Palaeogeography, Palaeoclimatology, Palaeoecology 461 (2016) 432–448

Contents lists available at ScienceDirect

Palaeogeography, Palaeoclimatology, Palaeoecology

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

Nearshore euxinia in the photic zone of an ancient sea: Part II – The bigger picture and implications for understanding ocean anoxia

Mirosław Słowakiewicz [a,b,c,*], Maurice E. Tucker [c,d], Katja Hindenberg [e], Mike Mawson [f], Erdem F. Idiz [g], Richard D. Pancost [a,c]

[a] Organic Geochemistry Unit, School of Chemistry, University of Bristol, Cantock's Close BS8 1TS, UK
[b] Polish Geological Institute, Rakowiecka 4, 00-975 Warszawa, Poland
[c] Cabot Institute, University of Bristol, Cantock's Close, Bristol BS8 1UJ, UK
[d] Department of Earth Sciences, University of Bristol, Bristol BS8 1RJ, UK
[e] Institute of Bio- and Geosciences (IBG-3), Forschungszentrum Jülich GmbH, D-52425 Jülich, Germany
[f] Department of Earth Sciences, Durham University, Durham DH1 3LE, UK
[g] Department of Earth Sciences, University of Oxford, South Parks Road, Oxford OX1 3AN, UK

A R T I C L E I N F O

Article history:
Received 5 June 2016
Received in revised form 31 August 2016
Accepted 5 September 2016
Available online 7 September 2016

Keywords:
Nearshore euxinia
Anoxia
Lipid biomarkers
Organic matter
Carbonate rocks
Zechstein
Late Permian

A B S T R A C T

Biomarker, palaeontological and isotopic evidence suggests that the Late Permian carbonate seas, i.e. the Northern (NPB) and Southern (SPB) Permian basins of northern Pangea, were characterized by significant spatial and temporal variations in the palaeowater-column redox state. This is particularly the case with regard to the deposition of the Lopingian Zechstein cycle 2 carbonate rocks. A shelf to basin reconstruction of environmental conditions was achieved by analysing nearly 400 core samples from 49 wells. This allowed an evaluation of the spatial variations in facies and broad oceanographic conditions at the basin scale. Specifically, in the lower slope and shallow-basin facies of the northern margin of the SPB (present-day northern Poland and eastern Germany), highly variable concentrations of the green sulphur bacterial biomarkers chlorobactane and isorenieratane (and their likely degradation products, C_{15} to C_{31} 2,3,6-aryl isoprenoids, indicative of photic zone euxinia) and homohopane indices (indicative of anoxia), combined with the presence of a benthic fauna and bioturbation, indicate a variable but occasionally anoxic/euxinic water column. Locally in lagoonal facies in the northern and southern margin of the SPB, euxinic conditions also developed but these were likely associated with localised conditions or benthic production in association with microbialites. The presence of gammacerane in the eastern SPB (south-eastern Germany and eastern Poland) suggests elevated salinities there, compatible with the restricted configuration of the basin. However, a lack of these signatures in basinal settings of the eastern SPB indicates that strongly reducing conditions were restricted to the lower slope and shallow-basin locations and restricted lagoons, and were not developed in the basin centre. Moreover, this anoxia/euxinia in marginal settings is restricted to the north-eastern part of the SPB. The south-eastern part of the SPB (SE Poland), in contrast, is devoid of evidence for PZE. The southern margin of the SPB is also characterized by generally oxic-suboxic conditions, with local anoxia limited to more restricted embayments, and elevated salinities limited to restricted oxic-anoxic lagoons. In the western SPB (NE England and adjacent offshore) and the NPB (Outer Moray Firth, offshore Scotland) the water columns were oxic-suboxic. Overall, it appears that high but episodic primary bioproductivity of organic matter was concentrated on (or even limited to) the lower slopes of the SPB's north-eastern margin and the restricted lagoons and shallow basin of its southern margin, leading to the formation of source rocks for petroleum in these areas. In addition, the temporal and geographical restriction of anoxia appears to have prevented the accumulation of large and more widespread quantities of organic matter; in fact TOC contents exhibit a poor correlation with ecological and anoxia indicators. Crucially, this work confirms that the strong evidence for PZE observed in shelf and lower slope/shallow-basin facies of the north-eastern SPB need not be associated with widespread, basin-scale anoxia; this conclusion has implications for organic matter burial, carbon cycling and biotic crises during other times in Earth history.

