Organic matter sources and paleoenvironmental changes in a devonian epeiric sea (Pimenteiras Formation, Parnaíba Basin): an integrated study of well logs, C/N ratio, and stable isotopes.

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Abstract

Epicontinental seas are shallow seas that lie over a continental block and can be differentiated from shelfs by their depth and topographic irregularity. During Devonian time, the occurrence of black organic-rich shales can be related to the extinction event known as the Kellwasser event. In the Parnaíba Basin, the Pimenteiras Formation is the main hydrocarbon source, composed of organic-rich shales deposited during the Frasnian-Famennian period. This work focus on description and integration of well logs and carbon/nitrogen ratio data from the Late Devonian of the Parnaíba Basin. The Pimenteiras Formation was divided into five shale intervals, from top to the base: A, B, C, D and E. Total nitrogen (TN) shows an enrichment pattern towards the top of the section, reaching its maximum value in the Interval D (B) (0.168 wt%). δ^{15}N also exhibits a trend of enrichment towards the top, while the total organic carbon (TOC) displays the highest values in the base of the interval B (D) and the top of D (B) (5.58 wt%). TOC/TN ratio is extremely high at the base of the studied well, gradually depleting toward the Upper Pimenteiras Formation. The data integration suggests that the organic matter source was predominantly terrestrial in the Lower Pimenteiras Formation (Intervals E and D), being gradually converted by marine source in the upper unit (B and A). In this marine interval, the black shales present the geochemical characteristics of the Kellwasser event (Frasnian-Famennian biotic crisis): the TOC/TN ratio presents the highest value; the $\delta^{13}C_{org}$ presents a value of -26.37‰; the TOC a value of 5.85 wt%; and the δ^{15}N depletion of 9.04‰.

Introduction

The extinction in the Frasnian-Famennian (Late Devonian) was one of the "big five" mass extinctions registered in the Earth (Sepkoski, 1996; McGhee et al., 2013). This event, known as the Kellwasser event (KWE), is associated with deposition of organic-rich shales in many ancient epeiric seas around the world (Uveges et al., 2019). The Appalachian Basin and the Illinois Basin in US, Peel Shelf in Canada, Canning Basin in Australia, and Madre de Dios Basin in Bolivia are some examples of the organic-rich shales associated with the KWE (Haddad et al., 2016; Spaak et al., 2018; Kabanov and Jiang, 2020).

In the Parnaíba Basin, NW Brazil, the occurrence of successions deposited in epeiric seas with high total organic carbon (TOC) content were registered in the Pimenteiras Formation (Rodriguel, 1994; Souza et al. 2017; Gonzalez; 2020; Mussa et al. 2021; Lessa et al., 2022). This unit deposited during the Devonian Period, originally lying on the northwestern margin of Gondwana and connected adjacently to the Amazon and Saltpond-Kenta basins (Villeneuve, 2005; Menzies et al., 2018).

The Mesodevanian-Eocarboniferous succession is one of the five major depositional sequences of the Parnaíba Basin, and consists of five lithostratigraphic units: Itaim, Pimenteiras, Cabeças, Longá, and Poti Formations (Gois and Feijó, 1994; Vaz et al. 2007). The Pimenteiras Formation (middle to late Devonian) is the main hydrocarbon source in this basin (Souza et al. 2017). Rodrigues (1995) identifies three intervals of radioactive shales (Radioactive shales A, Radioactive shales B, and Radioactive shales C) deposited during the Devonian, with the radioactive shale C associated with a global anoxic event. The effect of this event (or events) on the sedimentary organic matter sources and paleoenvironmental changes in the Pimenteiras Formation is little-documented.

According to Lamb *et al.* (2006), Freire *et al*. (2012), and Freire and Monteiro (2013), when TOC/TN values are higher than 20, the $\delta^{13}C_{org} < -25‰$ and the δ^{15}N values are negative, we can associate to terrestrial OM source;on the other hand, when TOC/TN are lower than 20, $\delta^{13}C_{org} > -22‰$, and δ^{15}N values are positive we can associate to in situ marine OM. Mixtures can be interpreted as coastal zones.

The objective of this study is to integrate the interpretations of geophysical well logs and the carbon and nitrogen data in the shales of the Pimenteiras Formation to understand the paleoenvironmental variations in the basin during the Late Devonian. Carbon and nitrogen isotopes give us clues about the dynamics of the carbon cycle and the source of organic matter (OM), the nitrogen and his isotopes help us understand the dynamics of nutrients present in the environment, the source of biologically available nitrogen, and redox processes (Uveges et al., 2019). Together, they provide the necessary data to reach our objectives.

