



Research paper

Geochemical paleogradient in pore waters controlled by AOM recorded in an Oligocene laminated limestone from the Outer Carpathians

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ARTICLE INFO

Article history:

Received 20 April 2011

Received in revised form 2 November 2011

Accepted 4 November 2011

Available online 18 November 2011

Keywords:

Methane seepage

Authigenic carbonate

Stable C and O isotopes

Pelagic limestone

Oligocene

Outer Carpathians

ABSTRACT

A 20-cm thick laminated limestone of Oligocene age from the Outer Carpathians is composed mainly of coccoliths and authigenic calcite. $\delta^{13}\text{C}$ values unequivocally indicate that the authigenic calcite precipitated as a result of methane oxidation. The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values change gradually from the base to the top of the bed from -38.0‰ to -17.6‰ and from -1.1‰ to -5.7‰ , respectively. This trend reflects a geochemical gradient which developed in the zone of anaerobic oxidation of methane (AOM) due to the consumption of sulfate by methane. This gradient was related to an inverse relationship between the concentrations of both compounds in the pore waters of the AOM zone. Methane was the source of isotopically light carbon. It was accompanied by heavy oxygen-containing water liberated from decomposition of gas hydrates. The methane-bearing fluids migrated upwards to the base of the sulfate reduction (SR) zone, where methane was oxidized ($\text{CH}_4 + \text{SO}_4^{2-} \rightarrow \text{HCO}_3^- + \text{HS}^- + \text{H}_2\text{O}$) and the AOM zone developed. The bicarbonate produced in this reaction was significantly depleted in ^{13}C and ^{16}O . In the SR zone organic matter was oxidized by sulfate: $2\text{CH}_2\text{O} + \text{SO}_4^{2-} \rightarrow \text{H}_2\text{S} + 2\text{HCO}_3^-$. The bicarbonate released in that reaction was the source of isotopically heavier C and lighter O. The proportion of bicarbonate produced by oxidation of methane to bicarbonate produced by oxidation of organic matter decreased upwards. The resultant isotopic composition of bicarbonate dissolved in the pore waters changed upwards towards higher $\delta^{13}\text{C}$ and lower $\delta^{18}\text{O}$ values and has been recorded in the limestone's isotopic composition.

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1. Introduction

In marine basins, anaerobic oxidation of methane (AOM) occurs in the sediment column, where methane-charged fluids seep through the diagenetic zone of sulfate reduction (SR). There, methane is oxidized by sulfate ions: $\text{CH}_4 + \text{SO}_4^{2-} \rightarrow \text{HCO}_3^- + \text{HS}^- + \text{H}_2\text{O}$. This reaction is microbially mediated by chemosynthetic consortia of archaea and sulfate-reducing bacteria (Boetius et al., 2000; Orphan et al., 2001). The resultant liberation of bicarbonate ions to the pore waters often leads to the precipitation of authigenic carbonates (e.g. Ritger et al., 1987; Sakai et al., 1992; Von Rad et al., 1996; Bohrmann et al., 1998; Cavagna et al., 1999; Peckmann and Thiel, 2004; Conti and Fontana, 2005; Teichert et al., 2005; De Boever et al., 2006; Campbell et al., 2008; Lim et al., 2009). Such methane-derived seep carbonates occur preferentially along continental margins and are commonly associated with fine-grained sediments. They vary strongly in size, form, mineralogic composition and fabric and no single petrographic feature can be regarded as diagnostic. They are recognized in modern environments by a set of petrographic features, biomarker composition, and stable C isotope ratios (Campbell, 2006). Sometimes,

they also contain characteristic faunal assemblages. However, recognition of seep carbonates in the fossil record is hindered due to the diagenetic alteration of primary petrographic features and maturation of organic matter during burial. If chemosynthetic faunal assemblages are not present and the rocks experienced significant burial, the only unequivocal evidence of their origin may be unique stable C isotope ratios. Therefore, identification of ancient seep deposits requires a multi-disciplinary approach, but the stable isotopic composition is the most frequently employed method (Campbell, 2006).

Bicarbonate dissolved in pore waters from the SR zone yields fairly negative $\delta^{13}\text{C}$ values about -25‰ (Irwin et al., 1977; Curtis and Coleman, 1986). Bicarbonate liberated from oxidation of hydrocarbons is strongly depleted in ^{13}C and exhibits even lower $\delta^{13}\text{C}$ values, from about -40‰ down to -110‰ (Whiticar and Faber, 1986; Mozley and Burns, 1993; Campbell, 2006). Therefore, the $\delta^{13}\text{C}$ values of seep carbonates depend primarily on the original composition and the mass balance between bicarbonate from two sources, sulfate reduction and oxidation of methane. Addition of marine bicarbonate is also possible if they precipitate close to or on the seafloor.

Oligocene seep carbonates from the Polish Carpathians described by Bojanowski (2007a) comprise concretions, a carbonate build-up and a laminated limestone bed with abundant coccoliths. All these rocks exhibit very negative $\delta^{13}\text{C}$ values, as low as -39‰ . Samples

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from the limestone bed gave a surprisingly broad range, from -37 to -19% (Bojanowski, 2007a). This study has been undertaken to investigate the isotopic C and O compositions of the limestone bed in detail, with two main aims. The first was to understand the origin of the laminated limestone, which appeared debatable when petrographic features were combined with the isotopic data. Laminated pelagic limestones similar to the bed examined are found in the Oligocene series of the Outer Carpathians (e.g. Haczewski, 1989; Leszczyński et al., 1996). They are interpreted as the result of intensive pelagic sedimentation of carbonate ooze caused by seasonal coccolithophorid blooms. Indeed, the petrographic composition and sedimentary structures alone could suggest that pelagic sedimentation was the primary control of the formation of the limestone examined. However, the isotopic results show that a major portion of carbonate was authigenic and related to AOM. Therefore, the first goal was to assess the role of pelagic sedimentation and methane seepage in the formation of the limestone. The second was to explain the high variability of the isotopic composition and an inverse relationship between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values in the limestone bed. Moreover, an attempt has been made to precisely identify and quantify the sources of C and O in the carbonate material.

