

Preservation Factors during Cretaceous Oceanic Anoxic Events in the Espírito Santo Basin, Southeast Brazil

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Abstract: The oceanic anoxic events (OAEs) are characterized by enhanced accumulation of organic matter in marine sediments. However, there is still an ongoing debate regarding the interplay between production and preservation during these events. Moreover, few studies provide quantitative estimations of primary productivity and/or the amount of carbon preserved during the OAEs. Here, we used geochemical data from multiple wells located at the Espírito Santo Basin that cover the intervals of events OAE1d and OAE2 to provide quantitative estimates of preservation factors. Our results show enhanced preservation during OAEs compared to modern conditions and a stronger preservation during OAE1d compared to OAE2 in the Espírito Santo Basin. The amount of preserved carbon could reach up to 8.6% during OAE1d, depending on the productivity of the system. In addition, we show that such improvement in preservation is linked to the bottom water with low-O₂ concentrations and not due to fast burial caused by high sedimentation rates. Our findings are extremely relevant for organic carbon and source rock modelling studies since model simulations need quantitative estimations

Keywords: organic matter; total organic carbon; anoxia; Espírito Santo Basin; cretaceous

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1. Introduction

The oceanic anoxic events (OAEs) are characterized by an expansion and increased intensity of the oxygen minimum zones (OMZs) and enhanced accumulation of organic carbon in marine sediments [1,2]. These events were linked to global warming due to the release of CO₂ to the atmosphere because of the degassing resultant of large-scale volcanism and dissociation of methane hydrates [3]. During OAEs, there is an interplay between production and preservation of organic carbon in the marine realm, but there is still a debate regarding which of these processes is more important for the accumulation of organic carbon. Recent studies have pointed out that preservation might be more important than production during these events [4,5]. However, few studies so far have focused on providing estimations on the fraction of organic carbon that was preserved. Studies have estimated ca. 2% of preservation of organic carbon during mid-Cretaceous anoxic events [6,7], but other findings have shown that these values can be even higher [8].

The majority of the investigations about OAEs are derived from sedimentary basins in the Northern Hemisphere [9]. Nevertheless, some studies have shown the occurrence of such events during the Cretaceous in Brazilian sedimentary basins [10–13]. However, to our knowledge, none of these studies from the Brazilian basins have presented

quantitative estimations on the fraction of organic carbon that was preserved. Here, we present new data of organic carbon accumulation rate (OCAR) for several wells located in the Espírito Santo Basin during Cretaceous OAEs (OAE1d, ca. 100–98 Ma; and OAE2, ca. 94–92 Ma). These data allowed us to quantitatively estimate the preservation factor (PF) for these events, considering a range of possible values of primary productivity (PP). Our results show that organic carbon preservation was enhanced during OAEs compared to modern conditions, and in general, it was more intense during OAE1d than OAE2 in the Espírito Santo Basin.

2. Geological Settings

The tectonostratigraphic evolution of the eastern, southeastern, and equatorial margin basins of Brazil (and their respective African counterparts) are part of the evolutionary context of the opening of the South Atlantic Ocean during the final stage of the Gondwana supercontinent breakup, which occurred during the Lower Cretaceous as a result of the separation between the South American and African continents [14,15]. The Espírito Santo Basin is located in SE Brazil, limited to the north by the Mucuri Basin (geographic limit) and to the south by the early Miocene Vitória-Trindade High (a volcanic chain emplaced in early Miocene) [16], which separates the Espírito Santo Basin from the Campos Basin. To the east, the basin is limited by a 3000 m isobath (economic limit). The Espírito Santo Basin occupies approximately 41,500 km², from which 38,500 km² corresponds to the offshore portion. The basin is positioned on a Precambrian basement composed of migmatites, granulites, gneisses, and granites, which occur as faulted homocline blocks with eastward vergence [17]. The tectonostratigraphic evolution of the Espírito Santo Basin is commonly divided into three main supersequences: rift (Valanginian–Aptian), post-rift or transitional (mid-Aptian–early-Albian), and drift (mid- to late-Albian) [18]. In addition to the aforementioned volcanic event of Vitória-Trindade, which occurred during the Miocene, the basin experienced, throughout its evolution, two other important volcanic-magmatic events: the Cabiúnas volcanism (136–118 Ma), related to the rift phase [18], and the Abrolhos magmatism, which culminated in the formation of the Abrolhos plateau (Abrolhos Bank) during the Danian period (ca. 62 Ma) [18,19]. The oldest known source rocks of the Espírito Santo Basin are part of the Cricaré Formation, of Valanginian age (rift phase), which occur at the base of the basin's sedimentary stratigraphic succession and are attributed to a lacustrine environment [17]. The Cricaré Formation is superimposed by Mariricu Formation which, in turn, is composed of sandstones and alluvial conglomerates in its basal portion (Mucuri Member) superimposed by a sequence of evaporites, corresponding to Mb. Itaúnas [17,20]. During the Albian–Cenomanian, shallow carbonate platforms developed in the basin corresponding to the Barra Nova Formation, generating high- to low-energy carbonate rocks (Regência Member) and clastic rocks associated with fan-deltas (São Mateus Member). Finally, during the Upper Cretaceous and Paleogene, the deposition that occurred in the drift phase was controlled by thermal subsidence with general tilting to the east and intense salt tectonics. In this phase, there was a predominance of a second-order transgressive cycle, where thick layers of shales and marls were deposited in the marine environment, especially in the offshore region of the basin, composing the Urucutuca Formation. In this time interval, in the onshore portion of the basin, the deposition of turbidite intervals and the formation of submarine canyons incised at the edge of the continental shelf predominated during moments of relative fall in sea level [17]. Regarding petroleum systems, the Espírito Santo Basin has onshore and offshore proven systems. In the onshore realm, a lacustrine generator system of the rift phase, with traps associated with rift faults (Cricaré-Mariricu(!) system). In the marine portion of the basin, the main system is the so-called Urucutuca-Urucutuca(!), characterized by marine origin with migration and trapping strongly related to halokinetics and turbidite reservoirs conditioned or not by erosive troughs [21]. In addition to these, other important petroleum systems are observed in the basin, such as the Mariricu-Mariricu(!), Regência-Regência(!), and Regência-Urucutuca(!) systems. The prior knowledge of the main