Method

The lithological interpretations were made from the analyses of drilling cuttings and logs of the well 1-OGX-93-MA, located near the Parque dos Gaviões Gas Field, at Parnaíba Basin, NE Brazil (Figure 1). The software APPy was used to process and interpret the well logs. Initially, cuttings were separated, washed in a 0.53 mm sieve to remove residual drilling mud from the samples and described. After washing, samples were dried in a heater oven at 40°C and decarbonated in a weak-acid attack (HCl 10%). During the decarbonation process, samples were placed on a hotplate to remove both $CaCO_3$ and $MgCO_3$. Samples were decarbonated for approximately 24 hours. After that, samples were washed with deionized water to remove the acid remains and the generated salts after reaction (this process was repeated up to three times) and dried for 24 hours at room temperature and 24 hours inside a heater oven at 40ºC. After drying, 5 mg and 50 mg of the samples were weighed for TOC, TN, $\delta^{13}C$ and $\delta^{15}N$ analysis, and encapsulated in tin capsules and analyzed using a Thermo Finnigan Flash-EA, associate to a Delta Plus mass spectrometer at the laboratory of the Federal University of Rio Grande (FURG). TOC/TN ratio was calculated from the TOC and TN content, both in wt%.

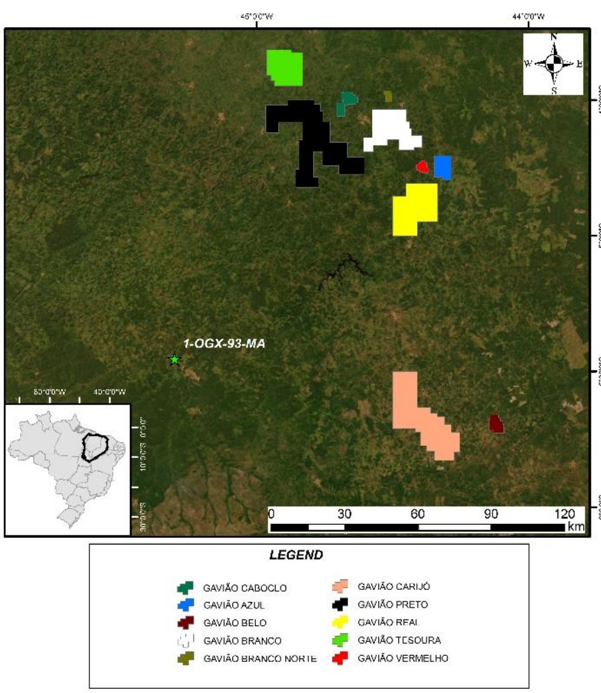

Figure 1 – Location map of the study area. Author.

Results

Well logs

The Pimenteiras Formation in well 1-OGX-93-MA has a thickness of approximately 768 m, including diabase sills and metasediments (*intertraps*) which correspond to 305 m of total thickness. The unit is basically composed of sandstones and shales, with a total thickness of 247 m of sandstones (53.3%) and 216 m of shales (46.7%).

The main shale intervals occur at the intervals 2475/2508m (Interval E), 2235/2277m (Interval D), 2130/2157m (Interval C), 1995/2109m (Interval B), and 1791/1800m (Interval A), as shown in Figure 2. Interval E (Figure 2E) is 33 m thick and consists of dark to light gray shales, locally silty shales with some trace minerals such as pyrite and micas. Below this interval occur sandstones of the Itaim Formation and above diabase sills. Throughout the interval, the gamma ray (GR) log remains high, ranging from 160 gAPI to 90 gAPI, with the highest values at the bottom of this interval and the lowest values at the top. The density log (RHOZ) values range from 2.95 g/cc at the bottom to 2.65 g/cc at the top of the succession. Although, the neutron log (NPOR) ranges from 27% (base of the interval) to 14% (top), and the sonic (DTCO) values, which are relatively low, range from 80 µs/ft (base) to 60 µs/ft (top).

