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The Central Paratethys during Oligocene as an ancient counterpart of the present-day Black Sea: Unique records from the coccolith limestones

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A B S T R A C T

Four isochronous Oligocene coccolith limestone horizons from the Carpathians were examined in order to reconstruct paleoceanographic conditions in the Central Paratethys. The dominance of small and size-uniform pyrite framboids, the occurrence of low-diversity dinoflagellate cysts and coccolithophorids and the presence of biomarker molecule 28,30-dinorhopane indicate that the water column was stratified with the upper water column being relatively well-oxygenated, but the bottom water being anoxic. The latter is confirmed by the fine and consistent horizontal laminations in various parts of the basin, scarcity of benthic organisms and their trace fossils. The limestones exhibit typical marine $\delta^{13}C$ values, but are significantly depleted in ^{18}O and enriched in ^{87}Sr relative to contemporaneous ocean water. These isotopic compositions result from a decreased salinity of the surface waters caused by an increased riverine input. This is confirmed by the lack or impoverishment of planktonic foraminifers, presence to abundance of goniodomid dinoflagellate cysts and massive occurrence of low-diversity nannoplankton assemblages, which indicates decreased salinities as low as 17‰ and high productivity in the upper water column. These observations indicate that the limestones were formed during periods when connection of the Central Paratethys with the global ocean was limited, which impeded water exchange causing the development of low-salinity conditions of surface water and bottom-water anoxia. During the deposition of the oldest Tylawa horizon, primary productivity was enhanced and chemocline was positioned exceptionally high in the water column. Moreover, decreased $\delta^{13}C$ values in both carbonates and organic matter of this horizon suggest that widespread methane venting took place in the basin during NP23. All these data show that during the Oligocene the Central Paratethys experienced similar conditions to those of the current Black Sea, which can be used as a modern analogue, especially for the Tylawa horizon. Therefore, the Tylawa horizon can be perceived as a potential effect of future post-depositional processes of coccolith marls analogous to those having been deposited in the Black Sea for 2.7 kyr.

1. Introduction

Large marginal basins having limited connections with the ocean provide unique settings for reconstructing past paleoceanography and climate, as they are susceptible to even subtle variations of global (e.g. eustatic) and regional (e.g. tectonic) phenomena. The sedimentary infills of such basins provide a valuable archive of these variations manifested in depositional, biotic and geochemical proxies that quickly and distinctly respond to changes of sea-level, water circulation, temperature, salinity, nutrient supply, redox conditions, riverine input etc. The Black Sea is currently the largest anoxic marginal basin on Earth. A weak connection with the Mediterranean and a large input of riverine water produce brackish conditions. The water column is stratified with respect to both O_2 concentration and salinity (Codispoti et al., 1991;

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Tuğrul et al., 1992) and anoxia reaches as high as the euphotic zone (< 100 m) in the distal parts (> 2000 m water depth) (Huang et al., 2000). This situation boosts primary productivity in the euphotic zone, which is mainly manifested by massive, seasonal coccolithophore blooms of *Emiliana huxleyi* (Eker-Develi and Kideys, 2003), and enhances the preservation of organic matter being transported to the seafloor (Calvert and Karlin, 1998; Stewart et al., 2007). As a consequence, micro-laminated coccolith- and organic C-rich sediments interspersed with dark fine-grained turbidites are deposited in the deep parts of the basin (Lyons, 1991; Arthur and Dean, 1998). Highly reducing conditions and high C_{org} content enable widespread methane production in the sediments (Reeburgh et al., 1991). Methane is liberated into the water column by fluid seepage (Peckmann et al., 2001; Thiel et al., 2001; Michaelis et al., 2002) where it is effectively being oxidized, mainly via anaerobic oxidation (Schouten et al., 2001; Wakeham et al., 2003).

Several authors have suggested that paleoceanographic conditions in Paratethys during the Oligocene, i.e. water-column stratification and low-salinity conditions in a restricted basin, were analogous to those in the present-day Black Sea (Báldi, 1984; Haczewski, 1989; Schulz et al., 2005; Sótak, 2010). The Paratethys was one of the seas that originated from the decay of the Tethys Ocean at the end of the Eocene (Báldi, 1984; Rögl, 1998). It was bordered to the south by rising collisional orogens and consisted of a series of marine basins whose extents, depths, mutual connections and connections with adjacent ocean basins were constantly changing. Fluctuations in sea-level, salinity, temperature and nutrient supply have been used to explain the alternating deposition of turbidites, organic C-rich mudstones, diatomites and coccolith limestones in the Paratethys (Rögl, 1998, 1999; Schulz et al., 2005; Sótak, 2010). A stratified water column, with stagnating bottom water and normal salinity with episodes of freshening near the sea surface, have been proposed to have occurred during deposition of organic C-rich mudstones (Vetö, 1987; Rögl, 1998, 1999; Melinte, 2005), which are important source rocks for oil and gas in the Alpine foreland, Carpathians and the Caspian Sea regions (Köster et al., 1998a; Schulz et al., 2005; Schmidt and Erdogan, 1996). Organic geochemical analyses of these rocks (Köster et al., 1998a, 1998b; Schulz et al., 2005) indicated that anoxicity reached even as high as the photic zone. The most comprehensive comparison between the Paratethys during Oligocene and present-day Black Sea was performed by Schulz et al. (2005). However, they studied the Dynów Marls, which are not the best possible Oligocene Paratethyan counterpart of the currently deposited laminated coccolith ooze in the Black Sea, as they lack the distinctive regular, fine lamination. Moreover, important paleoceanographic phenomena that take place in the Black Sea, i.e. methane seepage, anaerobic oxidation of methane, microbial sulfate reduction, were either not discussed or not verified for the Oligocene Paratethyan deposits in these studies. Thus, a reliable and systematic comparison between the Oligocene Paratethys and present-day Black Sea is needed, which is the scope of this work.

