

Chemostratigraphy (TOC, $\delta^{13}\text{C}$, $\delta^{18}\text{O}$) around the Pliensbachian/Toarcian boundary in the reference section of Peniche (Lusitanian Basin, Portugal)

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Resumo

Palavras-chave: Estratigrafia química, COT, Isótopos estáveis, Pliensbaquiano, Toarciano, Bacia Lusitânica, Portugal

São apresentados os resultados das análises quimioestratigráficas baseadas em carbono orgânico total (COT) e isótopos estáveis de oxigénio e carbono, em amostras de rocha total recolhidas ao longo do limite Pliensbaquiano–Toarciano do perfil de Peniche (parte superior da Formação de Lemed e parte inferior da Formação de Cabo Carvoeiro). Estes resultados fazem parte de um conjunto de estudos, em andamento, que incluem análises de $^{87}\text{Sr}/^{86}\text{Sr}$, $\delta^{18}\text{O}$, $\delta^{13}\text{C}$ e elementos maiores, menores e traços, tanto em rocha total como em belemnites.

Résumé

Mots-clés: Chimostratigraphie, COT, Isotopes stables, Pliensbachien, Toarcien, Bassin Lusitanien, Portugal

Sont présentés les résultats d'analyses chimostratigraphiques basées en carbone organique total (COT) et isotopes stables d'oxygène et de carbone, dans des échantillons de roche totale recueillis tout le long de la limite Pliensbachien–Toarcien de la coupe de Peniche (depuis la partie supérieure de la Formation de Lemed jusqu'à la partie inférieure de la Formation de Cabo Carvoeiro). Ces résultats font partie intégrante d'un ensemble d'études, en cours, qui englobent des analyses de $^{87}\text{Sr}/^{86}\text{Sr}$, $\delta^{18}\text{O}$, $\delta^{13}\text{C}$ et d'éléments majeurs, mineurs et trace, tant en roche totale qu'en des belemnites.

Abstract

Key-words: Chemostratigraphy, TOC, Stable isotopes, Pliensbachian, Toarcian, Lusitanian Basin, Portugal

This work presents the chemostratigraphy analysis based on total organic carbon (TOC) and the evolution of the carbon and oxygen stable isotopes in the whole rock samples around the Pliensbachian/Toarcian boundary in the Peniche section (uppermost part of Lemed Formation and lowermost part of Cabo Carvoeiro Formation). These are partial results which form part of a group of studies, being processed, that include isotope analyses of $^{87}\text{Sr}/^{86}\text{Sr}$, $\delta^{18}\text{O}$, $\delta^{13}\text{C}$ and major, minor and trace elements in whole rock and belemnites.

Introduction

The Lusitanian Basin (Portugal) is located on the western margin of the Iberian Plate, and belongs to a group of Atlantic Ocean marginal basins which began their formation during the rift phase at the Late Triassic. It has a NE-SW orientation and is almost 300 km in length and 150 km wide, including the offshore, with a maximum thickness of 5 km. These sediments belong to Upper Triassic–Upper Cretaceous, with Tertiary cover and is mainly Jurassic sediments.

The Lower Jurassic is particularly well represented in the Lusitanian Basin with various important geological outcrops. The Peniche region is one of the most important sections, due to the excellent exhibition of a continuous series of carbonates, with more than 450 m, deposited between Sinemurian to Toarcian.

The present study included the carbon and oxygen stable isotopes and total organic carbon (TOC) analysis in the whole rock samples around the Pliensbachian/Toarcian boundary in the Peniche section (uppermost part of Lameda Formation and lowermost part of Cabo Carvoeiro Formation). These are part of a multidisciplinary study that includes a group of chemostratigraphy analysis (TOC, “Rock-Eval” pyrolysis, biomarkers, carbon and oxygen isotopes, minor and major elements, on the whole rock, and carbon, oxygen and strontium isotopes on the belemnite fossil) and calcareous nannofossil biostratigraphy in the Pliensbachian–Lower Toarcian section of Peniche (OLIVEIRA & *al.*, 2005a,b).

