Latitudinal variability of preserved sedimentary organic matter along the Peruvian continental margin as inferred from petrographic and geochemical properties

Maricarmen Igarza, Mohammed Boussafir, Michelle Graco, Abdel Sifeddine, Jorge Valdés, Dimitri Gutiérrez

Journal Pre-proof

Latitudinal variability of preserved sedimentary organic matter along the Peruvian continental margin as inferred from petrographic and geochemical properties

Maricarmen Igarza, Mohammed Boussafir, Michelle Graco, Abdelfettah Sifeddine, Jorge Valdés, Dimitri Gutiérrez
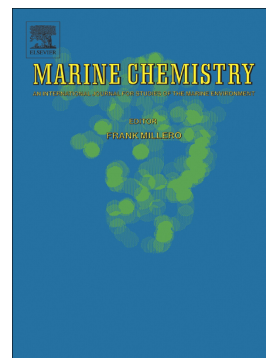
This is a PDF file of an article that has undergone enhancements after acceptance, such as the addition of a cover page and metadata, and formatting for readability, but it is not yet the definitive version of record. This version will undergo additional copyediting, typesetting and review before it is published in its final form, but we are providing this version to give early visibility of the article. Please note that, during the production process, errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

LATITUDINAL VARIABILITY OF PRESERVED SEDIMENTARY ORGANIC MATTER ALONG THE PERUVIAN CONTINENTAL MARGIN AS INFERRED FROM PETROGRAPHIC AND GEOCHEMICAL PROPERTIES

Maricarmen Igarza[1,4*], Mohammed Boussafir[2,3], Michelle Graco[1,4], Abdelfettah Sifeddine[5], Jorge Valdés[6], Dimitri Gutiérrez[1,4]

[1]Programa de Maestría en Ciencias del Mar, Universidad Peruana Cayetano Heredia, Lima, Perú.
[2]Institut des Sciences de la Terre d'Orléans, ISTO, UMR 7327
[3]Laboratoire GéoHydrosytèmes COntinentaux (GeHCO), E.A 6293, Faculté des Sciences et Techniques Université de Tours.
[4]Dirección General de Investigaciones en Oceanografía y Cambio Climático, Instituto del Mar del Perú, Callao, Perú.
[5]IRD-Sorbonne Université, LOCEAN (IRD, CNRS, Sorbonne Université, MNHN) Bondy-France
[6]Laboratorio de Sedimentología y Paleoambientes, Instituto de Ciencias Naturales A. von Humboldt, Facultad de Ciencias del Mar y de Recursos Biológicos, Universidad de Antofagasta, Chile

*Corresponding author:
Maricarmen Igarza
Email address: maria.igarza.t@upch.pe

Abstract

Processes controlling preservation and accumulation of organic matter (OM) in marine sediments are highly sensitive towards both natural and anthropogenic impacts. Thus, the sedimentary OM is considered a key proxy for the characterization of recent and past sedimentary environments. Along the Peruvian continental margin (PCM), high primary production and an intense oxygen minimum zone (OMZ) favor the accumulation and preservation of OM in sediments. Spatial variations in oceanographic conditions impact on both productivity and the redox conditions, in particular the OMZ intensity. These factors in turn lead to spatial differences in depositional conditions and OM accumulation and preservation. Therefore, this study aims at characterizing nature and types of recent sedimentary OM along the PCM covering a wide latitudinal and bathymetric range. With this purpose, a total of 29 surface sediment samples were collected from Tumbes (3°S) to San Juan (15°S) and analyzed by means of organic petrography (palynofacies analysis) and Rock-Eval pyrolysis. Results allowed characterizing the OM from recent sediments. Along the PCM, the sedimentary OM is predominantly amorphous, revealing its overwhelming marine origin. The highest abundances of gelified amorphous OM, total organic carbon, S1 and S2 Rock-Eval fractions occurred towards the southern part of the study area, especially off Callao (12°S) and Pisco (14°S), considered important upwelling and primary productivity centers. A principal component analysis performed allowed the description of main OM depositional environments. In the outer continental shelf of Callao (12°S) and OMZ of Pisco (14°S), accumulation of well-preserved OM occurs whereas in the inner shelf of Callao redox oscillations lead to less OM accumulation and pyrite formation in sediments. North of Callao, from Tumbes (3°S) to Huacho (11°S), a mixed signal of OM accumulation was observed. Finally, along the slope, transportation processes seem to play a key role in OM accumulation. This study also allowed the evaluation of certain proxies (e.g. Rock-Eval hydrogen index and oxygen index) routinely used in palaeoceanographic studies.

1. Introduction

In the ocean, phytoplanktonic production represents near 95% of total primary production and thus constitutes the main source of organic matter (OM, Killops and Killops, 2005). Only a small fraction of the OM produced in the photic area reaches the sea floor (1%, e.g. Hedges and Keil, 1995; Suess, 1980), where further degradation occurs via aerobic and anaerobic processes. In coastal areas, where phytoplankton production is high, near 10% of the total produced OM can reach the sediment (Hedges and Keil, 1995). The amount and composition of sedimentary OM directly depends on the production and supply in surface waters (Zonneveld et al., 2010), thus, the analysis of sedimentary OM provides key information for the characterization of present and past oceanographic conditions. In the last decades, techniques routinely applied in petroleum geochemistry, like organic petrography (palynofacies analysis) and Rock-Eval (RE) analysis (Espitalié et al., 1985), have been successfully employed in the study of OM deposited in both recent and past marine sediments from coastal and upwelling areas (Salvatteci et al., 2016; Hare et al., 2014; Valdés et al. 2009; Gurgel 2008; Marchand et al., 2008; Valdés et al., 2004; Pichevin et al., 2004). Moreover, the combination of both techniques has proven to be quite successful in the study of early diagenesis of marine OM (Gelin et al. 1995, Boussafir et al., 1995a, b, 1994; Lallier-Vergès et al., 1991) and lacustrine OM (Boussafir et al., 2012; Zocatelli et al., 2012).

The Peruvian upwelling system is among the most productive marine ecosystems in the world ocean (Chavez and Messié, 2009). In this system, upwelling takes place year-round (Bakun and Weeks, 2008), maintaining high primary production and therefore high rates of OM sedimentation. This situation, alongside with circulation patterns and water mass age, promotes the formation of an intense oxygen minimum zone (OMZ) off the coasts of Peru (Helly and Levin, 2004). In places where this OMZ impinges the sea floor, bioturbation is inhibited (Gutiérrez et al., 2008) and thus OM preservation is favored. Along the Peruvian continental margin (PCM), latitudinal changes of primary production, bottom dissolved oxygen and coastal shelf morphology determine the presence of different depositional environments, and thus affect the accumulation of sedimentary OM (Calienes et al., 1985; Delgado and Gomero, 1995; Gutiérrez et al., 2008; Scheidegger and Krissek, 1982).

In the PCM, previous organic geochemical studies analyzed OM content and composition in ancient and recent sediments from one of the main productive areas (between 9°S and 15°S). Repeta (1989) and Repeta and Gagosian (1987) studied the distribution and degradation of carotenoids in sediment trap material, zooplankton fecal pellets and surface sediments. These studies revealed differences in the composition of carotenoids between sediment trap material and surface sediments, which the authors attributed to different reactivity of the organic material. Studies regarding lipid distribution and composition has also been performed in both core samples and surface sediments (Farrington et al., 1988; Volkman et al., 1987; Gagosian et al., 1983; Wakeham et al., 1983, 1984, 1985). The studies showed high variability in both lipid flux and composition, a variety of marine sources for the lipids, and little degradation of lipids that reach the seafloor. ten Haven et al. (1990) analyzed deep-sea ancient sediments between 9°S and 11°S by means of organic geochemical and organic petrography techniques. The study showed that OM preservation is favored in sediments underlying upwelling cells, and that marine plankton and bacteria are the main contributors to the sedimentary OM. Farrimond et al. (1990) also reported the predominance of lipids of marine origin in sediment samples collected at 15°S, with terrigenous lipids being minor components of the sedimentary OM. Lückge et al. (1996) reported that the sedimentary OM deposited between 11°S and 12°S was mainly derived from phytoplankton degradation and had undergone an important degree of sulphate reduction. The authors also proposed sediment transport processes to be an important factor to explain high OM

2

accumulation in deep sediments outside the upwelling area. Likewise, Arthur et al. (1998) proposed, based on the use of both isotopic and RE analyses, that bottom currents and redeposition could exert an important control on organic carbon concentration. More recently, the studies of Salvatecci et al. (2016, 2014) and Gutiérrez et al. (2009) showed that isotopic analyses and organic geochemical proxies used in modern biogeochemistry are good indicators of climate and ocean ecosystem variability. As evidenced by the previous studies, the analysis of the OM deposited in sediments of the PCM provides a valuable tool to infer changes in ocean productivity and climate.

