Palaeogeography, Palaeoclimatology, Palaeoecology 410 (2014) 316–336

Contents lists available at ScienceDirect

Palaeogeography, Palaeoclimatology, Palaeoecology

journal homepage: www.elsevier.com/locate/palaeo

Organic facies variability in the Posidonia Black Shale from Luxembourg: Implications for thermal maturation and depositional environment

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ARTICLE INFO

Article history:
Received 2 August 2013
Received in revised form 2 June 2014
Accepted 4 June 2014
Available online 13 June 2014

Keywords:
Lower Toarcian
Thermal maturity
Biomarkers
Luxembourg
Depositional environment
Oil shale

ABSTRACT

Posidonia Shale (Lias ε, Lower Toarcian, "Schiste bitumineux") samples were obtained from a well in southern Luxembourg (Esch-sur-Alzette). Elemental composition and organic facies were studied along the cores, and accordingly the thermal maturity and depositional environment were evaluated. The organic matter content is high with an average of 7.2%, ranging between 2.8% and 13.5%. The average vitrinite reflectance value is ca. 0.55%, indicating an early stage of oil generation. Several biomarker based maturity parameters support the low thermal maturity including OEP values and C_{29} 5α, 14α, 17α (H)-steranes 20S/(20S + 20R).

Rock-Eval data and microscopy observations reveal that the organic matter is composed of hydrogen-rich type II kerogen derived from alginite. Small algal bodies derived from nannoplankton predominate, but large telalginite (*Tasmanales*) also occurs. Pyrites are abundant and fish bones are frequently observed, characterizing a marine depositional environment where strong sulfate reduction occurred. Small amount of autochthonous vitrinite observed microscopically, combined with predominance of short-chain *n*-alkanes over long-chain *n*-alkanes, as well as a low terrigenous/aquatic ratio (TAR), indicate a low input of terrigenous organic matter. Sterane distribution is in good agreement with an origin from a marine carbonate depositional environment which corresponds to the general marlstone lithology. Additionally, C_{30}-24-propyl-14α(H), 17α(H)-cholestane (20R) was detected, supporting the marine origin.

The depositional environment was strongly oxygen-depleted in bottom water, as indicated by low concentrations of C_{35} homohopane, fair to low Pr/Ph ratios (slightly less than 1.0) and high sulfur content (ca. 3 wt.% on average) and sulfur/organic carbon ratios, with only few interruptions of dysoxic to suboxic conditions during deposition of the Posidonia Shale in Luxembourg. Gammacerane detected in low abundance reveals that a stratified water column existed and water salinity was slightly enhanced in the paleoenvironment. The highest C_{27}/C_{29} sterane ratio due to more algal input indicates a maximum flooding during the upper *falciferum* zone of the Lower Toarcian in Luxembourg, which fits well to the global sea level curve and might correspond to a productivity-oceanic anoxic event (P-OAE). Furthermore, Toarcian greenhouse climate led to generally low oxygen concentration in bottom water of the shallow sea.

1. Introduction

The Lower Toarcian black shale (Posidonia Shale, Lias ε, "Schiste bitumineux") has been a focus of scientific interest for more than 100 years, as a proven petroleum source rock, rich in organic matter and as a treasure keeping excellent remains of the Lower Jurassic Sea World (Röhl et al., 2001). In the Paris Basin, the Posidonia Shale (PS) reaches depths of more than 2000 m. It was subject of conventional petroleum exploration in the 1970s and recently became focus of exploration for unconventional shale oil (Tissot and Welte, 1984; Chatallier and Urban, 2010). Because of the widespread distribution and richness in organic matter, the Posidonia Shale (PS) is regarded as one of the potential oil and gas shales in Europe (Bruns et al., 2013). However, it still needs to be clarified what kind of shales could generate and store enough gas for industry production. Key parameters for shale gas and shale oil systems include thermal maturity, total organic carbon (TOC) content, organofacies type, mineralogical composition and petrophysical properties (Curtis, 2002; Bowker, 2003; Jarvie et al., 2007; Horsfield and Schulz, 2012).