Methodology

The analyses used 71 samples collected along 25 meters of the section (Figs. 1 and 2). All samples were pulverized in a porcelain dish to obtain particles smaller than 80 mesh. Of these, 68 samples were submitted to the total organic carbon analyses (TOC) and in 38 samples the values of stable isotope carbon ($\delta^{13}\text{C}$) and oxygen ($\delta^{18}\text{O}$) were obtained from the whole rock carbonate fraction. The analyses were performed at the Petrobras Research Center (Cenpes, Brazil) laboratories. The determinations of the TOC values were made in the LECO-SC444 and oxygen and carbon isotopic values were obtained using a Kiel Carbonate Device III coupled to a MAT 252 Thermo Finnigan mass spectrometer.

The results of TOC were expressed as a percentage (%) and on every tenth analyzed sample a duplicated analysis was made. The equipment was calibrated daily with standards, before initiating the analyses. This process uses approximately 10 mg of sample, which was placed in a vacuum chamber and heated to 70 °C and reacted with phosphoric acid for 6 minutes. The water and carbon dioxide generated were captured at -170°C with liquid nitrogen. Then this mixture was brought to -110°C when the subsequently released pure CO₂ was again collected at -170°C with liquid nitrogen.

All oxygen and carbon isotopic results are reported in parts per mil (‰) relative to PDB and calibrated by routine preparation and analysis by the carbonate

standard NBS-19 ($\delta^{13}\text{C}=1.95\text{‰}$, $\delta^{18}\text{O}=-2.20\text{‰}$). Day to day precision ($\pm 1\sigma$) based on NBS-19 analyses was ± 0.05 for $\delta^{13}\text{C}$ and ± 0.08 for $\delta^{18}\text{O}$.

Results and discussion

Isotopic analysis: In the marl-limestone succession that encompasses the Pliensbachian/Toarcian boundary in Peniche, the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values decrease, gradually, from the middle part, up to the uppermost part of Spinatum Zone, with smaller values in the lowermost part of the Polymorphum Zone, with an absolute variation of around -2.0‰ (fig. 1).

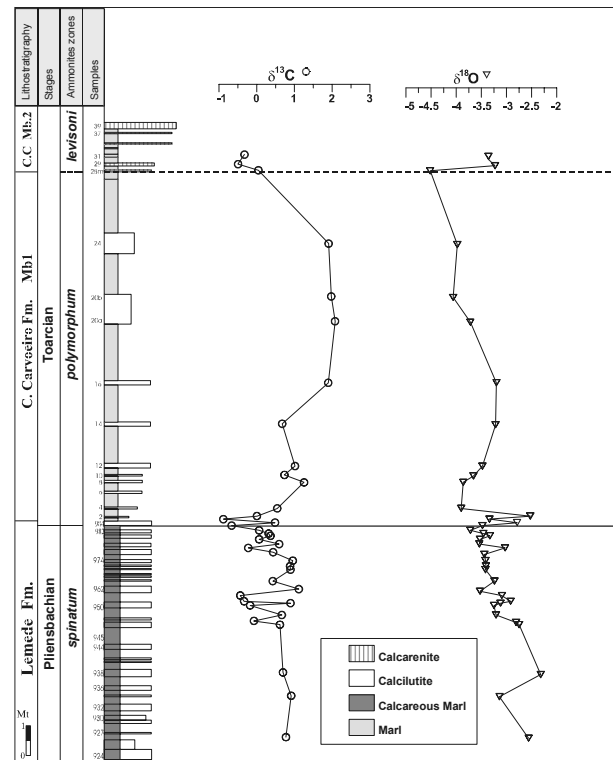


Fig. 1 – Carbon and oxygen isotope values around the Pliensbachian/Toarcian boundary in Peniche.

