Sedimentary Geology 364 (2018) 71–88

Contents lists available at ScienceDirect

Sedimentary Geology

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

Origin of red pelagic carbonates as an interplay of global climate and local basin factors: Insight from the Lower Devonian of the Prague Basin, Czech Republic

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A R T I C L E I N F O

Article history:
Received 5 September 2017
Received in revised form 7 December 2017
Accepted 8 December 2017
Available online 13 December 2017

Editor: Dr. B. Jones

Keywords:
Red pelagic carbonates
Pragian stage
Spectral reflectance
Geochemistry
Palaeoceanography
Bottom redox conditions
Trophic levels

A B S T R A C T

Red pelagic sediments are relatively common in the Phanerozoic. They are often interpreted as products of sea-bottom oxidation during greenhouse climate showing a conspicuous alternation with black shales and thus carrying important palaeoceanographic information. The Lower Devonian (Pragian) carbonate strata of the Prague Basin, Czech Republic (Praha Formation) contain a marked band of red pelagic carbonate, up to ~15 m thick, which can be correlated for several tens of km. We investigated seven sections (17 to 255 m thick) of the Prague Basin using the methods of facies analysis, outcrop gamma-ray logging, diffuse reflectance spectroscopy, optical microscopy, element geochemistry, magneto-mineralogy and electron microprobe analysis. The aim was to find the mineral carriers of the red colour, investigate the stratigraphic context of the red carbonates and evaluate the local and global prerequisites for their formation. The red pigmentation represents enrichment by hematite with respect to goethite. Approximately 31% of the total reflectance falling in the red colour band represents a threshold for red coloration. The red pigmentation is carried by submicronic hematite dispersed in argillaceous pelagic calcilutite and/or inside skeletal allochems. Gamma-ray log correlation indicates that the red carbonate band developed in stratigraphic levels with low sedimentation rates, typically from 1 to 7.1 mm/kyr, which are comparable to the Mesozoic Rosso Ammonitico facies. The red beds and the whole Praha Formation (Pragian to early Emsian) are characterized by low TOC values (<0.05%) and low U/Th, Mo/Al, *V*/Al, Zn/Al, Cu/Al and P/Al ratios indicating oligotrophic, highly oxic sea-bottom conditions. This period was characterized by global cooling, a drop in silicate weathering rates and in atmospheric pCO_2 levels. The lower Devonian successions of the Prague Basin indicate that switching between two greenhouse climatic modes, colder oligotropic and warmer mesotrophic, may have been responsible for the alternation of red and grey carbonate strata, respectively.

1. Introduction

Red coloured carbonates, cherts and mudstones (oceanic red beds, ORB) are important constituents of the pelagic depositional systems in both the present-day oceans and in the fossil record (Jenkyns and Hsü, 1975; Scholle et al., 1983; Wang et al., 2005; Hu et al., 2005, 2012). The main mineral carrier of red colour is hematite; consequently, the origin of the ORB is attributed to various ways of hematite enrichment. The threshold amount of hematite is unclear. A minimum of 1.5% of hematite has been claimed as the threshold for red coloration of siliciclastic mudstones (Franke and Paul, 1980), while in red pelagic carbonates, the hematite concentrations responsible for the red coloration can range between 0.13 and 0.82% (Li et al., 2011) and concentration of total iron can be as low as 350 ppm (Mamet and Préat, 2006). Apart from the infrequent examples of eolian input of detrital hematite from continents and red colouration due to post-depositional telogenetic alteration (Giosan et al., 2002; Mamet and Préat, 2006; Cai et al., 2009 and references therein), the main causes of red colouration are related to iron redox states during the deposition or early diagenesis. Mamet and Préat (2003, 2006) and Préat et al. (1999, 2005) explained the formation of hematite by the activity of Fe^{2+} oxidizing bacteria in environments with limited oxygen supply. On the contrary, many authors