The Posidonia Shale belongs to the laminated, usually calcareous black–gray to gray–brown marlstones and argillaceous marlstones with high contents of TOC. The carbonate content is on average 40%, showing variation between 20 and 60% (Geyer and Gwinner, 2011). The Posidonia Shale mainly contains Type II kerogen, having a very high petroleum generation potential according to previous studies by Littke et al. (1988); Rullkötter et al. (1988) and Leythaeuser et al.

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http://dx.doi.org/10.1016/j.palaeo.2014.06.002
0031-0182/

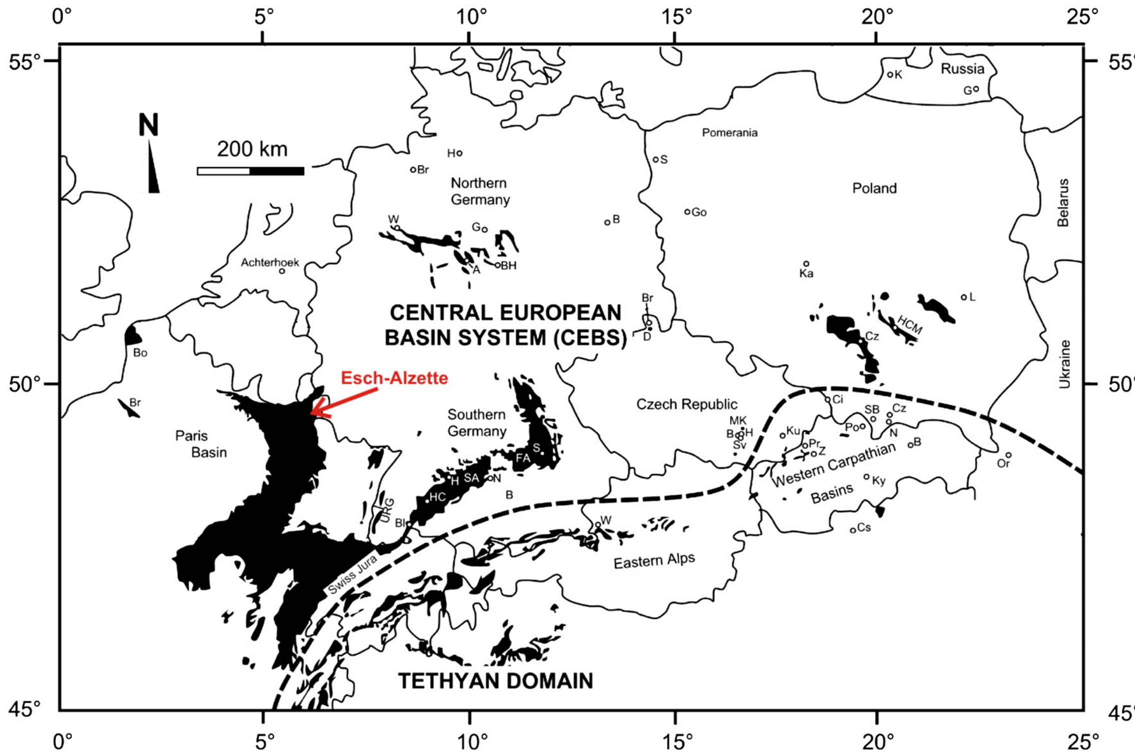

Fig. 1. Location of the studied well in Esch-Alzette, Luxembourg. Black areas are Jurassic outcrops.
Modified from Pienkowski et al. (2008).

(1988). Nevertheless, organic richness and facies are variable, both vertically and laterally to some extent (Littke et al., 1991a).

