types of figured organic elements, despite the contrasting chemical composition of these elements that should affect both Tmax and HI parameters. This observation suggests that the dominating presence of marine AOM mutes the chemical impact of the variations of figured elements. In this view, the decrease in TOC and HI with depth can be attributed to a progressive degradation of OM.

The small size of brown AOM particles and their brittle aspect indicate a relatively poor preservation state. The figured elements are dominated by brown and black phytoclasts that are refractory constituents, and correlatively poor in more labile constituents such as leaf cuticles or epidermis. This selective enrichment in the more resistant figured elements is unexpected for a depositional setting that is close to the Mississippi River mouth, suggesting that OM underwent some degradation that removed most of the more labile fraction of the figured elements [14].

Consequently, our results indicate that the organic assemblage underwent some degradation; however the bottom sea water and porewaters in the Orca Basin are strictly anoxic and one would expect OM preservation to be favored under such conditions (of course other factors are involved in OM preservation; see e.g., [26] for a recent review). At least, one would expect AOM to show some fluorescence, which is not the case. The release of appreciable amounts of biogenic iodine at the pycnocline was observed, inducing that settling OM is trapped at the stable pycnocline long enough to undergo extensive degradation [17,29]. No published data allow estimating this residence time at the pycnocline. The effect of degradation that we independently observe on the organic assemblage is consistent with the results of these authors. The strong density contrast affecting the water column would retain the settling OM at the pycnocline for some time. At the pycnocline, OM would remain in contact with the overlying oxygen-rich water mass. The contact would last long enough to favor OM degradation, which may explain the relatively poor preservation of AOM and the selective enrichment in the more refractory fraction of the figured elements.

The relative degradation of OM could at least partly explain why the rate of bacterially-mediated sulfate reduction is rather low in the Orca Basin. The low rate was already reported, despite abundant dissolved sulfate and appreciable OM [17,22]. According to the study by Porter et al. [10], high salinity cannot be suspected as the cause of lower sulfate reduction rates. Consequently, it is suggested that relatively degraded OM could not sustain extensive sulfate reduction.

5.2. Influence of the land-derived supply

Our study of the palynofacies assemblage and of its co-variations with the clay-mineral spectrum reveals the significant inputs of land-derived OM to the Orca Basin, though the marine-produced organic fraction is dominant. A prominent feature in the stratigraphic distribution of the figured elements is the covariation of the opaque debris and clay minerals (Fig. 5). The main source of the land-derived clay minerals deposited in the Orca Basin is the Mississippi River catchment. Clay minerals originating from the weathering of continental source rocks are formed on a time scale of about 500,000 yrs [4,21], that is, on a time scale much longer than the age of the sediments studied here. Because the studied sediments are of Holocene age, variations in the clay mineral composition must therefore reflect different source regions over the very large river catchment rather than climate-induced evolution of constant sources. Consequently, the correlation between the terrigenous constituents of the palynofacies and the land-derived clay mineral assemblage indicates that the variations affecting palynofacies must be ascribed to fluctuations of the land-derived inputs and not to variations of the OM-preservation conditions. The Mississippi River catchment may be divided into various areas that are each characterized by their peculiar clay mineral assemblage [20]. It is inferred that the composition of the clay-mineral assemblage of the sediments of the Orca Basin may be influenced by the way the Mississippi River catchment undergoes erosion. According to the main areas of the catchment (and consequently the inventories of clay minerals) that are subjected to erosion, the dominant clay minerals delivered to the Gulf of Mexico, and thus the Orca Basin, will change with time in conjunction with the remobilized inventory of organic particles. Thus, our results suggest that further studies could help to

determine the modalities of erosion of a large part of the North American continent through the Holocene.

6. Conclusions

Though the anoxic bottom conditions should favor preservation, OM is rather degraded in the Orca Basin sediments and its degradation must be accounted for, at least in part, by extended residence of the OM particles at the stable brine-sea water interface at 2230–2250 m water depth, where OM is subjected to oxic conditions. The degradation deduced from the release of abundant biogenic iodine at the pycnocline is confirmed by the relatively low HI values, the low fluorescence of the kerogens found within the sediment at all levels, including at the sediment-water interface, and the visual aspect of AOM. Usually, OM preservation and accumulation are reputed to depend on several factors including: productivity, magnitude of sedimentation rate, oxygenation level/redox status of bottom and pore waters, biochemical nature of OM. Several works also stressed the influence of remineralization processes occurring during organic-particle settling through the water column (e.g., [2,28], and references therein). The present study shows that OM may be degraded within the water column when it is retained durably at the pycnocline. Thus, high productivity coupled to strictly anoxic conditions cannot guarantee significant OM accumulation if a marked pycnocline strongly slows down organic-particle settling. Our results may apply to any basin characterized by a sharp density contrast within its mater mass.

This study also illustrates that a relative variability may be detected within the flux of land-derived organic particles whereas this variability does not correspond to major or even moderate fluctuations of hydrological conditions in the Gulf of Mexico or global climate affecting the emerged lands drained by the Mississippi River (almost half of the conterminous United States). The modest (regional scale) variations in Holocene climatic conditions (reputedly largely equable) on emerged lands can – in fact – induce appreciable variations in the sedimentary organic record. These observations must be kept in mind while studying ancient geological series: one is exposed to ''over-interpreting'' mineralogical variations when reconstructing paleoenvironments at the geological scale.

Acknowledgements

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