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https://doi.org/10.1016/j.sedgeo.2017.12.007
0037-0738/

suggest that hematite is formed by early diagenetic iron oxidation in oxidizing conditions on the sea floor or at shallow burial depths (Franke and Paul, 1980; Channell et al., 1982; Eren and Kadir, 1999; Wang et al., 2005). The essential factors for sea-bottom hematite formation are well oxygenated bottom conditions and low sedimentation rates, typically from a few mm/kyr to ~26 mm/kyr (Wagreich and Krenmayr, 2005; Wang et al., 2005; Jansa and Hu, 2009). The ORB are therefore considered important indicators of sea-bottom oxygenation and rates of sediment input. In addition, geochemical investigations suggest that the ORB are associated with decreasing values of organic productivity proxies and organic matter and probably require oligotrophic conditions (Franke and Paul, 1980; Neuhuber et al., 2007). The ORB occur in different times during the Phanerozoic. However, they are particularly abundant in the late Devonian (Tucker, 1975; Wendt and Aigner, 1985; Préat et al., 1999; Devleeschouwer et al., 2015), early Jurassic (Varol and Gokten, 1994; Gawlick et al., 2006; Myczyński and Jach, 2009), late Jurassic/earliest Cretaceous (Jenkyns, 1975; Martire, 1992; Clari and Martire, 1996; Cecca et al., 2001; Mamet and Préat, 2003; Martire et al., 2006; Šmuc and Rožič, 2010; Főzy et al., 2011) and in the Cretaceous (Wagreich and Krenmayr, 2005; Wang et al., 2005; Neuhuber et al., 2007; Jansa and Hu, 2009). The Cretaceous oceanic red beds (CORB), in particular, show close spatial and temporal pairing with the deposition of black shales of the ocean anoxic events (OAE). The deposition of the CORB in the aftermath of the OAE1a was explained by carbon burial, decrease of atmospheric $p\mathrm{CO_2}$, global climatic cooling and the formation of cold deep water with a high oxidizing capacity (Wang et al., 2011; Hu et al., 2012). There is indirect evidence for global cooling after the OAE1 (Hu et al., 2012 and references therein). The typically greenhouse-world periods, Cretaceous, Jurassic and Devonian, are prone to developing the ORB associated with black shale successions (in particular, the Kellwasser, annulata and Hangenberg black shale events in the Upper Devonian, Walliser, 1986; Mc Ghee Jr, 1996; Isaacson et al., 1999; Kaiser et al., 2006). On short-term (biozone) scale, however, the ORB tend to be rather diachronous (Hu et al., 2012, p. 223). Consequently, the ORB might represent an example of time-specific facies, which are particularly related to climatically driven sea bottom redox conditions (cf., Brett et al., 2012).

The carbonate successions of the Prague basin, Czech Republic, the classical region of Lower Devonian stratigraphy, contain a marked band of red pelagic carbonate, up to ~15 m thick, of Early Devonian (earliest Emsian) age. The red band (situated in the upper levels of the Praha Formation) can be correlated for several tens of kilometres, providing an important local stratigraphic key level. A prominent set of black shale laminae and dark carbonates referred to the 'Bohemian graptolite event' or the 'basal Emsian anoxic event' is located slightly above the red carbonates (Hladil et al., 1996; Chlupáč et al., 1998). This coincidence of the ORB and black shales, which shows some similarities with the Cretaceous OAE – ORB transitions may indicate a common forcing during the early Devonian greenhouse climatic mode (cf., Copper and Scotese, 2003; Saltzman, 2005; Lubeseder, 2008; Joachimski et al., 2009). The Early Devonian was indeed a period of palaeoclimatic fluctuations (Simon et al., 2007; Joachimski et al., 2009), which were possibly associated with high speciation and extinction rates of vascular plants, rapid colonization of terrestrial environments and thick phytodebris accumulations (Xiong et al., 2013; Kennedy et al., 2014; Morris and Edwards, 2014). In marine shelf environments, increasing levels of marine species richness and growing oxygen levels are noted worldwide within the Lochkovian and Pragian stages (Frey et al., 2014). Lubeseder (2008) argued that the abrupt transition from Lochkovian low oxygen shelf sediments into Pragian well oxygenated facies in Morocco can be related to changes in circulation and the end of upwelling due to the rise in water temperature and ocean-water stagnation. These changes can be related to an enhanced greenhouse effect starting from the Pragian times (Saltzman, 2005).