1. Introduction

The geographical distribution of O_2 in the marine water column is governed by a wide range of controls, including climate, nutrient supply, molecular diffusion, photosynthesis, respiration, global ocean

* Corresponding author at: Organic Geochemistry Unit, School of Chemistry, University of Bristol, Cantock's Close BS8 1TS, UK.
E-mail address: m.slowakiewicz@gmail.com (M. Słowakiewicz).

http://dx.doi.org/10.1016/j.palaeo.2016.09.003

circulation, localised upwelling and downwelling processes, and the configuration of the basin (e.g., Canfield et al., 2005). These govern O_2 content and organic matter (OM) burial via their impact on bioproductivity, the biological pump, sediment deposition, and deep water ventilation (Ducklow and Steinberg, 2001; Hain et al., 2014).

Processes other than anoxia and productivity which have been invoked to modulate the preservation potential of OM include sedimentation rate (Müller and Suess, 1979; Henrichs, 1992), grain size (Bergamaschi et al., 1997), mineral adsorption (Mayer, 1994), and anaerobic respiration. The last might be as effective in OM recycling as oxic metabolic pathways (Canfield, 1994).

The relative influence of factors controlling O_2 distribution and OM burial has been widely debated (e.g., Sarmiento et al., 1988; Pedersen and Calvert, 1990; Canfield, 1994; Hedges and Keil, 1995; Mayer, 1995; Tyson, 1995; Kenig et al., 2004; Kuypers et al., 2004a; Jenkyns, 2010), but today water column anoxia is largely restricted to oxygen minimum zones which form beneath areas of high productivity. Anoxia also occurs in chemically-stratified epeiric basins, such as the modern Black Sea where euxinic conditions extend into the photic zone (Overmann et al., 1992; Repeta, 1993; Sinninghe Damsté et al., 1993). The Black Sea model has been directly invoked as an analogue for ancient euxinic basins (Arthur and Sageman, 1994), and it is implicitly invoked when observations of anoxia in marginal settings are extrapolated to infer basin-scale anoxia (Joachimski et al., 2001; Grice et al., 2005). Although geochemical records of some Mesozoic oceanic anoxic events (OAEs) suggest that ocean anoxia does extend into deep basins (Sinninghe Damsté and Köster, 1998; Wagner et al., 2004; Pancost et al., 2002; van Breugel et al., 2006), recent work suggests that this was not necessarily associated with basin-scale stratification (Kuypers et al., 2002, 2004a, 2004b; Monteiro et al., 2012). Moreover, the evidence for anoxia in many ancient basins is interpreted as restricted to nearshore settings (e.g. Jenkyns, 1985, 1988; Wignall and Newton, 2001). Crucially, some of these authors have invoked a counter-model to the Black Sea – the bath-tub ring model of deposition in which anoxia in stratified basins is largely restricted to nearshore settings (Frakes and Bolton, 1984; Wignall and Newton, 2001). Both models are useful for extrapolating spatially limited geological data, especially in Palaeozoic settings, to infer larger-scale basinal characteristics. However, those respective interpretations have vastly different implications for understanding past environmental changes, biotic crises and source rock formation.

Here, we explore these models using organic geochemical analyses of over 400 rocks from 49 boreholes, collected from the Southern and Northern Permian basins of northern Europe. The Late Permian is characterized by a greenhouse climate with a vast intra-continental desert, an absence of polar ice-caps and average temperatures being >15 °C higher than today (Khiel and Shields, 2005; Roscher et al., 2011). Such climatic conditions, as well as the restricted character of tectonic depressions largely fed by seawater and their subtropical location, favoured the formation of carbonate and evaporite sediments in many epeiric seas in the northern hemisphere, including the Northern Permian (NPB) and Southern Permian (SPB) basins in NW Europe. However, although extensively studied, the controversy and speculation towards the overall biogeochemistry and organic matter (OM) productivity of the basins in Lopingian (Zechstein) time still remain. It has long been thought that the Zechstein water-column was salinity stratified with anoxic bottom waters (Brongersma-Sanders, 1971; Turner and Magaritz, 1986; Grotzinger and Knoll, 1995; Taylor, 1998). Although it is well established that the initial transgressive lowermost Zechstein mudrock (Kupferschiefer, i.e., base of the first Zechstein cycle, Z1, Fig. 2) was deposited under such conditions with euxinia extending into the photic-zone (Oszczepalski, 1989; Schwark and Püttmann, 1990; Gibbison et al., 1995; Grice et al., 1996a, 1996b, 1997; Pancost et al., 2002; Paul, 2006), the subsequent deposition of carbonate and evaporite sediments of the Z1 took place under varied oxic/suboxic to anoxic bottom-water conditions (Kluska et al., 2013; Peryt et al., 2015; Słowakiewicz et al., 2015). This clearly shows that the epicontinental Zechstein Sea experienced euxinia periodically in the Z1 cycle, but it remains unclear as to how extensive this was spatially and what governed the apparently pronounced temporal variations in this and the Z2 and Z3 cycles.