petroleum systems of the basin motivated the realization of stratigraphic modeling within the Albian-Turonian interval, with known generating potential in the offshore region, attributed to the Urucutuca Formation shales. The six wells that are investigated in this work are located in the southern offshore portion of the Espírito Santo Basin, which, in turn, is situated in the western boundary of the South Atlantic subtropical gyre (Figure 1).

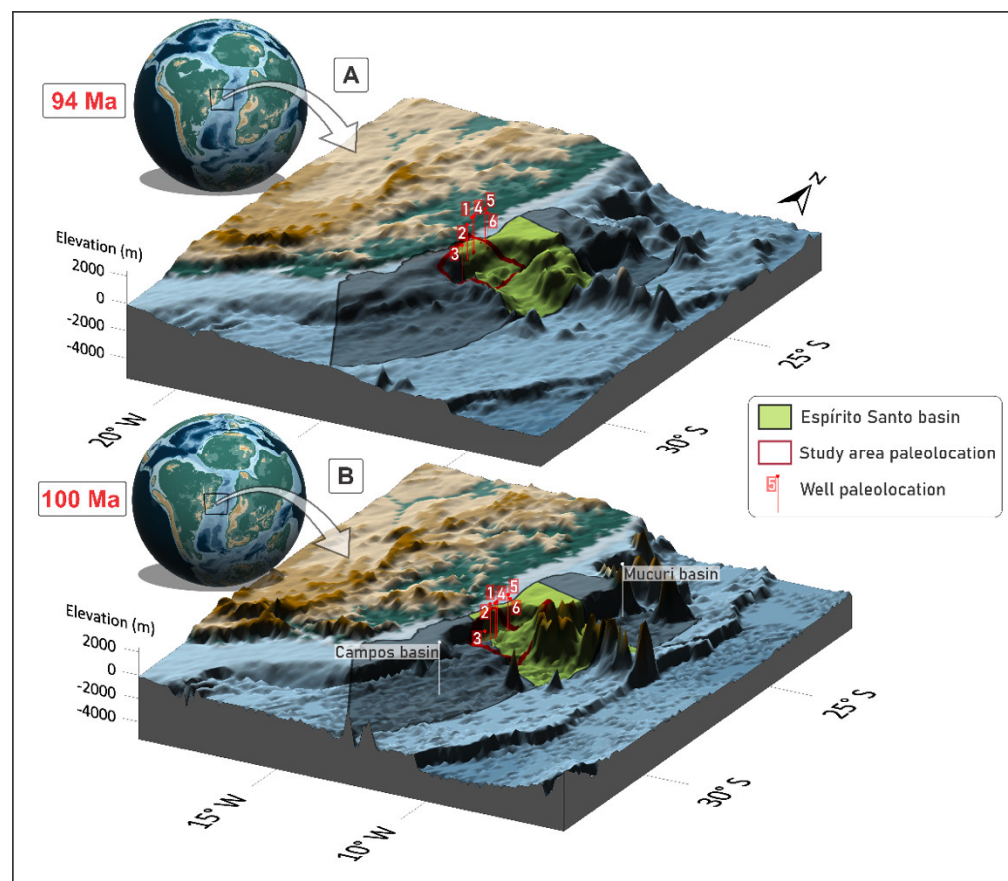


Figure 1. Paleolocations of the wells (ES-1 to 6) during the oceanic anoxic event 1d (OAE1d) (A) and oceanic anoxic event 2 (OAE2) (B) of the Cretaceous. Paleobathymetry is derived from [22].