Given the predominance of marine sources for the sedimentary OM along the PCM, changes in OM accumulation and composition should essentially be the result of diagenetic processes. Nevertheless, none of the studies already performed has characterized the sedimentary OM in areas north of 9°S where fluvial input to the ocean is more important compared to the south (Scheidegger and Krissek 1982). Additionally, latitudinal changes in primary production and variability in the intensity of the OMZ should affect OM composition and accumulation in sediments. Thus, two questions arise, do marine sources still contribute largely to the sedimentary OM deposited in northern areas of the PCM? Should we expect a difference in composition and accumulation of sedimentary OM at different latitudinal and bathymetric levels? In order to understand the processes controlling spatial variations in OM accumulation and composition along the PCM, we have conducted a study that characterized the nature and state of preservation of OM from recent sediments and allowed to determine the main OM depositional environments. With this purpose, surface sediment samples were collected along the PCM covering a wide bathymetric and latitudinal range, and then analyzed by organic petrography (palynofacies analysis) and RE pyrolysis.

2. Materials and Methods

2.1 Study area and sample collection

Along the PCM, the main upwelling and primary productivity centers are located in the central/southern part between 10°S and 12°S, and between 14°S and 15°S (Calienes et al., 1985; Zuta and Guillén, 1970). OM-rich sediments (>10% organic matter) in these areas reflect highly productive surface waters and depositional conditions favoring OM preservation (Reimers and Suess, 1983).To the north of 10°S, more ventilated conditions in the water column and less primary production prevent high accumulation of OM (Delgado and Gomero, 1995; Mollier-Vogel et al., 2012).

In the present study, a total of 29 surface sediment samples from the PCM were collected covering a wide bathymetric (48 m – 2607 m) and latitudinal (3°S – 15°S) range under different conditions of primary production and bottom dissolved oxygen (Figure 1, Table 1). In all cases, a multi-corer (MUC) device was used to recover undisturbed surface sediment samples. Only the top 0.5 cm of each core was used for the different analyses. After collection, all samples were stored at low temperature (8 ºC) until the laboratory analyses.

All the geochemical data obtained from both the petrographical and RE analyses were discussed with respect to the environmental variables depth (m) and dissolved oxygen (mL L^{-1}). The dissolved oxygen values used in this study were measured at the bottom of each collection site by means of an oxygen sensor coupled to a CTD before the retrieval of the sediment samples.

2.2 Analytical techniques

Prior to all analyses, all the samples were dried in an oven at 60ºC for four days and then homogenized and powdered in an agate mortar.

2.2.1 Organic petrography (palynofacies analysis)

The palynofacies analysis involves the observation and relative quantification of organic particles under transmitted light microscopy (Combaz, 1980). This analysis was carried out on the total OM previously isolated from the carbonate and silicate phases of the sediment by acid treatments. Ca. 1 g sediment underwent acid treatment with both hydrochloric and hydrofluoric acids in order to remove the mineral matrix (Combaz, 1980). The resulting organic residue was then examined using transmitted and reflected light microscopy, allowing the description of different organic fractions. Additionally, observations under UV excitation were performed, allowing the identification of phytoplankton material, which is sometimes invisible in transmitted white light but well observed by fluorescence of hydrocarbon-rich fractions (Boussafir et al., 2012). The absolute quantification of organic particles was performed using a pollen standard (10 mg mL^{-1}). The proportion of each organic fraction was estimated by counting more than 1000 surface units per microscope slide. Afterwards, a calculation of the absolute abundance of organic particles was done using an in-house macro function, which allows the estimation of a threshold in which the percentages of each compound do not vary anymore.

2.2.2 Rock-Eval6® (RE) pyrolysis

RE pyrolysis is a widely used method to screen rock samples and evaluate its potential for hydrocarbon generation (Peters, 1986). In the last decades, its applications have extended to recent marine and lacustrine sediments (e.g. Baudin et al., 2015; Hare et al., 2014; Boussafir et al., 2012), providing valuable qualitative and quantitative information concerning accumulation and characterization of sedimentary OM. For further description of the method and of the parameters that can be obtained, please refer to Lafargue et al. (1998). Briefly, the RE analysis determines the amount of hydrocarbons (HC) that are released from a given sediment sample during a progressive heating that usually goes from 200°C to 600°C under N_2 gas vector. Afterwards, certain parameters can be calculated. Since the recent OM-rich samples analyzed in this study are thermally labile, with possible presence of biogenic carbonate minerals weakly crystallized and sea salts (NaCl, sulfate), we did not use the classical RE program (Bulk-rock or pure OM modes) usually used for petroleum source rock samples, but a modified RE pyrolysis program adapted to our samples. The pyrolysis program used in this study started with an isothermal stage at 200 ºC for 2 minutes, then the oven temperature was raised at a rate of 30 ºC min^{-1} to 650 ºC (held 3 min). The oxidation phase (pyrolysis under purified air) corresponded to an isothermal stage at 400 ºC, then a ramp at 30 ºC min^{-1} to 850 ºC (held 5 min). This method is very close to the one proposed by Baudin et al. (2015) as standard mode for the analysis of recent OM. The proposed method avoids misleading interpretation of the RE data and makes it possible to intercompare the results regardless of the RE device used. Prior to the analysis, powdered samples were rinsed twice in demineralized water and dried at low temperature, then about 50 to 100 mg of this powder was used for the RE6® analysis (Vinci Technologies, Rueil Malmaison).

The RE parameters obtained during the pyrolysis and used in this study were:

1. Total organic carbon (TOC), which reflects the quantity of OM in a given sediment sample in percentage.

4

2. Fraction S1 (mg HC g^{-1} sediment), represents the amount of free HC that can be thermo-evaporated from the sample before 300°C.

3. Fraction S2 (mg HC g^{-1} sediment), represents the amount of HC that can be generated by pyrolytic degradation of the sample between 300°C – 600°C.

4. Hydrogen index (HI, mg HC g^{-1} TOC), represents the amount of HC produced during pyrolysis relative to TOC content (HI = S2/TOC x 100) and indicates the hydrogenated quality of the OM.

5. Oxygen index (OI, mg CO_2 g^{-1} TOC), represents the amount of oxygen produced as CO_2 during pyrolysis of a given sample relative to TOC (OI = S3/TOC x 100) and indicates either the oxygenated quality of OM or its degree of oxidation.

6. TpS2, represents the temperature of the maximum S2 hydrocarbon generation in RE 6 analysis and indicated either the labile or refractory character of the OM.

2.3 Data treatment and statistical analyses

All statistical analyses were performed using the R statistical platform (version 3.3.0). For generation of plots, the R package *ggplot2* (Wickman, 2006) and the Sigmaplot software (version 13.0) were used.

To analyze the bathymetric variability, samples were grouped in four groups, continental shelf (0 – 180m), OMZ (180 -350m), lower edge OMZ (350 – 600m) and slope (600 – 3000m). Additionally, samples were also grouped according to latitude (Table 1) in two groups, north (3°S – 9°S) and south (11°S – 15°S) for comparison purposes. Comparison of a given variable among different groups of samples was done either with a Student t-test or a Mann-Whitney test depending on the type of statistical distribution.

To analyze the relationship among variables, a Pearson product-moment correlation was performed using the package *Hmisc* (Harrel et al., 2016). The relationship among variables and sites was analyzed by means of a Principal Component Analysis (PCA) and a Cluster analysis in order to determine depositional environments of OM along the PCM. PCA aims at representing major features in a dataset by using a reduced number of axes (Borcard et al., 2011). The PCA was performed using the package *vegan* (Oksanen et al., 2016). Since the variables included in the PCA had different dimensions, a standardization was made before the PCA analysis.