In the Lower Toarcian studied section (Polymorphum Zone and lowermost part of Levisoni Zone) the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values show an inverse behavior compared to the Upper Pliensbachian section (middle to uppermost part of Spinatum Zone). In the Lower Toarcian the $\delta^{13}\text{C}$ data shows a positive trend (a spread of +2.0‰) with a maximum value in the middle-upper portion of the Polymorphum Zone and a minimum in the lowermost part of the Levisoni Zone. This event, recently confirmed by S. HESSELBO & *al.* (2007), was verified previously in the Coimbra area (DUARTE & *al.*, (2004a) and in other distal sectors of the Lusitanian Basin (DUARTE & *al.*, 2007). Similar variations were observed by B. VAN DE SCHOOTBRUDGGE & *al.* (2005) and I. ROSALES & *al.* (2004), in the Llanbedr Mochras Farm Borehole (Wales) and in the Basque-Cantabrian Basin, respectively. In spite of our study just using whole rock samples, and the studies of B. VAN DE SCHOOTBRUDGGE & *al.* (2005) and I. ROSALES & *al.* (2004) used belemnites, the absolute variation was similar, around -2.0‰.

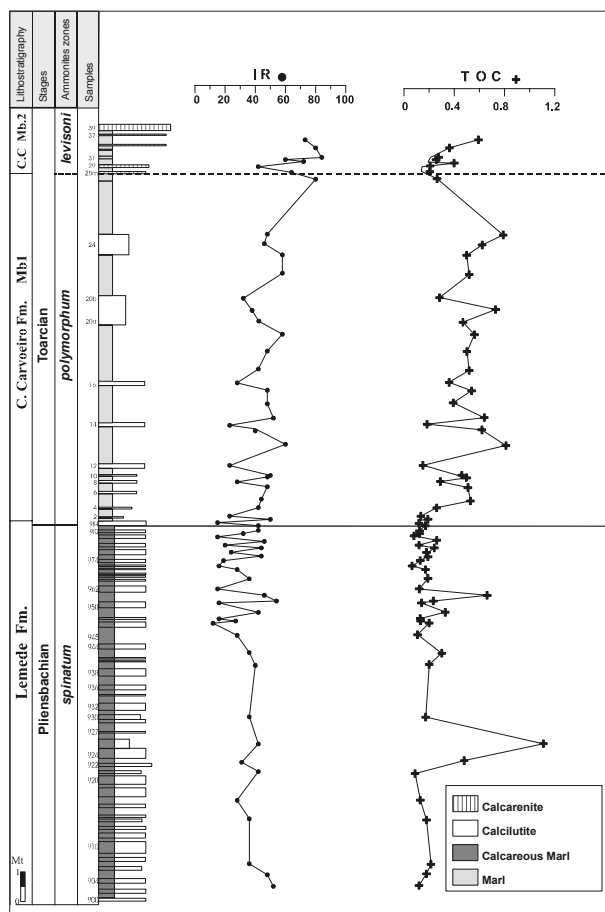


Fig. 2 – TOC and insoluble residue values around the Pliensbachian-Toarcian boundary in Peniche.

The $\delta^{18}\text{O}$ values, in spite of the positive excursion immediately observed after the Pliensbachian/Toarcian boundary, show a general tendency to decrease within the Polymorphum Zone, with the smallest values

observed in the lower portion of the Levisoni Zone, followed by a sudden reversion to higher isotopic values. Similar isotopic behavior was verified by I. ROSALES & *al.* (2004) for the Basque–Cantabrian Basin, suggesting a good correlation between Peniche and North Spain sections. In the Peniche section, the lowest isotopic values found in the lowermost part of the Levisoni Zone, would correspond to the smallest values registered in the lowermost part of the Serpentinus (= Levisoni) Zone, in the Spanish section.

TOC analysis: In general, the TOC values are low, around 0.2% in the Spinatum Zone, further upwards they increase to 0.5% in the Polymorphum Zone, whilst they decrease again to 0.2% in the lowermost Levisoni Zone (fig. 2).

The low TOC values registered in the Polymorphum-lowermost part of Levisoni Zone interval of Peniche don't coincide with the high values observed in the same interval of North-European area (JENKYN & *al.*, 2002). In fact, the Lower Toarcian series of the Lusitanian Basin are characterized by the absence of black shales as a result of local sedimentary conditions (DUARTE, 1997; DUARTE & *al.* 2004ab, 2005).