3. Materials and Methods

Wells are located in a bathymetric range from 1332 to 2081 m below sea level. The chronology of well ES-1 was built through astronomical tuning, and full details can be accessed in [23]. The authors used the frequency ratio method [24] to interpret the most likely wavelength associated with the 405 kyr long eccentricity cycle, also known as the “metronome” [25]. The selected frequency was separated via Gaussian bandpass filtering, and peaks were associated with the maximum 405 ka long eccentricity cycles [26] to determine the floating astronomical time scale. Subsequently, the time scale was anchored at 66.0 Ma using an abrupt shift in the natural gamma ray (NGR) associated with the regional transition between the Cretaceous and Paleogene sections [23]. This age model placed two total organic carbon peaks near the bottom of well ES-1 during OAE1d and 2. We then took advantage of the proximity among the wells investigated here to propagate the ES-1 astronomical age model (Figure 2). We completed this by anchoring the TOC peaks identified near the bottom of each well with a mean age corresponding to OAE1d (ES-2 and ES-4) or OAE2 (ES-3, ES-5, and ES-6). To check the reasonability of this strategy, we filtered the resulting 405 ka cycle from the NGR of each well. The longest ES-2, ES-3, and ES-4 (beyond the already solved ES-1) own 25–27 405 ka cycles between ~89 and 100 Ma, which agrees fairly well with the La2010d astronomical solution [26]. The same occurs for the shortest ES-5 and ES-6 for their covered interval. This find reinforces

the notion of relative completeness of these sediment packages during the Cenomanian-Turonian period [23].