3. Results

3.1. Organic petrography (palynofacies analysis)

3.1.1 Palynofacies observations and quantification

Following the description of Pichevin et al. (2004) and Boussafir et al. (2012), a total of eight organic particles were identified according to texture and morphology (Table 2). The particles were organized in three groups.
1. The amorphous OM (AOM) group mainly characterized by organic particles with no-define edges and an amorphous shape. These organic particles have been previously

5

linked to phytoplankton production (e.g. Pichevin et al. 2004; Boussafir et al. 1995a; Lallier-Vergès et al., 1993). Within the AOM group, we differentiated between gelified homogeneous AOM, gelified granular AOM and flaky AOM.

2. The terrestrial group is composed of lignocellulosic debris and cuticles and spores. These organic particles are easily distinguishable and originate from fluvial and/or aeolian transport.

3. A third group composed by framboidal pyrite, evidence of anoxic conditions in sediments (Pichevin et al., 2004), and gelified spherules, which show a perfectly round shape and do not show agglomeration, contrary to the gelified granular AOM.

The quantitative palynofacies analysis showed a clear predominance of the AOM group along the PCM (Table 3). Within this group, the most abundant organic particle was the gelified homogeneous AOM, evidencing the high phytoplanktonic production of the study area, followed by flaky AOM and gelified granular AOM. Among the non-amorphous organic particles, pyrite and gelified spherules showed the highest average abundance, while lignocellulosic debris and cuticles and spores, representing the terrestrial organic particles, were the less abundant.

3.1.2 Latitudinal and bathymetric distribution of palynofacies

Within the AOM group, all fractions showed a trend to increase from north (3°S – 9°S) to south (11°S – 15°S) (Figure 2), although significant differences were only found for the latitudinal distribution of flaky AOM and gelified granular AOM (Mann Whitney test, $p < 0.05$). The samples retrieved from the continental shelf and OMZ between Huacho (11°S) and San Juan (15°S) showed the highest abundances of the AOM group, up to 120.5 mg g^{-1} sed. Along the slope, an increase in the abundance of the AOM group was observed from north to south.

Along the PCM, terrestrial organic particles increased from north to south (Figure 2). The abundance of cuticles and spores showed significant differences (Mann Whitney test, $p < 0.05$) between north (3°S – 9°S) and south (11°S – 15°S), dominating the terrestrial fraction in the north. Towards the south, lignocellulosic debris increased, although no significant differences were found. At the bathymetric level, the highest abundances of the terrestrial fraction were found in the continental shelf between Huacho (11°S) and San Juan (15°S) where lignocellulosic debris dominated (up to 5.2 mg g^{-1} sed off Pisco), and along the slope where cuticles and spores dominated (Figure 2).

The highest abundances of pyrite and gelified spherules were found in the continental shelf and OMZ between Huacho (11°S) and San Juan (15°S) (12.3 mg g^{-1} sed and 7.6 mg g^{-1} sed respectively) (Figure 3). In the inner shelf (< 100 m depth) between 11°S and 12°S (Huacho - Callao) pyrite dominated, while in the outer shelf (> 100 m depth) and OMZ between 14°S and 15°S (Pisco - San Juan) gelified spherules dominated (Figure 3). Overall, in other areas of the PCM, the abundance of pyrite and gelified spherules was quite low, except for one sample from the OMZ of Piura (5°S) and the slope of Chimbote (9°S).

3.2 Bulk geochemistry (Rock-Eval analysis)

3.2.1 Rock-Eval (RE) parameters

The RE analysis allowed to obtain parameters for both OM accumulation (TOC, fractions S1 and S2) and OM geochemical quality (HI, OI and TpS2). Along the PCM, TOC values varied between 1% to 12%, with a maximum value of 11.6 % off Callao (12°S) (Table 3). Fraction S2 (25.5 ± 13.7 mg HC g^{-1}) was on average twenty times higher than fraction S1 (0.1 ± 0.1 mg HC g^{-}

6

[1]) in surface sediments of the PCM (Table 3). Despite the dominance of fraction S2, both fractions showed a significant positive correlation (r = 0.85, $p < 0.05$) (Supplementary Table S1). Aditionally, both fractions showed a positive significant correlation with TOC (r = 0.85 and r = 0.97 respectively, $p < 0.05$; Supplementary Table S1), evidencing its important contribution to the TOC along the PCM. TpS2 values ranged between 434°C and 464 °C (Table 3), typical for recent sediments (Boussafir et al., 2012). TpS2 showed a negative significant correlation with fraction S2 (r = -0.6, $p < 0.05$; Supplementary Table S1), thus a decrease in temperature is associated to an increase in the production of fraction S2.

A classical representation of both HI and OI is usually done using a modified van Krevelen diagram, in which both indexes are plotted against each other (Supplementary Figure S1). Along the PCM, the HI was comprised between 300 and 500 mg HC g^{-1} TOC, whilst OI values ranged between 100 and 190 mg CO_2 g^{-1} TOC (Table 3). These values are typical for OM of marine origin (Peters et al., 2005). The distribution of the samples in the modified van Krevelen diagram (Supplementary Figure S1) showed that the OM from surface sediments of the PCM is characterized by a similar signature to that of type II sedimentary OM, although slightly more oxygenated. During the diagenetic evolution of the recently deposited OM, it will first lose its oxygenation function leading to a general decrease in OI. Afterwards, this OM will correspond perfectly to the classic signal of OM deposited in a marine environment, which is considered mainly from algal origin (Bordenave et al., 1993; Tissot and Welte 1984).

3.2.2 Latitudinal and bathymetric distribution of RE parameters

OM accumulation parameters (TOC, fractions S1 and S2) showed a trend to increase from north to south of the PCM (Figure 4A, 4B). Highest values were found in two samples from the outer continental shelf of Callao (100 m – 215 m) and in samples from the OMZ of Callao (12°S) and Pisco (14°S). Lowest values corresponded to samples from the slope except for one sample from the continental shelf of Chimbote (9°S). The HI also showed a similar trend as the accumulation parameters (Figure 5A), with high values towards the south of the PCM compared to the north (Figure 5A). High values of HI occurred in the continental shelf and OMZ of Callao (12°S) and Pisco (14°S), and lowest values in the slope. The OI showed higher variability compared to the HI (Figure 5B), with no evidence for an increase/decrease related to latitude. Lowest OI values were found off Piura (5°S) and in one sample from the lower edge of the OMZ of Pisco (14°S). The highest OI value occurred in the inner continental shelf of Callao (12°S) and in the lower edge of the OMZ of Huacho (11°S). TpS2 increased from south to north of the PCM and from the continental shelf towards the slope (Figure 6). Low values of TpS2 occurred in the continental shelf and OMZ of Callao (12°S) and Pisco (14°S), while high values occurred between Tumbes (3°S) and Trujillo (8°S).

3.3 Principal component analysis (PCA)

In order to determine the main depositional environments of OM along the PCM, a principal component analysis (PCA) was performed (Figure 7). This analysis provided an overview of the relationships between petrographical (palynofacies analysis), geochemical (RE analysis) and environmental variables (dissolved oxygen and depth). Since the absolute quantification of organic particles revealed the AOM fraction was at least 10 times higher compared to the terrestrial fraction (Figure 2, Table 3), changes in OM composition and accumulation along the PCM are mainly the result of diagenetic processes. Therefore, the terrestrial organic particles have been excluded from the PCA analysis.

7

The PCA showed that the two first components (i.e. axes) explained 66% of the variability in the data. Principal component 1 (PC1) accounted for 47% of the total variability, while principal component 2 (PC2) accounted for 19%. The PCA performed displays variables as vectors and a circle of equilibrium contribution (Figure 7). The variables whose vectors are longer than the radius of the circle have a larger contribution to the variability of the data than those whose length is shorter (Borcard et al., 2011). Therefore, the most important variables were gelified homogeneous AOM, flaky AOM, pyrite, TOC, fraction S2, depth and dissolved oxygen.

The PCA analysis showed a bathymetric gradient from left to right (Figure 7), starting with samples from the continental shelf and OMZ of Callao (12°S) and Pisco (14°S), and ending with samples from the slope. Following this gradient, four groups of samples were identified and associated to specific variables. This grouping was further confirmed by a cluster analysis performed using the factor scores obtained from the PCA analysis (Supplementary Figure S2). A first group was formed by samples from the outer continental shelf of Callao (> 100 m depth) (12°S) and OMZ of Pisco (14°S), which plotted to the left side of the biplot (Figure 7, Figure S2). This group of samples displayed high values of S1, S2, TOC, HI, gelified spherules, gelified granular AOM and gelified homogeneous AOM. A correlation analysis showed good positive correlations ($p < 0.05$) among these variables, except for HI that showed overall low correlation coefficients compared to the other RE parameters (Supplementary Table S1). The samples in this group also showed low values of TpS2 (Figures 6 and 7). DO values varied between Callao and Pisco, the samples from the outer continental shelf of Callao were characterized by suboxia (DO < 0.1 mL L^{-1}, Karstensen et al., 2008), while off Pisco DO values ranged from 0.1 to 0.4 mL L^{-1}.