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References

- DUARTE, L. V. (1997) – Facies analysis and sequential evolution of the Toarcian-Lower Aalenian series in the Lusitanian Basin (Portugal). *Comun. Inst. Geol. Mineiro*, Lisboa, t. 83, pp. 65-94.
- DUARTE, L. V., OLIVEIRA, L. C. V. & RODRIGUES, R. (2007) – Carbon isotopes as a sequence stratigraphic tool: examples from the Lower and Middle Toarcian marly limestones of Portugal. *Bol. Geol. Min.*, Madrid, n° 118 (1), pp. 3-18.
- DUARTE, L. V., PERILLI, N., DINO, R., RODRIGUES, R. & PAREDES, R. (2004a) – Lower to Middle Toarcian from the Coimbra region (Lusitanian Basin, Portugal): Sequence Stratigraphy, Calcareous Nannofossils and stable-isotope evolution. *Riv. Ital. Paleont. Stratigrafia.*, Milano, n° 110, pp. 115-127.
- DUARTE, L. V., RODRIGUES, R., OLIVEIRA, L. C. V. & SILVA, F. (2005) – Avaliação preliminar das variações do carbono orgânico total nos sedimentos margosos do Jurássico inferior da Bacia Lusitânica (Portugal). *XIV Sem. Geoquímica & VIII Congr. Geoquímica Países Língua Portuguesa*, Aveiro, pp. 39-43.
- DUARTE, L. V. (Coord.), WRIGHT, V. P., FERNÁNDEZ-LOPÉZ, S., ELMÍ, S., KRAUTTER, M., AZERÊDO, A. C., HENRIQUES, M. H., RODRIGUES, R. & PERILLI, N. (2004b) – Early Jurassic carbonate evolution in the Lusitanian Basin: facies, sequence stratigraphy and cyclicity. In: DUARTE, L. V. & HENRIQUES, M. H. (Eds.), Carboniferous and Jurassic Carbonate Platforms of Iberia. *23rd IAS Meet. Sedimentology*, Coimbra, *Field Trip Guide Book*, vol. I, pp. 45-71.

- HESELBO, S. P., JENKYN, H. C., DUARTE, L. V. & OLIVEIRA, L. C. V. (2007) – Carbon-isotope record of the Early Jurassic (Toarcian) Oceanic Anoxic Event from fossil wood and marine carbonate (Lusitanian Basin, Portugal). *Earth Plan. Sc. Letters*, Amsterdam, n° 253, pp. 455-470, 5 fig.
- JENKYN, H. C., JONES, C. E., GRÖCKE, D. R., HESSELBO, S. P. & PARKINSON, D. N. (2002) – Chemostratigraphy of the Jurassic System: applications, limitations and implications for palaeoceanography. *J. Geol. Soc. London*, vol. 159, pp. 351-378.
- OLIVEIRA, L. C. V., DUARTE, L. V., PERILLI, N., RODRIGUES, R. & LEMOS, V. B. (2005) – Estratigrafia química (COT, $\delta^{13}\text{C}$, $\delta^{18}\text{O}$) e nanofósseis calcários na passagem Pliensbaquiano-Toarcião no perfil de Peniche (Portugal). Resultados preliminares. *Pesq. Geociências*, Porto Alegre, n° 32 (2), pp. 3-16.
- OLIVEIRA, L. C. V., DUARTE, L. V. & RODRIGUES, R. (2005) – Estratigrafia química (COT, $\delta^{13}\text{C}$ e $\delta^{18}\text{O}$) na passagem Pliensbaquiano-Toarcião no perfil de Peniche (Portugal). Resultados Preliminares. *XIV Sem. Geoquímica & VIII Congr. Geoquímica Países Língua Portuguesa*, Aveiro, pp. 185-188.
- ROSALES, I., QUESADA, S. & ROBLES, S. (2004) – Paleotemperature variations of Early Jurassic seawater recorded in geochemical trends of belemnites from the Basque–Cantabrian basin, northern Spain. *Palaeogeogr., Palaeoclim., Palaeoecol.*, Amsterdam, n° 203, pp. 253-275.
- VAN DE SCHOOTBRUGGE, B., BAILEY, T. R., ROSENTHAL, Y., KATZ, M. E., WRIGHT, J. D., FEIST-BURKHARDT, S., MILLER, K. G. & FALKOWSKI, P. G. (2005) – Early Jurassic Climate change and the radiation of organic-walled phytoplankton in the Thetys Ocean. *Paleobiology*, London, vol. 31, pp. 73-97.