The aim of this paper is to gain insight into the genesis of the Devonian ORB and their palaeoclimatic meaning, based on a multidisciplinary study of the red horizon and its stratigraphic framework. Our primary aim is to discuss whether the red pelagic facies of the early Devonian greenhouse world and their palaeoclimatic and palaeoceanographic context share any common features with their Jurassic-Cretaceous greenhouse/supergreenhouse counterparts. Moreover, it is not clear why red pelagic facies tend to occur in well constrained, usually narrow time windows of the Devonian period, i.e., whether they indeed represent time-specific facies (cf. Brett et al., 2012) that would be related to global climate-driven factors such as sea-bottom oxygenation and oligotrophy (cf. Franke and Paul, 1980; Hu et al., 2012). The Prague Basin offers a fine example of well-exposed and almost complete Lower Devonian marine sedimentary succession with horizons of red pelagic facies. Although the red pelagic carbonate was previously identified by Koptíková et al. (2010a) at the Požáry section, little is known about its position in the stratigraphic architecture of the Prague Basin, its mineralogy, geochemistry, sedimentation rates and the global palaeoclimatic context of its formation. In this effort, we use detailed facies logging of seven sections (~17 to ~250 m thick) of the Prague basin, supported by outcrop spectral gamma-ray logging, visible-light spectral reflectance, quantitative carbonate constituent analysis, element geochemistry, total organic-carbon concentrations, magneto-mineralogy and electron-microprobe analyses. Particular aims are to find the mineral carriers of the red colour and investigate the conditions of their genesis, to examine the prerequisites for the red pigmentation, to locate the red horizon in the sea-level cycle and to interpret the local palaeogeographic/bathymetric context of its formation.

2. Geological settings and stratigraphy

We studied seven sections of the Prague Basin (Fig. 1) located in the southwestern outskirts of Praha (Prague), Czech Republic: 1) Čertovy schody near Koněprusy, eastern quarry (49°54′38.180"N; 14°4′7.272″E; all co-ordinates referenced to WGS-84 ellipsoid); 2) Na Chlumu quarry (49°56′45.946"N; 14°8′2.842″E); 3) Branžovy quarry (49°59′0.197"N; 14°10′43.668″E); 4) Požáry quarry (50°1′39.974"N; 14°19′37.916″E); 5) Na Hvížďalce quarry (49°59′38.481"N; 14°19′36.546″E); and 6) Na Homolce quarry (Lochkovian/Pragian boundary GSSP) (50°0′52.846"N; 14°22′21.348″E) and 7) Pod Barrandovem section (50°2′17.703"N; 14°24′14.767″E).

The study area consists of Neoproterozoic to Middle Devonian volcano-sedimentary successions of the Teplá-Barrandian area (Bohemicum, Bohemian Massif, Cháb et al., 2008). The rocks were deformed and partly metamorphosed at the end of the Cadomian orogeny (~551 to ~540 Ma) and consequently deformed in the fold-and-thrust tectonic style and buried in several steps during the Variscan orogeny (Glasmacher et al., 2002; Suchý et al., 2002; Melichar, 2004; Cháb et al., 2008). The Prague Basin (Prague synform sensu Melichar, 2004) is an erosional relict of unmetamorphosed Lower Ordovician to Middle Devonian volcano-sedimentary successions, which rest on the Neoproterozoic and Cambrian successions of the Teplá-Barrandian area with angular unconformity (Chlupáč et al., 1998). The Prague Basin developed on the Armorican Terrane Assemblage of the Rheic Ocean domain (Chlupáč et al., 1998; Plusquellec and Hladil, 2001).

The lower Devonian of the Prague Basin is formally subdivided into the Lochkov, Praha, Zlíchov and Daleje-Třebotov formations (Fig. 2) (Chlupáč, 1953; Chlupáč et al., 1998). Two distinct facies successions are recognized, one in the Praha-Beroun area encompassing the sections Na Chlumu, Branžovy, Požáry, Na Hvížďalce, Velká Chuchle and Pod Barrandovem, and the other in the Koněprusy area (Čertovy schody section), which are tectonically juxtaposed (Melichar, 2004). The Lochkov Formation (lower Lochkovian to lowermost Pragian) is composed of thin bedded and/or nodular limestones locally with chert nodules, which alternate with marl laminae and thick-bedded, coarse-grained crinoidal calcarenites and calcirudites (Chlupáč et al., 1998; Carls et al., 2007; Slavík et al., 2007, 2012). The formation is subdivided