A second group was formed by two samples from the inner shelf (< 100 m depth) of Callao (12°S) (Figure 7, Figure S2). Both samples displayed high values of pyrite and flaky AOM (Figure 7). The most coastal sample at 48 m depth displayed the highest OI, while the sample at 92 m depth displayed the second highest value of HI. DO showed minimum values for both samples, while TpS2 showed intermediate values (Figure 6). A third group of samples plotted around the center of the biplot (Figure 7, Figure S2) and was formed by samples from the outer continental shelf of Chimbote (9°S) and Pisco (14°S), the OMZ of Tumbes (3°S) and Piura (5°S), the lower edge of the OMZ and two samples from the slope. All the samples in this group showed intermediate to low values for all measured variables and were not spread out by axes 1 and 2 of the PCA. Finally, a fourth group was formed by samples plotting at the lower right of the biplot (Figure 7, Figure S2). These samples corresponded entirely to the slope. Overall, the samples in this group displayed high values of DO (up to 2.0 mL L^{-1}), TpS2, and low values of flaky AOM, TOC, fractions S1 and S2, and HI.

4. Discussion

4.1 Variability of organic and geochemical parameters along the PCM

The predominance of the AOM fraction, linked to phytoplankton production (e.g. Pichevin et al. 2004; Boussafir et al. 1995a; Lallier-Vergès et al., 1993), revealed an overwhelming marine origin for the OM deposited in surface sediments along the PCM (Figure 2). Previous studies in the area (Gurgel, 2008; Lückge et al., 1996; Powell et al., 1990; ten Haven et al., 1990) and in the upwelling systems of Benguela (Pichevin et al., 2004) and Chile (Valdés et al., 2009) also revealed an overwhelming predominance of the AOM fraction in sediments. Thus, this non-structured OM aggregate is a typical proxy of high productivity areas. The latitudinal distribution of the AOM fraction along the PCM further confirms this, with high productivity areas located south of 10°S (Calienes et al., 1985) characterized by higher absolute abundances of the AOM

8

fraction compared to less productive areas north of 10°S (Calienes et al., 1985) characterized by lower absolute abundances (Figure 2).

The present study is unique since it presents an absolute quantification (mg g^{-1} sed) of the organic particles, contrary to past studies in the PCM (Gurgel, 2008; Lückge et al., 1996; Powell et al., 1990; ten Haven et al., 1990) and studies from other regions (Valdés et al., 2009, Pichevin et al., 2004) where a relative quantification was performed. An absolute quantification of organic particles allows a better interpretation of OM composition and preservation. Among the identified AOM particles, the gelified homogeneous AOM showed the highest absolute abundance (Table 3, Figure 2). Gelified AOM has also been identified in palynofacies from the upwelling systems of Benguela (Pichevin et al., 2004) and Chile (Valdés et al., 2009), and has been associated to sedimentary environments that favor OM preservation. In sediments from the PCM, Gurgel (2008) reported the gelified AOM fraction represented more than 50% of all identified OM fractions. According to Boussafir et al. (1995a) the relative contribution of the gelified AOM fraction to the total OM increases with an increase in organic productivity. In the PCM, the high positive correlation between the gelified homogenous AOM and TOC (r = 0.89, p < 0.05; Supplementary Table S1) further confirms this organic particle is associated to high accumulation of OM. The gelified AOM fraction showed an increase in absolute abundance towards the south of the PCM (Figure 2), characterized by conditions of high primary production (Calienes et al., 1985). Furthermore, the dominance of this fraction in the outer continental shelf (> 100 m depth) of Callao (11°S – 12°S) and in the OMZ of Pisco and San Juan (14°S – 15°S) (Figure 2) suggest these areas promote the accumulation and preservation of OM in sediments.

Amorphous aggregates along the PCM were not only present as gelified particles, but also as flaky AOM (Table 2). Gurgel et al. (2008) previously reported the presence of this organic particle in ancient sediments from the PCM, although its relative abundance was lower compared to the gelified AOM. Valdés et al. (2009) also reported the presence of a diffusive, yellow AOM particle (similar to the identified flaky AOM), which was linked to low productivity environments. The lack of significant correlation between the flaky AOM and TOC values in this study (Supplementary Table S1) suggests indeed that this organic particle is linked to environments that promote OM degradation. Thus, the dominance of flaky AOM among the amorphous aggregates in the inner shelf (< 100 m depth) of Huacho and Callao (11°S – 12°S) (Figure 2) indicates this area does not promote OM accumulation.

Gelified spherules were also identified among the palynomorphs of the PCM (Table 2). Gutiérrez et al. (2009) and Lückge et al. (1996) already reported the presence of gelified spherules in ancient sediments from the PCM. Pichevin et al. (2004) and Gurgel (2008) related the presence of gelified spherules to high productivity in upwelling areas, whereas Lallier-Vergès et al. (1993) considered them as framboidal pyrite precursors. In the present study, the good positive correlation found between gelified spherules with the gelified AOM fractions and TOC (Supplementary material Table S1) indicates their presence indeed characterizes high productivity environments. In fact, highest abundances of gelified spherules were reported in the outer continental shelf (> 100 m depth) of Callao and OMZ of Pisco, further evidencing these areas promote OM preservation (Figure 3).

Along the Peruvian coast, terrigenous material reaches the continental shelf mainly by aeolian transport (Saukel et al., 2011), but also by fluvial transport. Fluvial input to the ocean varies according to river discharge, being more important in the northern coast where large rivers dominate compared to the south (Scheidegger and Krissek, 1982). Coastal currents then play an important role by distributing this allochthonous material along the PCM (Montes et al., 2010). High absolute abundances of terrestrial particles towards the south (Figure 2) where fluvial input is less important (Scheidegger and Krissek, 1982) and the AOM fraction dominates the identified

9

palynomorphs, indicate that indeed coastal currents play a primary role in distributing the allochthonous material along the PCM. Additionally, the presence of terrestrial particles in the slope (Figure 2) far away from the continent further confirms transportation processes play a key role in the distribution of organic particles, as was previously proposed by past studies (Arthur et al., 1998; Lückge et al., 1996) The latitudinal distribution of terrestrial particles reported in this study demonstrates that marine sources still contribute largely to the sedimentary OM deposited in northern sediments of the PCM.

Along the PCM, TOC values were higher than the mean value obtained in surface sediments of Chile (e.g. Valdés et al., 2009; Niggemann et al., 2007) and in the same range obtained for ancient sediments of Peru (ten Haven et al., 1990). Carrie et al. (2012) reported fraction S1 to be composed of small organic molecules (<500 Da) considered as the free hydrocarbon fraction corresponding to the light extractable bitumen. Lipids and remains of phyto- and zooplankton tissues composing the AOM contributed more to the pyrolyzed insoluble proto-kerogen and heavy bitumen expressed in fraction S2. Along the PCM, fractions S1 and S2 had a major contribution to the sedimentary OM in the south (11°S – 15°S), especially in the outer continental shelf (> 100 m depth) of Callao and OMZ of Pisco, where the highest values of TOC, fractions S1 and S2 were found (Figure 4A, 4B). According to Boussafir et al. (2012), a negative correlation between fraction S2 and TpS2 evidences the deposit of easily pyrolyzable OM, possibly fresh and/or slightly degraded. Low TpS2 values occurred towards the south of the PCM (11°S – 15°S) in the outer shelf (> 100 m depth) of Callao and OMZ of Callao and Pisco (Figure 6), further suggesting this area as ideal for OM preservation and accumulation. Furthermore, high HI values in this area (Figure 5A) confirm enhanced preservation of lipid-rich OM occurs (Arthur et al., 1998). Towards the slope, higher pyrolytic TpS2 (Figure 6) shows that the OM transported and redeposited to deeper parts experience a higher degree of degradation and thus is more recalcitrant.