While the great majority of studies on the paleoenvironment of the Paratethys was based on investigations of the laterally variable and strongly diachronous Oligocene facies, isochronous marker horizons traceable across the different facies zones and tectonic units should be central for studies on the sedimentary history of the Paratethys, as they represent a snapshot of paleoceanographic conditions in different and distant parts of the basin. The most useful among them are thin intervals of pelagic, finely laminated coccolith limestones, traceable over the whole Outer Carpathians and adjacent basins (Koszarski and Żytko, 1961; Jucha, 1969; Haczewski, 1989; Krhovský et al., 1992; Melinte, 2005; Schulz et al., 2005; Kotlarczyk et al., 2006). They occur as distinct thin interbeds within predominant siliciclastic gravity-flow deposits and organic C-rich shales. They were formed by intensive pelagic carbonate sedimentation induced by phytoplankton blooms within a large part of the Paratethys analogous of the recent Black Sea sediments. Krhovský et al. (1992), based mainly on the analysis of nannoplankton assemblages, maintained that during the deposition of the coccolith limestones, the basin was brackish for most of the time with only short episodes of salinity rising to near-normal marine values. Kotlarczyk et al. (2006) and Bieńkowska-Wasiluk (2010), based on the analysis of fish fauna, concluded that anoxia was intermittently present in the water column. Still, controversies exist concerning the specific paleoceanographic conditions that persisted in the basin and favored formation of these limestones (e.g. Haczewski, 1989; Krhovský et al., 1992; Ciurej, 2009).

The main purpose of this work is to constrain the paleoenvironmental conditions in the Central Paratethys at the time of the deposition of the coccolith limestones by a systematic examination of all four Oligocene horizons on a basin-wide scale employing a multiproxy approach. We have chosen a wide range of methods, i.e. examination of foraminifera and dinoflagellate cyst assemblages, measurements of pyrite framboid diameters, lipid biomarker analysis, isotopic analyses of C, O and Sr in carbonates, C and N in organic matter and S in framboidal pyrite, that are considered as robust and for which data exist from the current Black Sea and its recent sediments. The Black Sea is a particularly valuable natural laboratory in which many of these proxies have been in fact tested and calibrated for evaluating paleoenvironmental conditions. The data obtained in this study are discussed with respect to paleoceanographic reconstructions and point-by-point compared to the relevant major characteristics of the Black Sea today and its sediments deposited over the last 2.7 kyr.

2. Geological settings

The Oligocene coccolith limestones from different areas of the Outer Carpathians (22 sections: 18 from Poland, 4 from Romania) and from the Transylvanian Basin (one section) were examined (Fig. 1). The Oligocene deposits of the Outer Carpathians lie in the upper part of an Upper Jurassic-Lower Miocene sedimentary sequence folded and thrust in a pile of nappes onto the outer foredeep of the Carpathian orocline. Dark, organic C-rich shales intercalated with siliciclastic gravity mass-flow deposits are the most distinctive Oligocene facies. Two main facies zones are defined by clastic sediments predominating in volume over the dark shales: the outer zone with the Kliwa Sandstone supplied from the external margin of the basin and the inner zone with the Krosno Beds (equivalent to Fusaru Sandstone, Pucioasa Beds and Vineţişu Beds in Romania). The facies with the Krosno Beds appeared first in the internal parts of the basin and prograded outwards as is shown by the changing position of the limestone horizons relative to the major facies (Fig. 2). Two southernmost sections (Buciumeni and Suslăneşti) represent transitional zone between the outer nappes (the Skole-Tarcău unit) and the foreland (Puglisi et al., 2006). The Fântânele section in the Transylvanian Basin, on the rear side of the orocline, represents a sedimentary realm separated from the Outer Carpathian part of the Paratethys, but with the equivalents of the Outer Carpathian coccolith horizons.

Four coccolith limestone horizons are traced over the nearly whole length of the Outer Carpathians: Tylawa (TL-1), Jasło (JL-2), Sokoliska (SL-3) and Zagórz (ZL-4) limestones. Each horizon is isochronous, which makes them valuable chronostratigraphic markers in the Oligocene strata. TL-1 lies in the middle of the nannoplankton NP 23 zone (Krhovský et al., 1992; Melinte, 2005). Biostratigraphical positions of JL-2 and ZL-4 fall within the NP24 zone (Krhovský, 1981; Bąk, 2005; Melinte, 2005; Švábenická et al., 2007). Bąk (1999) placed ZL-4 in the foraminiferal zone P21, which is in agreement with an earlier work by Olszewska (1984). SL-3 lies between JL-2 and ZL-4, closer to the former, and thus also represents the NP24 zone (see also Ciurej and Haczewski, 2016). Therefore, JL-2, SL-3 and ZL-4 were laid down during the Rupelian-Chattian transition within merely a few tens of thousands years (Haczewski, 1989).