2. Geological setting

The Outer Carpathians are a Miocene thrust-and-fold orogenic belt, stretching from Romania through Ukraine and Poland to Slovakia. It is composed of a thick, mainly turbiditic succession. The Polish part is in the northernmost part of the Carpathian range. It is composed of several main nappes. Magura, the uppermost nappe, is thrust over the Obidowa-Słopnice, the Grybów, the Dukla and the Silesian nappes. The Obidowa-Słopnice and the Grybów nappes emerge only in tectonic windows (Fig. 1).

The rocks examined here are exposed in the Świątkowa Wielka tectonic window (Fig. 1) (e.g. Kozikowski, 1956; Karnkowski, 1963; Koszarski, 1985; Oszczytko-Clowes and Oszczytko, 2011). This small tectonic structure is located in the Beskid Mały Mountains, about 5 km west of Krempna village (Fig. 1). The rocks of the window

unit are strongly folded and sliced (Mastella and Rubinkiewicz, 1998; Oszczytko-Clowes and Oszczytko, 2011). The southernmost slice contains dark, calcareous shales of the Oligocene Krosno Formation, which are between 80 and 110 m thick. The succession was deposited on a bypass slope in relatively stable conditions: turbiditic sediments were laid down episodically, whereas the background hemipelagic sedimentation was continuous throughout (Bojanowski, 2007b). There were, however, periods when pelagic sedimentation prevailed and deposition of carbonate ooze was intensive. The Krosno Fm. was deposited in a basin a few hundred meters deep, in the upper bathyal zone (Książkiewicz, 1975, Olszewska, 1984, Poprawa et al., 2002).

The succession is full of various authigenic carbonates, dispersed throughout the profile. Those in the uppermost part of the profile were formed as a result of methane seepage (Bojanowski, 2007a). These seep-carbonates (GPS position: N between 4931'620 and 4931'690, E between 2124'150 and 2124'650) comprise early-diagenetic concretions, a laminated limestone bed and a carbonate build-up. The build-up is composed of intraformational carbonate breccia. Unique features related to the hydrocarbon seepage have been documented in the breccia, e.g. pseudomorphs of gas-hydrate particles, calcified microbial biofilms and fossils of giant sulfur bacteria (Bojanowski, 2007a). The carbonate build-up thins gradually into a bed of laminated limestone. The thickness of the bed decreases away from the carbonate build-up from one meter to about 20 cm. It is strongly brecciated on the flanks of the build-up. This work is mainly focused on the limestone bed sampled away from the build-up, where it is about 20 cm thick and not brecciated. The exact age of the laminated limestone and the overlying shales was determined on the basis of dinoflagellates. It is restricted to *Dinoflagellata* zones D14b and the uppermost part of D14a (Barski and Bojanowski, 2010) encompassing the time span between 31.2 and 30.2 Ma, which corresponds to the upper part of calcareous nannoplankton zone NP23 (Ogg et al., 2008). The Outer Carpathian basin was at that time isolated from Parathetys and experienced anoxicity, low-salinity and cool-water conditions (Melinte, 2005; Švábenciká et al., 2007).

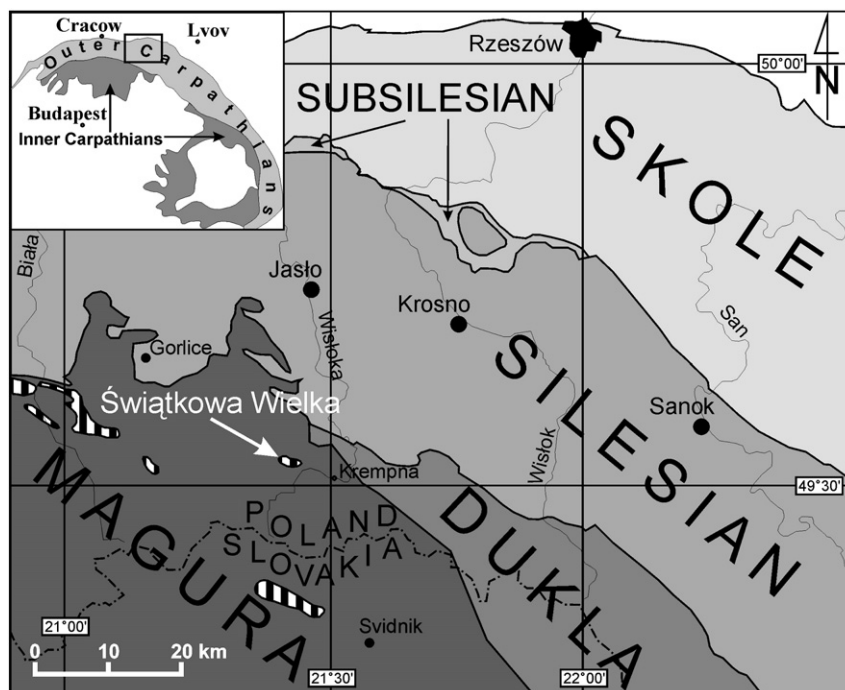


Fig. 1. General map of tectonic units of the eastern part of the Polish Outer Carpathians. The Grybów and Obidowa-Słopnice units (stripes) are covered by the Magura nappe and emerge only in tectonic windows. The rocks studied here occur in the Świątkowa Wielka tectonic window (arrow).

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