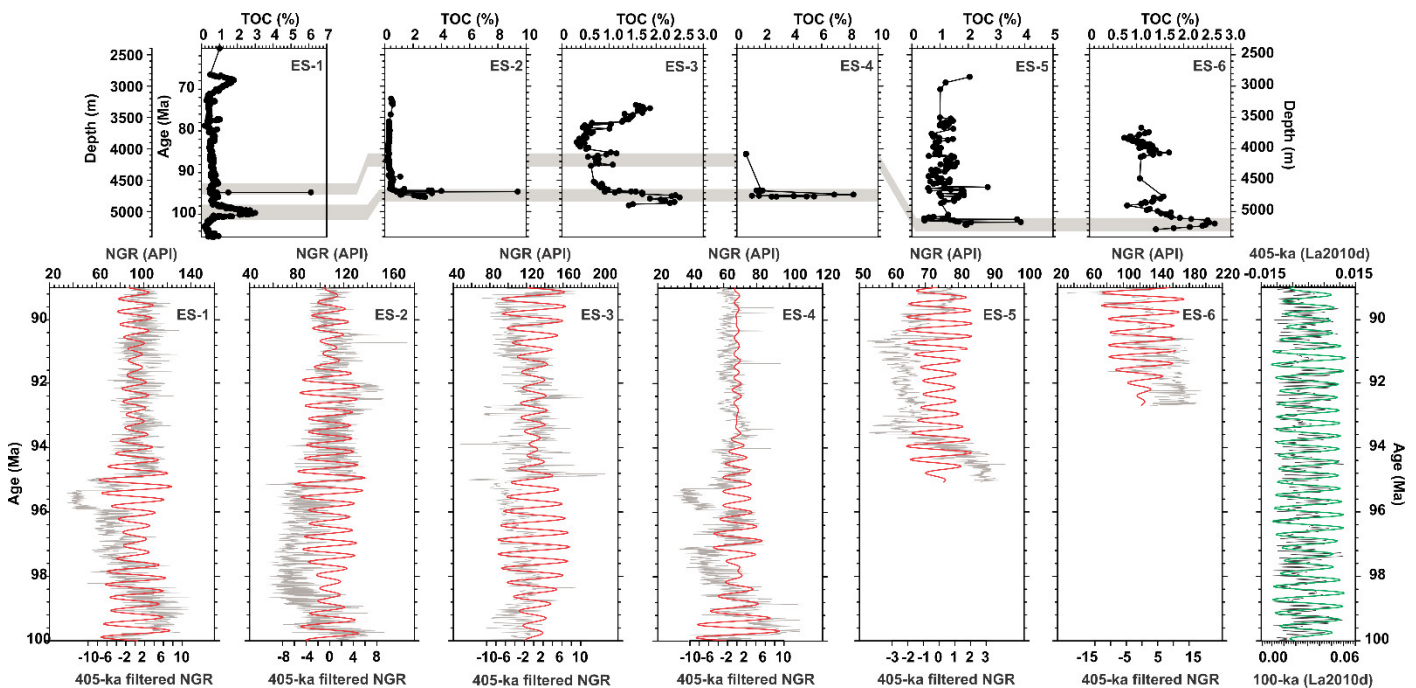


Figure 2. Propagation of the ES-1 astronomical age model to the other wells of the Espírito Santo Basin. The graphs at the top show the TOC (%) data for each well and the correspondence of the peaks between them. The graphs at the bottom show the filtered 405 ka cycle from the NGR of each well.

The Brazilian oil company Petrobras provided geochemical and geophysical data for these wells. A total of 145 measurements of total organic carbon (TOC) is used in this study. Rock samples were dried at 40 °C and then grounded to a fine powder with subsequent carbonate dissolution with HCl and organic carbon combustion using a LECO WR 112 Carbon Analyzer to determine the TOC content. Density (RHOB) data were extracted from the log data of the wells.

To obtain the estimations of organic carbon accumulation rate (OCAR) for each well, we used the following equation:

$$\text{OCAR} = \text{TOC} \times \text{SR} \times \rho, \quad (1)$$

where OCAR has units in gC/m²/yr, sedimentation rate (SR) has units in m/Myr, and sediment bulk density (ρ) has units in g/cm³. Sedimentation rate (SR) values for the wells are derived from the age-depth models following the same methods described in [23] for well ES-1.

The preservation factor (PF) was estimated using the following equation:

$$\text{PF} = \text{OCAR}/\text{PP}, \quad (2)$$

where primary productivity (PP) has units in gC/m²/yr. For PP, we used values that are consistent with the modern range of the PP within the Espírito Santo Basin (ESB) [27].

We used these data to calculate the mean values of the chosen parameters for the time intervals of OAE1d (ca. 100–98 Ma) and OAE2 (ca. 94–92 Ma). OAEs were identified by correlating the peaks in TOC and the age-depth models of each well (Figure 2).

4. Results

For the wells located in the Espírito Santo Basin, we obtained results for bulk density (ρ), sedimentation rate (SR), and total organic carbon (TOC) (Figure 3). For bulk density, the values vary from 1.99 to 2.68 g/cm³. Sedimentation rates values range from 31.4 to 119.3 m/Myr. Total organic carbon values range from 0.37 to 9.40%.