Several depositional models for Lower Toarcian black shales have been proposed (Pompeckj, 1901; Jenkyns, 1985; Wignall, 1991). Sundararaman et al. (1993) proposed an upwards increasing oxygenation of the environment due to the presence of Ni- and VO^{2+}-porphyrins in northern Germany. Röhl et al. (2001) reconstructed a time-averaged oxygen curve based on high-resolution geochemical, sedimentological and palaeoecological parameters. 4th-order sea-level cycles were proposed to explain the observed facies variability in Dotternhausen and Schesslitz, Southern Germany (Röhl and Schmid-Röhl, 2005).

In this paper, we present a detailed description and analysis of the organic facies of the Posidonia Shale in Luxembourg, as well as information on its thermal maturity and depositional environment based on a series of geochemical parameters. Results are put into a context of sea level fluctuation and depositional environment, and consequences for shale oil and shale gas exploration are discussed and compared to other Posidonia Shale profiles in Western Europe.

2. Geological background

The Posidonia Shale, being divided into three ammonite-biozones (*tenuicostatum*, *falciferum* and *bifrons* in upward order) (Riegraf et al., 1984), belongs to the early Jurassic (Toarcian) and is mainly composed of fine-grained calcareous shales and marlstones with some interbedded thin limestones (Littke et al., 1991a). Samples for the present study originate from Luxembourg (Esch-Alzette, well FR-210-006), located in the northeastern Paris Basin (Fig. 1), between the Ardennish–Rhenish Mountains and the Vosges. During the Lower Jurassic the present-day Europe was located on the broad and extensive Laurussian continental shelf that opened to the deep Tethyan Ocean towards the southeast (Ziegler, 1982). The Posidonia Shale was assumed to be deposited under an anoxic or oxygen depleted environment (Littke et al., 1991a; Jenkyns and Clayton, 1997; Jenkyns, 2010). Küspert (1982) observed significant depletion in ^{13}C in carbonates and organic matter coinciding with the widest regional occurrence of bituminous rocks in Europe. Such a negative $\delta^{13}C_{org}$ excursion ($\delta^{13}C_{org}$ ca.-32‰ PDB) has been observed in Toarcian shales throughout Europe (Hollander et al., 1991; Hesselbo et al., 2000; Jenkyns, 2010). Janicke (1990) assumed that an anoxic deep water layer probably prevailed during deposition of the PS in the Paris Basin, with the evidence of the lack of bioturbation.

The studied Posidonia Shale in Luxembourg covers a sequence of about 33 m thickness, including the *bifrons* and *falciferum* ammonite biozones (Fig. 2). The upper 11 m of the sequence belong to the biozone of *hildoceras bifrons*; they are composed of black laminated mudstones with some calcareous interbeds that are vertically cracked and locally include small pyrite nodules. The biozone of *harpoceras falciferum* ranges from 11 m to 33 m. The upper section between 11 m and 16 m is composed of locally laminated argillite with small nodules of pyrite (>0.1 vol.%) which showed signs of alteration (bleached, disintegration in the laboratory during drying). The *bifrons* and upper *falciferum* zones can be compared to the bituminous mudstone facies of the Posidonia Shale of southern Germany (Röhl et al., 2001). The *falciferum* section between 16 m and 33 m is composed of laminated dark gray marlstones with local inclusions of pyritic nodules concentrated in fossil beds (belemnites) and isolated pyrite grains and pyritized fossils. Abundant Bositra buchi were observed. This section is an analog to the laminated oil shale facies of the Posidonia Shale of southern Germany (Röhl et al., 2001). At a depth of 30.7 m a ca. 1 cm thick layer of amorphous solid bitumen is observed (sample 10-1093). Sometimes granular gypsum is found, indicating transformation of pyrite and weathering. Littke et al. (1991b) could show that weathering affects pyrite to even a greater extent than organic matter; i.e. that fresh pyrites prove the presence of unweathered organic matter. At the bottom of the section (33.2 m) the border between the *falciferum* and *tenuicostatum* biozones is represented by a gray fossil sandy loam (Fig. 2).