4.2 Depositional environments of OM along the PCM

Based on the observed trends and on the PCA and cluster results, we were able to identify three depositional environments of OM along the PCM corresponding to sample groups 1, 2 and 4 (Figure 7, S2). Group 3 was excluded as a depositional environment since it was not spread out by axes 1 and 2 from the PCA and was formed by samples from different depths ranging from the continental shelf to the slope. A first depositional environment corresponds to the outer continental shelf of Callao (> 100 m depth) (12°S) and OMZ of Pisco (14°S) (group 1 PCA – Figures 7, S2), characterized by high values of S1, S2, TOC, HI, gelified spherules and gelified AOM and low values of TpS2. Previous studies have linked the dominance of gelified AOM to areas that promote OM preservation, mainly characterized by suboxic conditions (Valdés et al., 2009; Pichevin et al., 2004). Additionally, low values of TpS2 have been associated to the presence of freshly produced or slightly degraded OM (Boussafir et al., 2012). Thus, this first depositional environment, corresponding to the outer continental shelf of Callao and OMZ of Pisco, favors OM accumulation and preservation under conditions of minimum DO (< 0.5 mL L^{-1}).

Variations in morphology of the continental shelf occur along the Peruvian margin. Of Callao, the continental shelf presents its maximum wideness, then it narrows of Pisco (14°S) (Teves and Evangelista 1976). Differences in OM accumulation between the continental shelf of Callao and Pisco were observed. Samples from the outer continental shelf of Callao (12°S) and OMZ of Pisco (14°S) correspond to the first depositional environment, while samples from the continental shelf of Pisco (14°S) correspond to group 3 of the PCA (Figure 7, S2), which has not been considered as a depositional environment. High OM accumulation occurs in the continental shelf of Callao (12°S), while of Pisco (14°S), more OM accumulates in the OMZ compared to the

10

continental shelf (Figures 4 and 7). According to Monteiro et al. (2011), areas where the shelf is narrow promote high export of particulate organic carbon towards the OMZ, while areas where the shelf is wide, promote retention of organic material and less export towards the OMZ. Therefore, the differential OM accumulation between the continental shelf of Callao and Pisco can be explained based on the wideness of the continental shelf.

A second depositional environment corresponds to the inner shelf of Callao (< 100 m depth) (12°S) (group 2 PCA - Figure 7, Figure S2), characterized by high values of pyrite and flaky AOM, intermediate values of TpS2 and minimum DO values. The presence of flaky AOM has been previously related to environments that promote OM degradation (Valdés et al., 2009). Pyrite formation in the sediments, indicative for anoxia and anaerobe OM degradation, is determined by the availability of dissolved Fe and the amount of metabolizable OM that reaches the sea floor (Berner, 1985). The inner shelf of Callao is characterized by high abundance of Fe (> 50 nM; Bruland et al., 2005), thus the supply of metabolizable OM to the sediments in this shallow environment could promote OM degradation via bacterial sulfate reduction producing H_2S and thus leading to pyrite formation. The inner shelf of the central Peruvian coast is also characterized by strong redox oscillations (Dale et al., 2015; Scholz et al., 2011), which promote intense OM degradation (Aller, 1994) and thus could explain high values of both HI and OI in this area (i.e. preservation of hydrogenated and oxygenated OM). Further evidence of OM degradation in the inner shelf of Callao is given by the high OI value. Overall, OI can indicate both OM origin and degradation. OM from marine sources contains fewer oxygen than OM from terrestrial origin, additionally OM oxidation leads to an increase in oxygen content (Hare et al., 2014). In the inner shelf of Callao, abundance of terrestrial organic particles is minimum (< 4 mg g^{-1} sed) compared to the AOM fraction (up to 56 mg g^{-1} sed) (Figure 2), thus changes in OI can be attributed solely to OM oxic degradation, leading to a decrease in TOC (Figure 5B).

High phytoplanktonic production and high input of metabolizable OM is key for the accumulation of hydrogen rich OM (Boussafir et al., 1995a). Among the AOM group, HI significantly correlated with both gelified homogenous AOM and flaky AOM (Supplementary Table S1). Additionally, HI showed good positive correlation with fractions S1 and S2, but no correlation was found with TOC, DO and depth (Supplementary Table S1). Off Trujillo (7°S) and Pisco (14°S), Emeis et al. (1991) found a close relationship between the increase of HI and the low availability of oxygen, possibly related to a preferential preservation of hydrogen-rich OM under suboxic conditions (Dean et al. 1986). Nevertheless, the pattern observed in both the first and second depositional environments indicate that different conditions of OM accumulation and preservation can lead to high HI, contrary to what has been observed in ancient sediments of the PCM (Salvatteci et al., 2016).

A third and final depositional environment corresponds to the slope (group 4 PCA – Figure 7, S2), characterized mainly by high values of DO (up to 2.0 mL L^{-1}) and TpS2 (Figure 6), low values of TOC and fractions S1 and S2 (Figure 4A, 4B). Thus, the slope is an area where low accumulation of OM occurs compared to the other defined depositional environments. Nevertheless, three samples from the slope of Piura (5°S), Chimbote (9°S) and Pisco (14°S) showed relatively high values of HI (Figure 5A). Along the PCM, OM preservation in deep sediments is favored in upwelling areas (ten Haven et al., 1990). Lückge et al. (1996) reported OM accumulation in sediments beyond the influence of upwelling and of the OMZ, proposing that transportation processes, like turbidity currents and mass flow, could be equally important as bioproductivity in the accumulation and preservation of OM in deep sediments of the PCM. Arthur et al. (1998) also proposed bottom currents could exert a control on OM accumulation by reworking surface sediments. Dale et al. (2015) reported high sedimentation rates and carbon burial efficiency at deep oxygenated sites, probably related to deposition of reworked material originating from sites higher up on the slope. Therefore, transportation processes along the slope

11

could explain the presence of OM with relatively high HI. Thus, the slope appears to be an area where i) less accumulation of OM occurs compared to the other depositional environments and ii) eventual accumulation of hydrogen-rich OM could occur related to downward transport processes.

The overall distribution pattern of both petrographical and geochemical features of the sedimentary OM responded to large-scale variability of oceanographic conditions along the PCM. Towards the south, increase in primary production and a more intense OMZ determine higher accumulation of OM, as evidenced by the distribution of the AOM fraction (Figure 2), gelified spherules (Figure 3), TOC, fractions S1 and S2 (Figure 4A, 4B) and HI (Figure 5A). Nevertheless, short-scale oceanographic variability determines specific patterns of OM distribution. Along the PCM, three well-defined depositional environments have been identified: i) outer shelf of Callao (12°S) and OMZ of Pisco (14°S), where high OM accumulation and preservation occur; ii) inner shelf of Callao (12°S), where redox oscillations promote intense OM degradation preventing high OM accumulation; and iii) the slope, where transportation processes promote a mixed signal of OM degradation and accumulation.

5. Conclusions

The present study characterized the OM deposited in surface sediments along the PCM by means of organic petrography and RE analysis, allowing the identification and description of three main OM depositional environments. Observations of isolated OM by light microscopy allowed to characterize the different types of OM and to show that the initial gelification process of phytoplanktonic OM is at the origin of the different preserved organic fractions in this environment. This observation shows that the OM preserved in oil prone sediments acquire its morphological and textural character, as well as its hydrogenated or oxygenated quality, early during sedimentation and diagenesis. This qualitative OM character is preserved and provides valuable information regarding environmental interpretations in marine sediment records.

Along the PCM, OM accumulation and preservation in recent sediments are influenced by factors such as primary production patterns, bottom dissolved oxygen, depth and transport processes. The best records of well-preserved OM are found in the outer shelf of Callao (12°S) and OMZ of Pisco (14°S), while in the inner shelf of Callao and along the slope less OM accumulates. Outside these areas, a mixed signal of OM accumulation and preservation is observed. This study also provided the opportunity to evaluate certain geochemical proxies routinely used in palaeoceanographic studies (e.g. HI, OI), putting in evidence that palaeoceanographic interpretations should be done with caution and using a multi-proxy approach. Indeed, the quantitative and qualitative variations obtained by the RE analysis showed a certain heterogeneity in the distribution of the OM preserved in surface sediments of the PCM, with an increase in the amount of bio resistant OM and an eventual transfer of part of the labile OM to deep areas.

12

crew of the RV Meteor, RV Galathea and RV *José Olaya Balandra* for their help in sample collection.