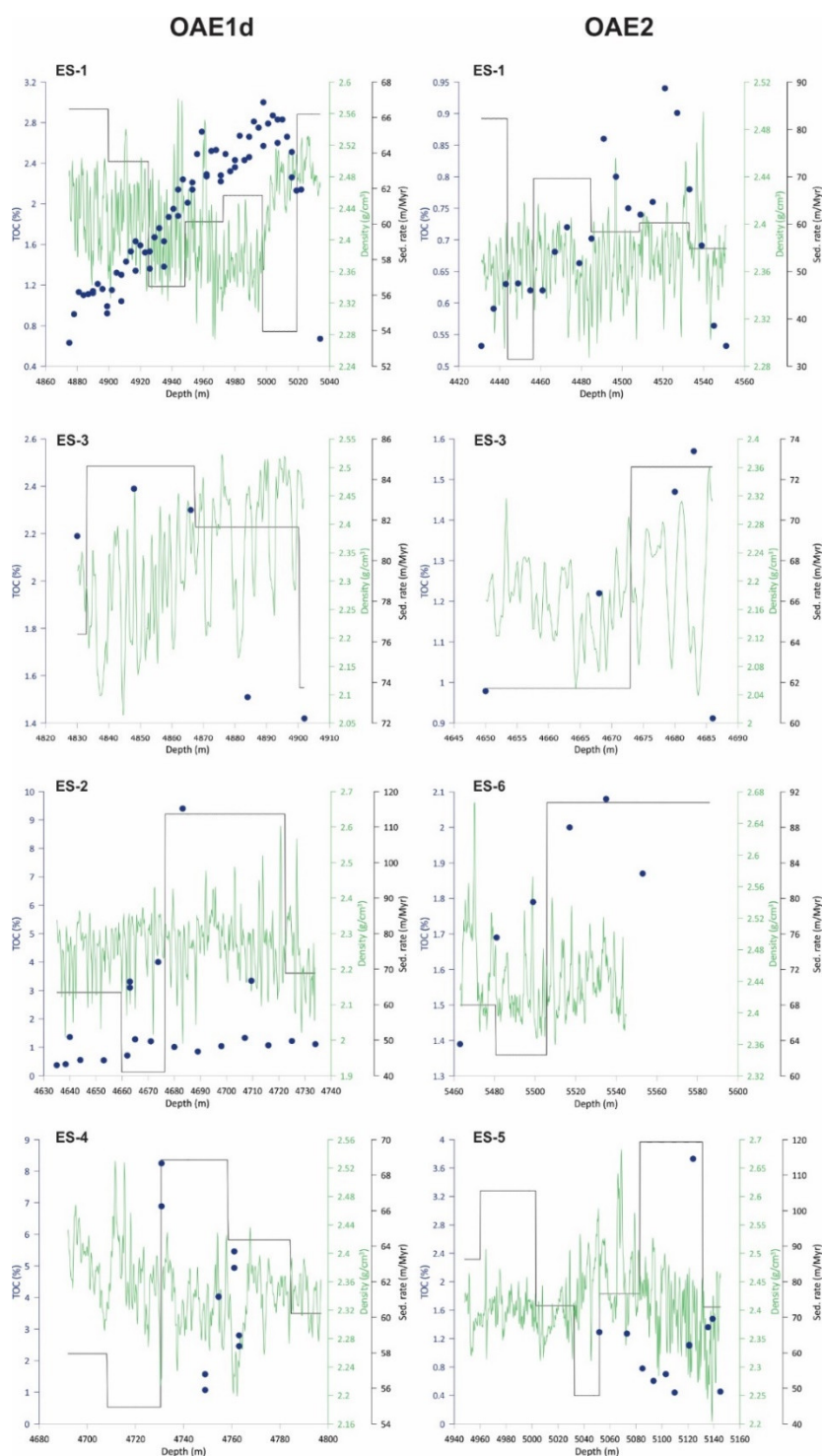


Figure 3. Results of total organic carbon (TOC, %), density (g/cm³), and sedimentation rates (m/Myr) for the wells (ES-1 to 6) located in the Espírito Santo Basin during OAE1d and OAE2. TOC values are shown as blue circles, density values are shown as green lines, and sedimentation rates are shown as black lines.

With the values of these variables for the intervals of OAE1d and OAE2, we generated mean values of each variable for each OAE recorded by the wells (Table 1). These mean values were used to calculate the mean organic carbon accumulation rate (OCAR) for each event recorded by the wells, following equation 1. Mean values of OCAR varied from 1.01 to 6.04 gC/m²/yr for the wells. The modern mean OCAR for the Esp rito Santo Basin is 0.11 gC/m²/yr.

These OCAR values were used to estimate potential values of preservation factor (PF), considering the range of modern PP values, for the OAEs recorded by the wells located in the Esp rito Santo Basin. PF values estimated for the wells varied from 0.08 to 8.64%. The maximum PF value for OAE1d was 8.64%, while for OAE2, it was 5.14%. Mean PF values for the OAEs were 0.96% for OAE1d and 0.53% for OAE2. Modern PF values for the ESB range from 0.01 to 0.45%, with a modern mean PF value of 0.07%.

Table 1. Table showing the mean values of ρ (g/cm³), SR (m/Myr), TOC (%), and OCAR (gC/m²/yr) for each event and well.

Well	Event	Mean ρ (g/cm ³)	Mean SR (m/Myr)	Mean TOC (%)	Mean OCAR (gC/m ² /yr)
ES-1	OAE1d	2.42	61.08	1.96	3.78
	OAE2	2.37	60.61	1.23	1.76
ES-2	OAE1d	2.26	83.63	1.86	3.52
ES-3	OAE1d	2.33	82.69	1.93	2.86
	OAE2	2.18	65.65	0.70	1.01
ES-4	OAE1d	2.35	62.06	4.15	6.04
ES-5	OAE2	2.41	90.39	1.19	2.60
ES-6	OAE2	2.44	81.74	1.80	3.60