The Interval D (Figure 2D) corresponds to a 42m thick succession, consisting of black to dark and light gray shales. GR is extremely high at the base of the interval, exceeding values of 300 gAPI, tending to decrease towards the top of the succession, reaching values of 120 gAPI. At the depth of 2269m, it shows the highest GR value in this interval. RHOZ values vary between 2.45 g/cc and 2.25 g/cc, gradually decreasing upward. NPOR log shows values near zero at the bottom of the succession, tending to decrease towards the top with values of up to -15%. At depth 2258m, the values tend to increase up to 3% and at depth 2243m it decreases with values ranging from -15 to -3 %. DTCO values remain low at the bottom (80µs/ft), tending to increase towards the top until the depth of 2257m, with a value of 33 µs/ft.

The Interval C (2130/2157m - Figure 2C) is composed of dark to light gray shales, locally micaceous and silty. GR tend to remain high at the base, with values of 135 gAPI to 195 gAPI, but at depth 2144m there is a significant increase, reaching 270 gAPI. RHOZ has values of 2.45 g/cc at the base and 2.06 g/cc at the top, while NPOR has values between 3% and -3%. At the depth of 2144m, NPOR decreases to the value of -15 %, maintaining this value until the top of the interval. DTCO vary between 60 and 80 µs/ft.

The Interval B (Figure 2B) corresponds to the thickest shale interval of the Pimenteiras Formation in this well (1995/2109m), with a total thickness of 114 m. Shales in this interval are dark to light gray colored, with subordinate layers of siltite and sandstones. GR has values between 120 gAPI and 180 gAPI in the interval 2059/2055m, and above this interval values decrease and are varied from 60 gAPI to 150 gAPI between 2055 m to the top of the interval (120 gAPI to 180 gAPI). RHOZ values are relatively high at the base of the interval, with values of approximately 2.90 g/cc, with a tendency to decrease towards the top, reaching 2.20 g/cc. From the depth 2087 m, the density tends to increase up to 2.75 g/cc, with some isolated intervals varying between 2.45 and 2.85 g/cc. Values of NPOR tend to increase towards the bottom to the top, in 2087m values decrease until 2056m, varying with values of 45% to 14%, from 2056m the values increase again towards the top until 2034m, reaching values of 45%, DTCO values are lowthroughout the interval, ranging from 60 µs/ft to 80 µs/ft.

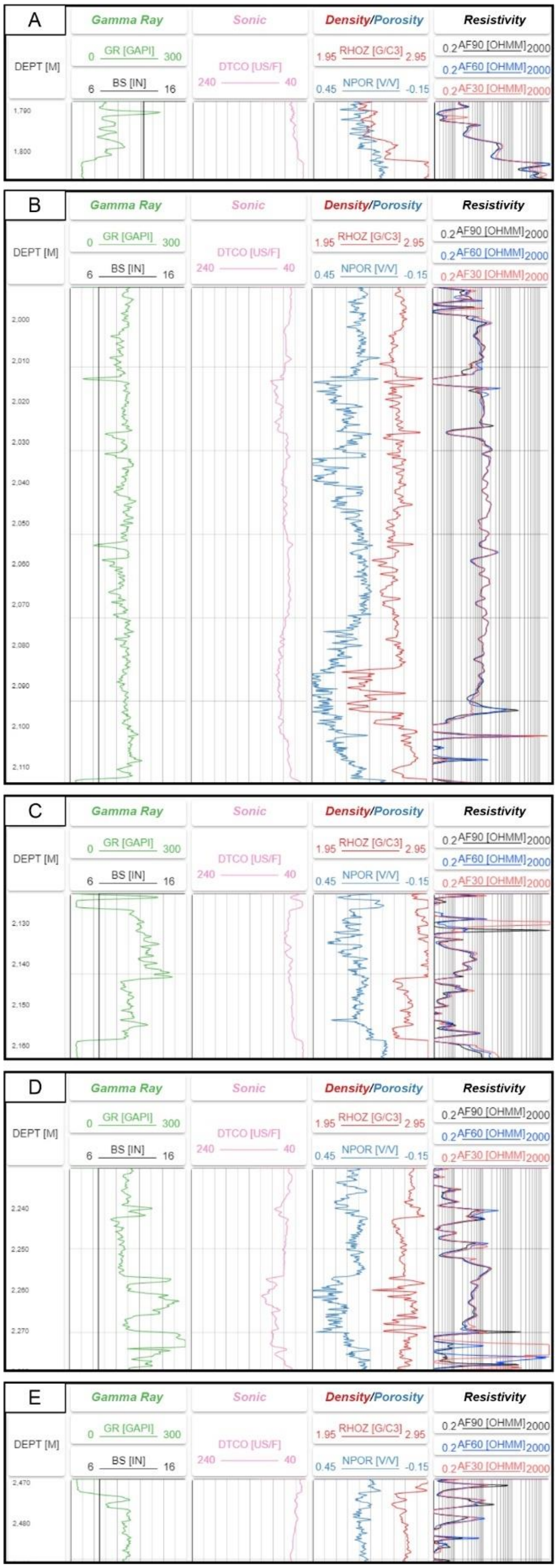

Figure 2 –Well logs of the five shale intervals (Pimenteiras Formation), from the top to the base: Interval A; Interval B; Interval C; Interval D; and Interval E.