Finally, we would like to thank the two anonymous reviewers whose comments greatly helped to improve the quality of the present research article.

Funding

References

Aller, R.C., 1994. Bioturbation and remineralization of sedimentary organic matter: effects of redox oscillation. Chem. Geol. 114, 331–345. https://doi.org/10.1016/0009-2541(94)90062-0

Arthur, M.A., Dean, W.E., Laarkamp, K., 1998. Organic carbon accumulation and preservation in surface sediments on the Peru margin. Chem. Geol. 152, 273–286. https://doi.org/10.1016/S0009-2541(98)00120-X

Bakun, A., Weeks, S.J., 2008. The marine ecosystem off Peru: What are the secrets of its fishery productivity and what might its future hold? Prog. Oceanogr. 79, 290–299. https://doi.org/10.1016/j.pocean.2008.10.027

Baudin, F., Disnar, J.R., Aboussou, A., Savignac, F., 2015. Guidelines for Rock-Eval analysis of recent marine sediments. Org. Geochem. 86, 71–80. https://doi.org/10.1016/j.orggeochem.2015.06.009

Berner, R. A., 1985. Sulphate reduction, organic matter decomposition and pyrite formation. Phil. Trans. R. Soc. Lond. A. 315, 25 - 38.

Borcard, D., Gillet, F., Legendre, P., 2011. Numerical Ecology with R, Springer, London.

Bordenave, M. L. (1993) Applied Petroleum Geochemistry. Editions Technip, Paris.

Boussafir, M., Lallier-Verges, E., Bertrand, P., Badaut-Trauth, D., 1994. Structure ultrafine de la matiere organique des roches meres du Kimmeridgien du Yorkshire (UK) Bulletin de la Société géologique de France 165 (4), 353-361.

Boussafir, M., Gelin, F., Lallier-Vergès, E., Derenne, S., Bertrand, P., Largeau, C., 1995a. Electron microscopy and pyrolysis of kerogens from the Kimmeridge Clay Formation, UK: Source organisms, preservation processes, and origin of microcycles. Geochim. Cosmochim. Acta 59, 3731–3747. https://doi.org/10.1016/0016-7037(95)00273-3

Boussafir, M., Lallier-Verges, E., Bertrand, P., Badaut-Trauth, D., 1995b. SEM and TEM studies on isolated organic matter and rock microfacies from a short-term organic cycle of the Kimmeridge Clay Formation (Yorkshire, GB), Organic matter accumulation, Springer, Berlin, Heidelberg , 15-515 30.

Boussafir, M., Sifeddine, A., Jacob, J., Foudi, M., Cordeiro, R.C., Albuquerque, A.L.S., Abrao, J.J., Turcq, B., 2012. Petrographical and geochemical study of modern lacustrine sedimentary

13

organic matter (Lagoa do Caçò, Maranão, Brazil): Relationship between early diagenesis, organic sedimentation and lacustrine filling. Org. Geochem. 47, 88–98. https://doi.org/10.1016/j.orggeochem.2012.03.013

Bruland, K.W., Rue, E.L., Smith, G.J., DiTullio, G.R., 2005. Iron, macronutrients and diatom blooms in the Peru upwelling regime: Brown and blue waters of Peru. Mar. Chem. 93, 81–103. https://doi.org/10.1016/j.marchem.2004.06.011

Calienes, R., Guillén, O., Lostaunau, N., 1985. Variabilidad espacio-temporal de clorofila, producción primaria y nutrientes frente a la costa peruana. Bol. Inst. Mar. Perú-Callao.

Carrie, J., Sanei, H., Stern, G., 2012. Standardisation of Rock-Eval pyrolysis for the analysis of recent sediments and soils. Org. Geochem. 46, 38–53. https://doi.org/10.1016/j.orggeochem.2012.01.011

Chavez, F.P., Messié, M., 2009. A comparison of Eastern Boundary Upwelling Ecosystems. Prog. Oceanogr. 83, 80–96. https://doi.org/10.1016/j.pocean.2009.07.032

Combaz, A., 1964. Les palynofaciès. Revue de Micropaléontologie 7, 205 – 218.

Dale, A.W., Sommer, S., Lomnitz, U., Montes, I., Treude, T., Liebetrau, V., Gier, J., Hensen, C., Dengler, M., Stolpovsky, K., Bryant, L.D., Wallmann, K., 2015. Organic carbon production, mineralisation and preservation on the Peruvian margin. Biogeosciences 12, 1537–1559. https://doi.org/10.5194/bg-12-1537-2015

Dean, W.E., Arthur, M.A., Claypool, G.E., 1986. Depletion of 13C in Cretaceous marine organic matter: Source, diagenesis, or environmental signal? Marine Geology 70, 119 – 157.

Delgado, C., Gomero, R., 1995. Atlas sedimentologico de la plataforma continental peruana, Boletín del Instituto del Mar del Perú

Emeis, K., Whelan, J., Tarafa, M. 1991. Sedimentary and geochemical expressions of oxic and anoxic conditions on the Peru shelf. In: Tyson, RV, Pearson, TH, editors. Modern and Ancient Continental Shelf Anoxia. Geological Society Special Publication 58, 155 – 170.

Espitalié J., Derro G., Marquis F., 1985. La pyrolyse Rock-Eval et ses aplications. Revue de l'Institut Français du Petrole 40, 563 – 579.

Farrimond, P., Poynter, J., Eglinton, G., 1990. Molecular composition of sedimentary lipids off the Peru Margin, Leg 112, in: Proceedings of the Ocean Drilling Program, Scientific Results, 539–546.

Farrington, J. W., Davis, A. C., Sulanowski, J., McCaffrey, M. A., McCarthy, M., Clifford, C. H., Dickinson, P., and Volkman, J. K., 1988. Biochemistry of lipids in surface sediments of the Peru upwelling area at 15°S. In Mattavelli, L., and Novelli, L. (Eds.), Advances in Organic Geochemistry 1987. Org. Geochem. 13, 607- 617.

Gagosian, R.B., Volkman, J.K., Nigrelli G. E., 1983. The use of sediment traps to determine sterol sources in coastal sediments off Peru. Adv. Org. Geochemistry, 369–379.

Gelin, F., Boussafir, M., Derenne, S., Largeau, C., Bertrand, P., 1995. Study of qualitative and quantitative variations in kerogen chemical structure along a microcycle: correlations with ultrastructural features, Springer, Berlin, Heidelberg, 31-47.

Gutiérrez, D., Enríquez, E., Purca, S., Quipúzcoa, L., Marquina, R., Flores, G., Graco, M., 2008. Oxygenation episodes on the continental shelf of central Peru: Remote forcing and benthic ecosystem response. Prog. Oceanogr. 79, 177–189. https://doi.org/10.1016/j.pocean.2008.10.025

Gutiérrez, D., Sifeddine, A., Field, D.B., Ortlieb, L., Vargas, G., Chvez, F.P., Velazco, F., Ferreira, V., Tapia, P., Salvatteci, R., Boucher, H., Morales, M.C., Valds, J., Reyss, J.L., Campusano, A., Boussafir, M., Mandeng-Yogo, M., Garca, M., Baumgartner, T., 2009. Rapid reorganization in ocean biogeochemistry off Peru towards the end of the Little Ice Age. Biogeosciences 6, 835–848. https://doi.org/10.5194/bg-6-835-2009

Hare, A.A., Kuzyk, Z.Z.A., Macdonald, R.W., Sanei, H., Barber, D., Stern, G.A., Wang, F., 2014. Characterization of sedimentary organic matter in recent marine sediments from Hudson Bay, Canada, by Rock-Eval pyrolysis. Org. Geochem. 68, 52–60. https://doi.org/10.1016/j.orggeochem.2014.01.007

Harrell Jr, F.E., with contributions from Charles Dupont and many others, 2016. Hmisc: Harrell Miscellaneous. R package version 3.17-4. https://CRAN.R-project.org/package=Hmisc

Hedges, J.I., Keil, R.G., 1995. Sedimentary organic matter preservation: an assessment and speculative synthesis. Mar. Chem. 49, 81-115 https://doi.org/10.1007/978-94-011-0739-6

Helly, J.J., Levin, L.A., 2004. Global distribution of naturally occurring marine hypoxia on continental margins. Deep. Res. Part I Oceanogr. Res. Pap. 51, 1159–1168. https://doi.org/10.1016/j.dsr.2004.03.009