5. Discussion

Our results show that OCAR and PF were higher during OAE1d and OAE2, when compared to the modern conditions, confirming that organic carbon preservation was enhanced in the Esp rito Santo Basin during these anoxic events (Figure 4). Our OCAR and PF values for OAEs are comparable to the ones reported by other studies [7,8]. Most notably, we were able to quantify, for the first time, the increase in preservation during OAEs for the Esp rito Santo Basin. Considering mean values of PF from modern conditions and for OAEs, preservation was approximately eight times greater than modern conditions during OAE2 and approximately fourteen times greater during OAE1d. By comparing PF values from both OAEs, it is also possible to indicate that preservation during OAE1d was in general higher than OAE2, and by considering mean PF values, the preservation was approximately two times greater during OAE1d compared to OAE2. In addition, the maximum PF during OAEs reached values of 5.14% for OAE2 and 8.64% for OAE1d, highlighting the higher potential of preservation during OAE1d compared to OAE2 for the Esp rito Santo Basin. Our maximum PF value for OAE2 is very similar to the one reported by [8] for the southern part of the proto-North Atlantic. A possible explanation for the more intense preservation of organic carbon during OAE1d compared to OAE2 in the Esp rito Santo Basin may reside on the important role of paleogeography preconditioning the ocean for organic carbon preservation [28]. As pointed out by [29], land–sea configuration affects the ease with which OAEs can develop; thus, the more restricted Atlantic Basin during OAE1d compared to OAE2 may have been more favorable for low-oxygen conditions, causing higher quantities of organic carbon to be preserved in the oceans [15].

Since our PF calculations are based on TOC and variable values of oceanic primary productivity, one could argue that our TOC has some fraction of terrestrial carbon and that changes in its proportion varied during the past, which could influence our estimations. Indeed, as pointed out previously in the work of [23], for one of our wells

investigated here, the fraction of continentally derived (terrigenous) carbon in the data is unknown but most likely contributes to the final TOC. However, we interpreted our PF values for the OAEs in comparison with modern values for the same basin. Since the TOC values of the modern samples also contain some fraction of terrestrial carbon, our calculations are already incorporating the bias introduced by the terrestrial fraction. This helps to minimize the impact of this issue in our interpretations. Furthermore, studies that analyzed organic facies during anoxic events of the Cretaceous in the Brazilian margin indicated that most of the organic matter is characterized as amorphous organic matter mostly composed of marine plankton [10,30]. In addition, during OAE1d and OAE2, the global sea-level was rising, and terrigenous sedimentation was probably reduced during transgressions [31]. Such an environmental scenario also minimizes the impact of terrestrial carbon on our PF estimations for OAE1d and OAE2. Thus, we understand that although our estimations of PF are influenced by this issue related to the terrigenous fraction, such influence is likely minor and does not significantly alter our calculations.