The Interval A (Figure 2A) occurs at the top of the unit (depth 1791m), reaching 9m of dark to light gray shales. GR oscillates with values from 70 gAPI to 120 gAPI; RHOZ values decrease towards the top (2.65 g/cc to 2.35 g/cc) and NPOR values vary from 14% to 32%. In the interval 1796,5/1795,0m it is possible to observe the *crossover* between RHOZ and HPOR curves. Throughout the interval, DTCO curve shows a slight increase towards the top of the succession, ranging from 40 µs/ft to 50 µs/ft.

Total Nitrogen and $\delta^{15}N$

Total nitrogen (TN) and nitrogen stable isotopic signature ($\delta^{15}N$) analyses were performed in five intervals of the Pimenteiras Formation (Figure 3). Interval E (2475/2508m), in the base of the interval, shows TN content constant, with very low values ranging from 0.030 wt% to 0.018 wt%, while the $\delta^{15}N$ values have a trend of enrichment towards the top of the interval, ranging between -8.33‰ and -2.45‰.

In interval D (2235/2277m), the TN content have a slight tendency to enrichin the interval, reaching values of 0.091 wt%. From this depth on, the TN content tends to deplete towards the top, reaching values of 0.014 wt%. The values of $\delta^{15}N$ have two main trends of variation: (i) in the interval 2259/2277m, with the shales tending to deplete in $\delta^{15}N$ to values of -6.83 ‰; and (ii) in the interval 2271/2259m in the top of the interval, with enrichment in $\delta^{15}N$ of the shales to values of 1.55‰ (Figure 3).

In the Interval C (2130/2157m), it is possible to observe a trend of enrichment in TN values from the bottom to the top of the succession, with a minimum value of 0.024% and a maximum of 0.038% (Figure 3). The values of $\delta^{15}N$ have a similar enrichment trend towards the top of the range with small oscillations, reaching minimum values of -4.7‰ at depth 2151m and maximum values of -0.99‰ at depth 2130 m.

In the Interval B (1995/2109m), the TN values have a general trend of enrichment towards the top of the succession. From the bottom of the interval to depth 2088 m, TN varies from 0.048 wt% to 0.141 wt%. The interval 2088/2076m, occur a depletion of TN to values of 0.091 wt%, subsequently gradually enriching to a maximum at depth 2013 m (0.168 wt%) and reducing until the transition to sandstones at depth 1995m (0.091 wt% - Figure 3). The values of $\delta^{15}N$ also follow a trend of enrichment from the base of the interval B to the depth of 2085 m, ranging from -2.60‰ to 0.43 ‰. Between 2085m and 2013m depth, the values of $\delta^{15}N$ decrease the rate of enrichment, maintaining high values until 2013m. From this depth to the top of the interval B, the values of $\delta^{15}N$ begin to deplete, reaching -5.56 ‰ (Figure 3).

In the Interval A (1791/1800m), TN content is low, with a maximum value of 0.108 wt% at depth 1797m and a minimum value of 0.071 wt% at depth 1794m. The values of $\delta^{15}N$ have a slight depletion trend from the bottom to the top of the interval, with values ranging from -6.80‰ (1797 m) to - 9.04‰ (1794 m).