Killops, S.D., Killops, V.J., 2005. Introduction to Organic Chemistry, second ed. Blackwell Publishing, US

Lallier-Vergès, E., Bertrand, P., Desprairies, A., 1993. Organic matter composition and sulfate reduction intensity in Oman Margin sediments. Mar. Geol. 112, 57–69. https://doi.org/10.1016/0025-3227(93)90161-N

Lallier-Vergès, E., Bertrand, P., Desprairies, A., Berner, U., 1991. Geochemical and optical investigations on degradation processes affecting organic matter in Celebes Basin sediments. Proc. Ocean Drill. Program. Sci. Results 124, 239–247

Lückge, A., Boussafir, M., Lallier-Vergès, E., Littke, R., 1996. Comparative study of organic matter preservation in immature sediments along the continental margins of Peru and Oman. Part I: Results of petrographical and bulk geochemical data. Org. Geochem. 24, 437–451. https://doi.org/10.1016/0146-6380(96)00045-9

Marchand, C., Lallier-Vergès, E., Disnar, J.R., Kéravis, D., 2008. Organic carbon sources and transformations in mangrove sediments: A Rock-Eval pyrolysis approach. Org. Geochem. 39, 408–421. https://doi.org/10.1016/j.orggeochem.2008.01.018

Marcio Gurgel. La sédimentation organique associée à deux systèmes d'upwelling en Amérique du Sud tropicale : implications paléocéanographiques et paléoclimatiques au cours de l'Holocène. Géochimie. Université d'Orléans, 2008. Français.

Mollier-Vogel, E., Ryabenko, E., Martinez, P., Wallace, D., Altabet, M.A., Schneider, R., 2012. Nitrogen isotope gradients off Peru and Ecuador related to upwelling, productivity, nutrient uptake and oxygen deficiency. Deep. Res. Part I Oceanogr. Res. Pap. 70, 14–25. https://doi.org/10.1016/j.dsr.2012.06.003

Montes, I., Colas, F., Capet, X., Schneider, W., 2010. On the pathways of the equatorial subsurface currents in the eastern equatorial Pacific and their contributions to the Peru-Chile Undercurrent. J. Geophys. Res. Ocean. 115, 1–16. https://doi.org/10.1029/2009JC005710

Niggemann, J., Ferdelman, T.G., Lomstein, B.A., Kallmeyer, J., Schubert, C.J., 2007. How depositional conditions control input, composition, and degradation of organic matter in sediments from the Chilean coastal upwelling region. Geochim. Cosmochim. Acta 71, 1513–1527. https://doi.org/10.1016/j.gca.2006.12.012.

Oksanen, J., F. Guillaume Blanchet, Michael Friendly, Roeland Kindt, Pierre Legendre, Dan McGlinn, Peter R. Minchin, R. B. O'Hara, Gavin L. Simpson, Peter Solymos, M. Henry H. Stevens, Eduard Szoecs and Helene Wagner. 2016. vegan: Community Ecology Package. R package version 2.4-0. https://CRAN.R-project.org/package=vegan

Peters K.E., 1986. Guidelines for evaluating petroleum source rock using programmed pyrolysis. American Association of Petroleum Geologists Bulletin 70, 318 – 329.

Pichevin, L., Bertrand, P., Boussafir, M., Disnar, J.R., 2004. Organic matter accumulation and preservation controls in a deep sea modern environment. An example from Namibian slope sediments. Org. Geochem. 35, 543–559. https://doi.org/10.1016/j.orggeochem.2004.01.018

Powell, A.J., Dodge, J.D., Lewis, J., 1990. Late Neogene to Pleistocene Palynological facies of the Peruvian Continental Margin Upwelling, Leg 112. Proc. Ocean Drill. Program, Sci. Results 112, 297–321.

Repeta, D. J., 1989. Carotenoid diagenesis in recent marine sedi- ments: II. Degradation of fucoxanthin to loliolide. Geochim. Cosmochim. Acta 53, 699-707.

Repeta, D. J., and Gagosian, R. B., 1987. Carotenoid diagenesis in recent marine sediments: I. The Peru continental shelf (15°S, 75°W). Geochim. Cosmochim. Acta 51, 1001-1009.

Salvatteci, R., Gutiérrez, D., Field, D., Sifeddine, A., Ortlieb, L., Bouloubassi, I., Boussafir, M., Boucher, H., Cetin, F., 2014. The response of the Peruvian Upwelling Ecosystem to centennial-scale global change during the last two millennia. Clim. Past 10, 715–731. https://doi.org/10.5194/cp-10-715-2014

Salvatteci, R., Gutierrez, D., Sifeddine, A., Ortlieb, L., Druffel, E., Boussafir, M., Schneider, R., 2016. Centennial to millennial-scale changes in oxygenation and productivity in the Eastern Tropical South Pacific during the last 25,000 years. Quat. Sci. Rev. 131, 102–117. https://doi.org/10.1016/j.quascirev.2015.10.044.

Saukel, C., Lamy, F., Stuut, J. B. W., Tiedemann, R., Vogt, C., 2011. Distribution and provenance of wind-blown SE Pacific surface sediments, Mar. Geol. 280, 130–142.

Scheidegger, K.F., Krissek, L.A., 1982. Dispersal and deposition of eolian and fluvial sediments off Peru and northern Chile. Geol. Soc. Am. Bull. 93, 150–162. https://doi.org/10.1130/0016-7606(1982)93<150:DADOEA>2.0.CO;2

Scholz, F., Hensen, C., Noffke, A., Rohde, A., Liebetrau, V., Wallmann, K., 2011. Early diagenesis of redox-sensitive trace metals in the Peru upwelling area - response to ENSO-related oxygen fluctuations in the water column. Geochim. Cosmochim. Acta 75, 7257–7276. https://doi.org/10.1016/j.gca.2011.08.007

Suess, E., 1980. Particulate organic carbon flux in the oceans - Surface productivity and oxygen

utilization. Nature 288, 260–263. https://doi.org/10.1038/288260a0

ten Haven, H.L., Littke, R., Rullkötter, J., Stein, R., Welte, D.H., 1990. Accumulation Rates and Composition of Organic Matter in Late Cenozoic Sediments Underlying the Active Upwelling Area off Peru. Proc. Ocean Drill. Program, Sci. Results 112, 591–606.

Teves, N., Evangelista E., 1976. Las 200 Millas de Mar Territorial Peruano y sus Fondos Marinos. Bol. Soc. Geol. Peru, 53 – 54, 59 – 74.

Tissot, B.P., Welte, D.H., 1984. Petroleum Formation and Occurrence, second ed. Springer-Verlag, Berlin.

Valdés, J., Sifeddine, A., Lallier-Verges, E., Ortlieb, L., 2004. Petrographic and geochemical study of organic matter in surficial laminated sediments from an upwelling system (Mejillones del Sur Bay, Northern Chile). Org. Geochem. 35, 881–894. https://doi.org/10.1016/j.orggeochem.2004.02.009

Valdés, J., Sifeddine, A., Ortlieb, L., Pierre, C., 2009. Interplay between sedimentary organic matter and dissolved oxygen availability in a coastal zone of the Humboldt Current System; Mejillones Bay, northern Chile. Mar. Geol. 265, 157–166. https://doi.org/10.1016/j.margeo.2009.07.004

Volkman, J.K., Farrington, J.W., Gagosian, R.B., 1987. Marine and terrigenous lipids in coastal sediments from the Peru upwelling region at 15°S. Sterols and triterpene alcohols. Org. Geochem. 11, 463–477. https://doi.org/10.1016/0146-6380(87)90003-9

Wakeham, S. G., Farrington, J. W., and Volkman, J. K., 1983. Fatty acids, wax esters, triacylglycerols and alkyldiaglycerols associated with particles collected in sediment traps in the Peru up- welling. In Bjor0y, M., et al (Eds.), Advances in Organic Geochemistry 1981: Chichester (Wiley), 185-197.

Wakeham, S. G., Farrington, J. W., and Gagosian, R. B., 1984. Variability in lipid flux and composition of particulate matter in the Peru upwelling region. In Schenck, P. A., de Leeuw, J. W., and Lijmbach, G.W.M. (Eds), Advances in Organic Geochemistry 1983. Org. Geochem. 13, 203-215.

Wakeham, S. G., 1985. Wax esters and triacylglycerols in sinking particulate matter in the Peru upwelling area (15°S, 75°W). Mar. Chem. 17, 213-235.