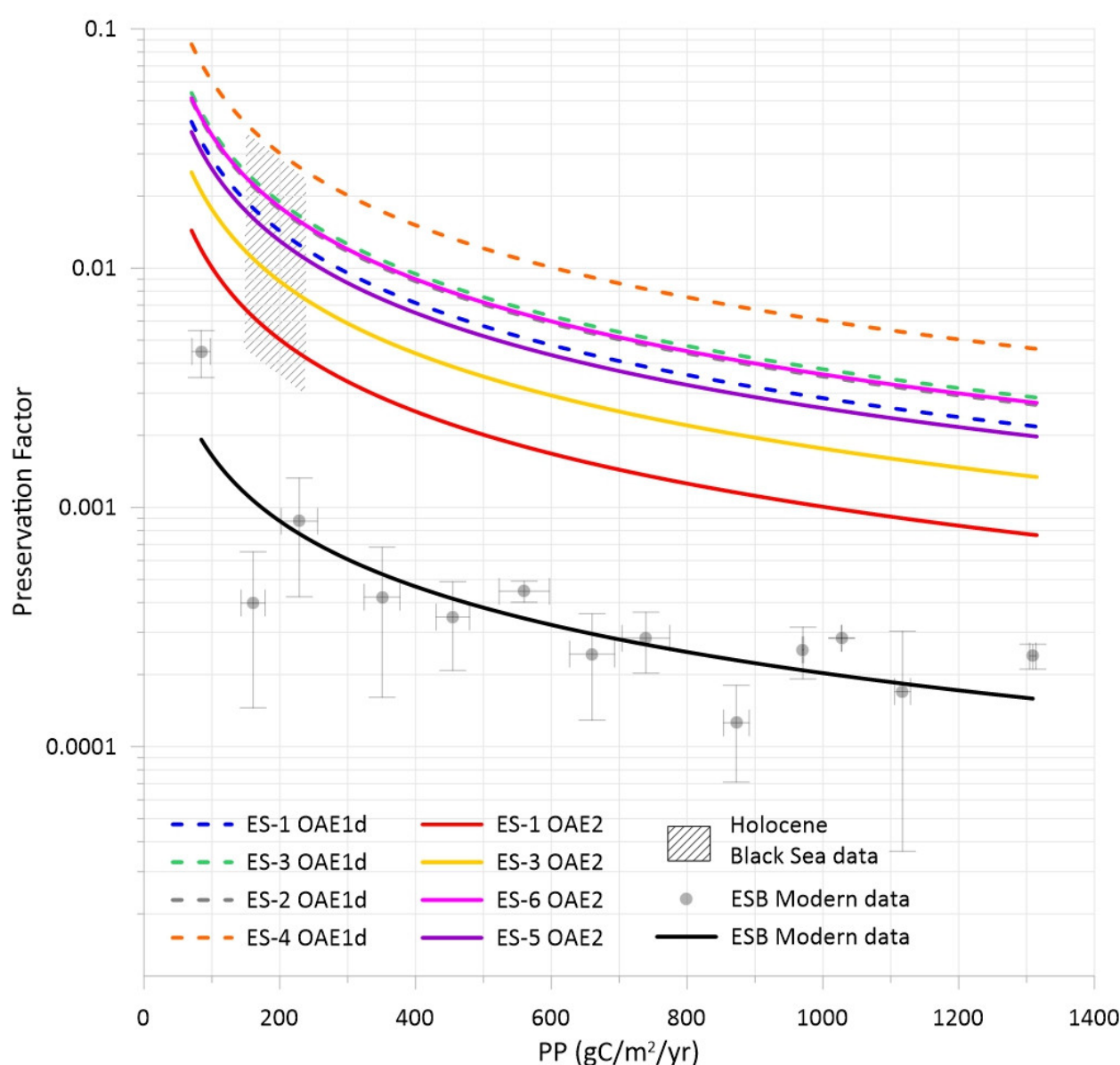


Figure 4. Preservation factors (fraction) for a range of primary productivities (PP) ($\text{gC/m}^2/\text{yr}$). Preservation factors were calculated from modern data (productivity data were binned in $100 \text{ gC/m}^2/\text{yr}$ intervals) from the Espírito Santos Basin (ESB modern data) derived from the modern dataset published in [27]; error bars are displayed, and a curve was fitted to the data (black solid

line). For the wells located in the ESB, preservation factors were estimated based on the mean organic carbon accumulation rate (OCAR) for each oceanic anoxic event (OAE1d and OAE2) and a variable PP considering the modern range of PP for the ESB. Solid colored lines show the calculated values for OAE2, and the dashed colored lines show the calculated values for OAE1d. The y -axis is in log-scale. The rectangle with forward slash filling exhibits the values for the Black Sea during the Holocene based on the results from [32,33].

Despite the discussions made above, there is still another issue regarding the enhanced OCAR during the OAEs in the Espírito Santo Basin. An increase in OCAR may be related either to improvements in production and/or preservation, which is an active debate in this field of research [34], and therefore requires further investigation. Indeed, considering the modern range of PF values for the Espírito Santo Basin, some higher values overlap with the lower limit of the distribution of estimated PF values for the OAEs (Figure 5). This means that preservation could be similar to modern conditions, and enhanced OCAR during OAEs could be caused by increased productivity. In fact, some studies highlight the importance of enhanced productivity as a key process to achieve high-TOC values during the Cretaceous in the South Atlantic [35,36]. However, we highlight that this is only true when considering the highest modern values of PF. If we consider the lowest modern values of PF, the values of productivity during OAEs would extrapolate the modern range for the Espírito Santo Basin. Thus, the values would be 6 to 37 times the modern productivity. This is not only unlikely, but it would also produce unreal productivity values that would be unmatched even considering modern productivity values of the entire Atlantic. Thus, this indicates that a shift in the whole distribution of possible PF values occurred during the OAEs, and that shift was towards higher values of PF (Figure 5). Therefore, it is clear that mean preservation conditions were enhanced during OAEs in the Espírito Santo Basin although we cannot completely discard that increased productivity, which may have occurred during these events, influenced to some extent the high observed values of OCAR.