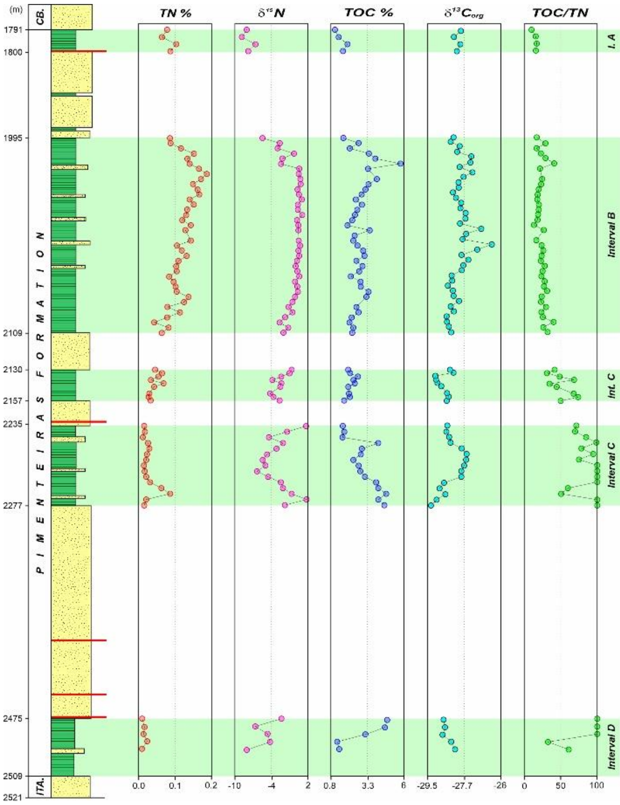

Figure 3 – Track1: Lithological log; Track 2: TN content (wt%); Track 3: $\delta^{15}N$ (‰); Track 4: TOC content (wt%); Track 5: $\delta^{13}C_{org}$ (‰); and TOC/TN ratio of the Pimenteiras Formation. Lithology legend: yellow - Deltaic sandstones; green - shallow marine shales; red lines (not in scale) - location of diabase sills.

Total Organic Carbon (TOC) and $\delta^{13}C_{org}$

Total organic carbon (TOC) and organic carbon isotopic signature ($\delta^{13}C_{org}$) analyses were performed in the entire interval of the Pimenteiras Formation (Figure 3).In Interval E (2475/2508m), TOC content shows enrichment from the bottom to the top of the succession, ranging from values of 0.95 wt% to values of 4.81 wt%. Although, the values of $\delta^{13}C_{org}$ have a reverse trend, depleting towards the top from values of -28.21‰ to -28.78‰ (Figure 3).

In the Interval D (2235/2277m), TOC content tends to decrease toward the top of the succession, ranging from 4.49 wt% at the bottom (2277m) to 1.27wt% at the top (2235 m - Figure 3). However, between depths 2253m and 2244m, an enrichment pattern occurs up to values of 4.02 wt%.The $\delta^{13}C_{org}$ values have a trend of enrichment from depth 2279m (-29.60‰) to 2250m (-27.64‰). After this interval, the values of $\delta 13C_{org}$ tend to deplete towards the top of the succession, reaching a value of -28.66 ‰ at depth 2235m.

In Interval C (2130/2157m) there is an enrichment in the TOC content from depth 2157m (1.36 wt%) to 2136 m (2.4wt%), showing smaller cycles of increasing and decreasing in the contents (Figure 3). From depth 2136m, TOC content tends to decrease towards the top of the interval, reaching values of 1.66 wt% at depth 2130m, just below the sandstone layers. The values of $\delta^{13}C_{org}$ show a trend of depletion from the base of the interval to depth 2136m, leaving values of -29.19‰ to -29.19‰. After this depth, the $\delta^{13}C_{org}$ again enriches towards the top reaching values of -28.30‰.

Interval B (1995/2109m) shows much oscillation in TOC content, but with a general trend of enrichment towards the top of the succession (Figure 3). At least three major enrichment cycles can be identified, with boundaries marked by an abrupt decreasing in TOC values: (i) from depth 2103m to 2085m,values change from 1.92 wt% to 3.36 wt%; (ii) from depth 2076m to 2049m, the change goes from 20.04 wt% to 3.48 wt%; and (iii) from depth 2046m to 2010m, has an increase from 1.77 wt% to 5.58 wt%. Above depth 2010m, the TOC content shows a large decreasing, reaching values of 1.46 wt% just below the sandstones. The values of $\delta^{13}C_{org}$ also show a lot of oscillation throughout the interval, but the cyclicity does not coincide with the TOC content variation curve. From the base of the interval (2109m) to depth 2082m, $\delta^{13}C_{org}$ shows intervals of enrichment at depths 2097m and 2091m, with values of -28.28‰ and -28.02‰ respectively, and depletion at depths 2100m, 2094m and 2082m, with values of -28.65‰, -28.43‰ and -28.58 ‰. After 2082m, the $\delta^{13}C_{org}$ presents a strong trend of enrichment until the depth of 2058m, reaching values of -26.37‰, after 2058m. To the top, the $\delta 13C_{org}$ presents a strong trend of depletion, presenting some points of enrichment in the depths 2049m, 2040m, 2016m and 2007m, with values of -26.90‰, -27.68‰, -27.34‰ and -27.42‰, respectively.