Our previous shelf-to-basin reconstruction of environmental conditions in the Polish sector of the SPB in Europe has shown that euxinic conditions were present during the deposition of lower slope carbonate strata on the SPB northeast margin during deposition of the Zechstein second carbonate cycle (Ca2) (Słowakiewicz et al., 2015). However, initial data from the basinal facies suggested that the euxinic conditions did not develop there, but only in the nearshore environments, thus not on a basin-wide scale. This initial study, therefore, indicated that a restricted epeiric basin, i.e. a Black Sea analogue, is not appropriate to understand the SPB.

To explore this further and to test whether the rest of the basin and other marginal settings were also oxygenated – despite the strong evidence for photic zone euxinia (PZE) in the north-eastern SPB (NW Poland) – we examined the Ca2 cycle further. Our new data include sediments deposited in the NPB and the western, southern and south-eastern parts of the SPB, allowing a detailed examination of spatial (both basin- and facies-scale) variations in organic matter source and depositional conditions. We have quantified derivatives of isorenieratene and chlorobactene, which are produced by the brown and green strains of photosynthetic anaerobic green sulphur bacteria (*Chlorobiaceae*), respectively, allowing us to assess the geographical occurrence of photic zone euxinia and assess models for basin oceanography and redox conditions. These data and interpretations are complemented by other biomarker signatures indicative of past redox and other environmental conditions (homohopane ratios, bisnorhopane and gammacerane abundances) and changes in OM source (hopane and sterane distributions). These, as well as palaeontological and carbon and oxygen isotopic data, are used to infer the connectivity of the NPB and SPB to the global ocean and to refine further basin-scale interpretations of productivity and anoxia.

2. Geological setting

Both the NPB and SPB were formed in the Late Carboniferous-Early Permian (Gast, 1988) and were located in the arid subtropical belt of Northern Pangea (Henderson and Mei, 2000; Legler and Schneider, 2008), at 15-20°N palaeolatitude, northwest of the Palaeo-Tethys Ocean, and south of the Boreal Sea (Fig. 1a). During the early Zechstein marine transgression (mid-latest Wuchiapingian, Szurlies, 2013), the subsiding basin was flooded with seawater from the Panthalassa Ocean entering through the Boreal Sea and a narrow strait between Greenland and Scandinavia, to form the vast epicontinental Zechstein Sea. The shallow sea (<350 m deep) is segmented into the NPB and SPB, partially separated by a series of Carboniferous palaeohighs, the Mid North Sea High and Ringkøbing-Fyn High (Fig. 1b). Both basins are of economic importance, containing a number of significant petroleum accumulations, mostly located in the SPB in what is today Germany, the Netherlands and Poland. The SPB comprises a series of connected sub-basins extending from eastern England across the North Sea into Poland and southern Lithuania, a distance of some 1700 km. Its width ranges from 300 to 600 km (Van Wees et al., 2000). The SPB had several narrow connections with adjacent basins (Sørensen and Martinsen, 1987) and possibly temporary connections with the Tethys domain to the southeast via the Polish-Dobrogea trough along a rift zone (Peryt and Peryt, 1977; Ziegler et al., 1997; Şengor and Atayman, 2009) and with small basins in the Inner Variscan domain (Kiersnowski et al., 1995) (Fig. 1). The sediments of the NPB were deposited in a smaller basin, located to the north of the Ringkøbing-Fyn High, which was connected to the SPB via the Bamble and Glückstadt troughs and the Central and Horn grabens, among others (Stemmerik et al., 2000; Glennie et al., 2003).

The SPB was subject to periodic intense evaporation. Up to seven (Z1–Z7) evaporitic cycles have been recognized in different parts of