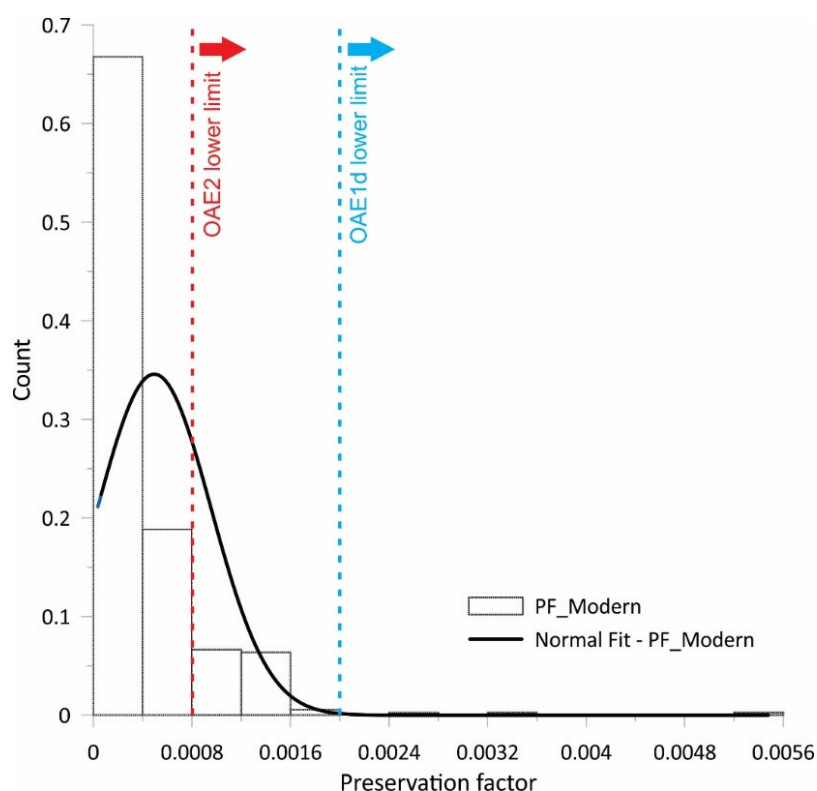


Figure 5. Histogram of modern preservation factor (PF) values and lower limits of the PF distributions for the OAEs.

As shown by our results, preservation was enhanced during OAEs in the Espírito Santo Basin, but we need to explore the causes of such improvement in preservation. In the work of [37], the author provides a discussion about the factors that influence the preservation of organic carbon in the marine realm. The author shows, using data from distinct depositional environments in terms of oxygen (O_2) concentrations and sedimentation, that preservation can be influenced by bottom-water O_2 concentrations depending on the conditions of sedimentation at these environments. In the work of [37], the authors concluded that in environments with sedimentation below $0.04 \text{ g/cm}^2/\text{yr}$, enhanced preservation is only observed for sediments deposited in low O_2 and euxinic environments, while at deposition rates above $0.04 \text{ g/cm}^2/\text{yr}$, similar preservation is observed in both the presence and absence of O_2 . Our mean values of sedimentation during the OAEs are below this threshold of $0.04 \text{ g/cm}^2/\text{yr}$, which implies that the observed enhanced preservation at the Espírito Santo Basin during these events was indeed caused by low O_2 concentrations. In addition, studies investigating changes in organic facies in sedimentary basins indicated that organic matter preservation is related to anoxic conditions during transgressions linked to sea-level rise, which is the case during these OAEs [38,39].

In summary, our results suggest that high OCAR values observed during OAEs in the Espírito Santo Basin were a consequence of enhanced preservation due to low O_2 concentrations. Our PF values for the OAEs at the Espírito Santo Basin are similar to Holocene values for the Black Sea [32,33], which supports our interpretation of enhanced preservation due to low O_2 concentrations, and also reinforces the quality of our PF estimations. Our PF estimations for the OAEs are also similar to the ones estimated for the mid-Cretaceous (ca. 2%) by [6] and for the late Cenomanian (ca. 5%) by [8]. Organic-rich layers linked to the OAEs were also observed in other basins along the Brazilian margin [3,10,13], and the high accumulation of organic carbon was also associated with enhanced preservation due to low O_2 concentrations. However, to our knowledge, our study is the first to provide quantitative estimations regarding the improvement in preservation during OAEs. Such quantitative estimations are extremely relevant for organic facies modelling studies since the amount of preserved carbon needs to be addressed during the model simulations [40–42].

6. Conclusions

Our results for the Espírito Santo Basin showed an increase in organic carbon accumulation during OAE1d and OAE2 compared to modern conditions. The high organic carbon accumulation rate values were associated to enhanced preservation due to the presence of bottom water with low O_2 concentrations and not due to fast burial caused by high sedimentation rates. Furthermore, we provided quantitative estimations of preservation by calculating preservation factor (PF) values for the OAEs. The estimations showed that PF values could reach up to 8.6% during OAE1d and 5.1% during OAE2. These results led us to conclude that OAE1d was probably a more intense anoxic event than OAE2 at the Espírito Santo Basin. We highlight that our results are relevant for organic facies modelling studies, which need to provide quantitative estimations of the amount of carbon preserved for their model simulations.

Author Contributions: Conceptualization, I.M.V.; methodology, I.M.V. and T.P.S.; formal analysis, I.M.V.; investigation, I.M.V. and A.L.B.; resources, A.S., I.V.S., and A.L.S.A.; writing—original draft preparation, I.M.V.; writing—review and editing, I.M.V., M.C.B., R.A.D., M.M., V.C.; visualization, I.M.V., T.P.S., and F.R.A.B.; supervision, A.S., I.V.S., and A.L.S.A.; project administration, A.S., I.V.S., and A.L.S.A.; funding acquisition, A.S., I.V.S., and A.L.S.A. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

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