

## **Oscillating redox conditions during deposition of Upper Sinemurian-Lower Pliensbachian black-shales in the Lusitanian Basin (Portugal)**

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The Polvoeira Mb of Água de Madeiros Fm (Upper Sinemurian to lowermost Pliensbachian) is one of the units in Lusitanian Basin with potential for hydrocarbon generation; it comprises alternations of marl/limestone with several black-shale levels [1]. Twelve samples representing different black shales were selected for whole-rock geochemistry. Two suites can be distinguished on the basis of TOC-S systematics and RSTE (e.g. Mo, U, V, Cd, Cu, Ni and Zn) relative content. Samples with TOC values up to ~7%: i) correlate positively with S (intercept close to the origin) and show TOC/S ratio  $\approx 4.0$ , close to the lower limit of the normal marine conditions field (at 3.6); ii) display low to moderate RSTE enrichments; and iii) have Mo/U ratios  $1\times$  to  $3\times$  of modern seawater, suggesting suboxic to anoxic bottom-waters with H<sub>2</sub>S limited to sediment pore-waters. Samples with TOC usually >7% but up to 15.4%: i) plot clearly below the field of normal marine conditions, showing TOC/S ratios (5.9-11.2) gradually higher with increasing TOC and a linear positive correlation that has low-slope and a positive S axis interception; ii) show high to extreme RSTE enrichments; and iii) have Mo/U ratios  $9\times$  to  $12\times$  modern seawater, indicating deposition under strongly euxinic conditions. The Mo-*EF* vs U-*EF* co-variation for the 12 samples follows a trend similar to that of organic-rich sediments from Cariaco Basin and Baltic Sea where a Mn-Fe oxyhydroxide particulate shuttle was suggested [2] as the mechanism to enhance Mo enrichment over U. The Mo/TOC ratios (10–22) for the euxinic black shale samples suggest moderate to strong deep-water mass restriction akin to those in Cariaco Basin and Framvaren Fjord [3]. Accordingly, the deposition of Upper Sinemurian-Lower Pliensbachian black-shales in the Lusitanian Basin indicates strong oscillating redox conditions in a weakly-restricted marine setting.

[1] Duarte et al. (2010) Geol Acta 8, 325-340. [2] Algeo and Tribovillard Chemical Geology 268, 211–225. [3] Algeo and Lyons (2006) Paleocyanography, 21, PA1016.