In the Interval A (1791/1800m), the TOC content shows a depletion trend towards the top of the succession, ranging from 1.67 wt% (1797m) to 0.67 wt% (1791m), and the $\delta^{13}C_{org}$ remains nearly constant with a mean value of -27.94‰ (Figure 3).

TOC/TN Ratio

In Intervals E (2475/2508m) and D (2235/2277m), the TOC/TN values are extremely high, sometimes above 100. In interval E, the TOC/TN ratio tends to increase toward the top, where at depth 2475m thevalue reaches 250,47. In interval D, the values oscillate greatly in increasing and decreasing, although it always remains extremely high. In the interval 2271/2277m, the TOC/TN values decrease, going from 206.95 to 51.30. From depth 2268m to 2259m, the values increase again, after which the values oscillate between 70 and 130 until depth 2235m.

In Interval C (2130/2157m), the TOC/TN values tend to deplete towards the top, but throughout the interval, it shows some peaks of increasing in the intervals 2154m, 2139m, and 2130m, with values of 74.4, 68.42 and 40.38.

In the Interval B (1995/2109m), the TOC/TN values tend to decrease toward the top, with small increasing oscillations with values ranging from 12.04 to 40.57. The highest increasing points are at depths 2103m and 2010m, and the highest decreasing values are at depths 2055m and 2046m. In the A Interval, the TOC/TNtends to decrease towards the top, reaching valuesof 8.02.

Conclusions

Considering the integration of geological, geophysical and geochemical data obtained from cuttings and logs of the Pimenteiras Formation in well 1-OGX-93-MA, we can infer the following:

In Interval E (2475/2508m), the TOC/TN values are extremely high towards the top, indicating a progressive increase of the terrestrial OM source. The depleted values of $\delta^{13}C_{org}$ and $\delta^{15}N$ corroborates with terrestrial OM influence. It can be related to a progradation or to humic periods with an increase in rivers discharges. This progradational event culminate with a thick deltaic sandstone, in the interval (2277/2474m).

The Interval D (2235/2277m) present an upward TOC/TN decreasing trend, with high values in the lower portion. The $\delta^{13}C_{org}$ values shows an enrichment middle, followed by a negative excursion towards the top of the interval, probably related to a progradational event. The $\delta^{15}N$ presents high values on the base and top of the interval, with lowest values in the middle. These trends indicate the dominance of terrestrial OM, with increase of marine contribution to the top, probably a flooding event.

In interval C (2130/2157m), the TOC/TN maintain a decreasing towards the top, while the $\delta^{13}C_{org}$ and $\delta^{15}N$ shows an enrichment characteristic of a transition between terrestrial and marine OM. In this interval, it is possible to notice the beginning of a possible sea level rise, as the TOC/TN starts to become very low, showing a higher increase in the influence of marine organic matter.

In the Interval B (1995/2109m), the TOC/TN ratio shows values above 20, but the $\delta^{13}C_{org}$, TOC, TN and $\delta^{15}N$ values shows a general trend of high values. This interval shows a possible major flooding interval of the epicontinental sea, interpreted based on the TOC/TN values below 20, an enrichment of the $\delta^{13}C_{org}$ values, higher TOC values, and a positive trend of the δ15N. This scenario refers to the increase in the anoxic water-column from the interval 2055/2025m. The increase of the TOC content between the interval 2025/2010m, as well as the increasing of the TOC/TN ratio, corroborates with the increase of the anoxic water column. In the depth 2010m, the TOC/TN ratio presents the highest value in interval B, the $\delta^{13}C_{org}$ presents a small negative excursion, the TOC a large positive excursion, and the $\delta^{15}N$ starts to deplete. These data can mark the Kellwasser event in the Frasnian-Famennian biotic crisis.

Three igneous intrusions have contact with the shales of the Pimenteiras Formation in this well. The influence of these intrusions remains uncertain. TN results near the intrusions exhibit a slight depletion, the $\delta^{15}N$ values show enrichment near the igneous rocks in all intervals. The TOC and $\delta^{13}C_{org}$ values do not follow a consistent pattern across all intervals. Further studies should be conducted to assess the extent of the influence of the igneous intrusions.

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