Wickham. H, 2016. ggplot2: Elegant Graphics for Data Analysis. Springer-Verlag New York.

Zocatelli, R., Turcq, B., Boussafir, M., Cordeiro, R.C., Disnar, J.R., Costa, R.L., 2012. Late Holocene paleoenvironmental changes in Northeast Brazil recorded by organic matter in lacustrine sediments of Lake Boqueirão. Palaeogeography, Palaeoclimatology, Palaeoecology 363, 127-134.

Zonneveld, K., Versteegh, G., Kasten, S., Eglinton, T., Emeis, K.-C., 2010. Selective preservation of organic matter in marine environments; processes and impact on the sedimentary record. Biogeosciences 7, 483–511.

Zuta, S., Guillén, O., 1970. Oceanografía de las aguas costeras del perú. Bol. Inst. Mar. Perú-Callao.

Tables

Table 1. Information from the 29 surface sediment samples collected along the Peruvian continental margin.

Site	Latitude	Depth (m)	Dissolved oxygen (mL L^{-1})	Distance to the coast (km)
Tumbes	3°S	350	0.53	29
		701	0.47	34
		995	1.06	31
Piura	5°S	307	0.46	29
		1252	1.54	41
		2607	2.18	51
Trujillo	8°S	359	0.29	103
		626	0.29	120
		1012	0.90	119
Chimbote	9°S	114	0.41	90
		437	0.79	111
		1107	1.20	147
Huacho	11°S	210	0.20	41
		424	0.24	63
		1933	2.09	99
Callao	12°S	48	0.08	8
		92	0.23	15
		117	0.06	25
		142	0.07	40
		175	0.11	57
		214	0.02	60
Pisco	14°S	120	0.24	10
		179	0.19	17
		303	0.14	25
		312	0.35	30
		396	0.36	33
		743	0.32	44
		1018	1.23	37
San Juan	15°S	290	0.29	28

18

Table 2. Description of organic particles (palynofacies) identified in surface sediments from the Peruvian Continental Margin.
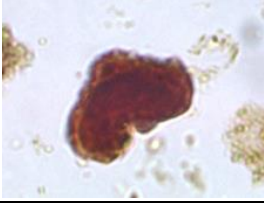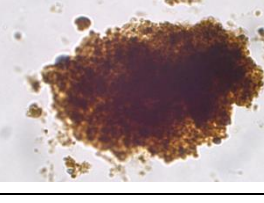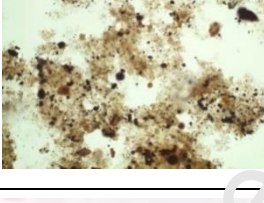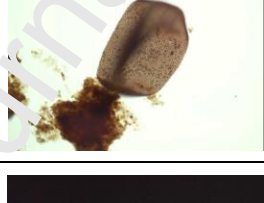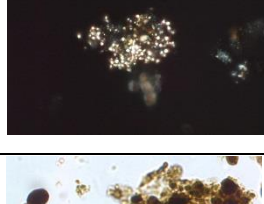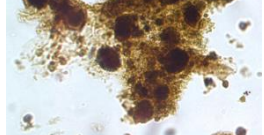
TYPE OF ORGANIC PARTICLE		Microscopic image	DESCRIPTION
AMORPHOUS ORGANIC MATTER (AOM) FRACTION	Gelified homogeneous AOM		Organic particle characterized by a perfectly amorphous texture, without an apparent structure. Can be orange, red, brown or black. Presents very define edge.
	Gelified granular AOM		Organic particle observed as aggregates formed by very little particles of gelified appearance
	Flaky AOM		Organic particle with a scatter amorphous texture, without define edge. General color is yellow.
TERRESTRIAL ORGANIC PARTICLES	Lignocelulosic debris		Fragments of tissue from vascular plants. Can be present in the form of gelified lignocelulosic debris or as opaque debris.
	Cuticles and spores		Well-structured tissues from terrestrial plants. Associated in this picture with gelified homogenous orange AOM.
PYRITE AND GELIFIED SHERULES	Pyrite		Pyrite in framboidal form observed under reflected light microscopy.
	Gelified spherules		Perfectly round spherules with well-defined edges. Can be black, brown or orange. Here included in gelified granular AOM.

19

Table 3. Descriptive statistics of all the variables derived from both the palynofacies analysis (organic petrography) and the Rock-Eval analysis.

	Variables	Average	Maximum	Minimum	Standard deviation
Palynofacies analysis (mg g^{-1} sed)	Gelified homogeneus AOM	49.3	120.5	0.8	28.5
	Gelified granular AOM	7.8	31.6	0.0	7.9
	Flaky AOM	19.7	56.2	5.6	10.4
	Lignocelulosic debris	1.0	5.2	0.0	1.4
	Cuticles and spores	1.5	8.5	0.0	2.2
	Pyrite	2.0	12.3	0.0	2.9
	Gelified spherules	1.6	7.6	0.0	2.1
Rock-Eval analysis	TOC (%)	5.8	1?6	1.5	2.7
	Fraction S1 (mg HC g^{-1})	0.1	0.?	0.0	0.1
	Fraction S2 (mg HC g^{-1})	25.5	??.?	6.4	13.7
	Hydrogen Index (mg HC g^{-1} TOC)	431	496	317	44
	Oxygen Index (mg CO$_2$ g^{-1} TOC)	133	191	105	18
	TpS2 (°C)	45?	460	434	6

Figure captions

Figure 1. Map showing the distribution of the 29 surface sediment samples collected along the Peruvian continental margin from Tumbes (3°S) to San Juan (15°S). The color scale represents average bottom dissolved oxygen from 1996 to 2006 (El Niño years have been excluded; source: Instituto del Mar del Perú - IMARPE; D. Gutiérrez, pers. comm).

Figure 2. Bathymetric and latitudinal variability of the amorphous organic matter (AOM) group formed by gelified homogeneous AOM (ghAOM), flaky AOM (fAOM) and gelified granular AOM (ggAOM), and the terrestrial organic fractions lignocellulosic debris (L. debris) and cuticles and spores (Cut. & Sp.) Organic particles were analyzed by palynofacies analysis (organic petrography). For further detail on these fractions, please refer to section 3.1.

Figure 3. Latitudinal and bathymetric variability of pyrite and gelified spherules (gsph) analyzed by palynofacies analysis (organic petrography). For further detail on these fractions, please refer to section 3.1.

Figure 4. Fraction S1 vs total organic carbon (A) and fraction S2 vs total organic carbon (B) for all samples collected along the Peruvian continental margin. The green color scale depicts the north sampling region (3°S – 9°S) and the blue color scale the south sampling region (11°S – 15°S). Symbols depict bathymetry. For more detail on the samples grouping please refer to section 2.3.

Figure 5. Hydrogen index vs total organic carbon (A) and oxygen index vs total organic carbon (B) for all samples collected along the Peruvian continental margin. The green color scale depicts the north sampling region (3°S – 9°S) and the blue color scale the south sampling region (11°S – 15°S). Symbols depict bathymetry. For more detail on the samples grouping please refer to section 2.3.

Figure 6. Fraction S2 vs TpS2 for all samples collected along the Peruvian continental margin. The green color scale depicts the north sampling region (3°S – 9°S) and the blue color scale the south sampling region (11°S – 15°S).Symbols depict bathymetry. For more detail on the samples grouping please refer to section 2.3.

Figure 7. Principal component analysis (PCA) performed among petrographical variables (excluding terrestrial organic fractions), geochemical variables, dissolved oxygen (DO) and depth. The green color scale depicts the north sampling region (3°S – 9°S) and the blue color scale the south sampling region (11°S – 15°S).Symbols depict bathymetry. For more detail on the samples grouping please refer to section 2.3. AOM: amorphous organic matter, fAOM: flaky AOM, ggAOM: gelified granular AOM, ghAOM: gelified homogeneus AOM, gsph: gelified spherules, TOC: total organic carbon, S1: fraction S1, S2: fraction S2, HI: hydrogen index, OI: oxygen index.

HIGHLIGHTS

Characterization of depositional environments of organic matter along the Peruvian continental margin.

Organic matter accumulation in outer shelf areas and oxygen minimum zone.

Low organic matter accumulation at inner shelf settings.

Transport processes affect organic matter accumulation at slope settings.