Palaeogeography, Palaeoclimatology, Palaeoecology 306 (2011) 1–14

Contents lists available at ScienceDirect

Palaeogeography, Palaeoclimatology, Palaeoecology

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

Molecular and petrographic indicators of redox conditions and bacterial communities after the F/F mass extinction (Kowala, Holy Cross Mountains, Poland)

Leszek Marynowski [a,*], Michał Rakociński [a], Ewelina Borcuch [a], Barbara Kremer [b], Brian A. Schubert [c], A. Hope Jahren [c]

[a] University of Silesia, Faculty of Earth Sciences, Będzińska Str. 60, 41-200 Sosnowiec, Poland
[b] Institute of Paleobiology, Polish Academy of Sciences, Twarda 51/55, 00-818 Warszawa, Poland
[c] Department of Geology and Geophysics, University of Hawaii, Honolulu, Hawaii, 96822, USA

ARTICLE INFO

Article history:
Received 27 November 2010
Received in revised form 22 February 2011
Accepted 18 March 2011
Available online 24 March 2011

Keywords:
Pyrite framboids
Cyanobacteria
Biomarkers
Redox conditions
Organic geochemistry
Mass extinction

ABSTRACT

Pyrite framboid diameter analysis and organic geochemistry of the *triangularis*/*crepida* boundary section at Kowala (Holy Cross Mountains, Poland) imply suboxic to oxic and sporadically euxinic bottom waters during the Lower Famennian. In addition, morphological web-like structures typical for microbial mats, as well as the recognition of 2α-methylhopanes and monomethyl-alkane cyanobacteria biomarkers is evidenced of microbial activity after the global Frasnian/Famennian (F/F) extinction event. The presence of cyanobacterial mats also suggests suboxic to oxic environments and at the same time photic bottom water conditions. However, isorenieratane and its derivatives were detected in almost all samples. The presence of this well-known biomarker of green sulfur bacteria implies that euxinic conditions were present in the upper part of the water column at least intermittently or that temporal euxinia occurred in the water column. Presence of euxinic conditions is confirmed by the occurrence of small-sized pyrite framboids which were particularly dominant in the lower part of the section. The shift towards low $\delta^{13}C$ values in both micritic limestones and in sedimentary organic matter seen at the beginning of the period of diminished photic zone, might reflect an influx of newly respired CO_2 to surface waters, caused by enhanced respiration at depth after the F/F transition in the Chęciny–Zbrza basin.

1. Introduction

Reduced animal diversity after mass extinction events gives rise to enhanced productivity of microbial communities (e.g. Sheehan and Harris, 2004; Xie et al., 2005) because mat-inhibiting animals have been removed from ecosystems and marine productivity is generally low. One example is the microbial expansion observed after the Permo/Triassic (P/Tr) mass extinction; this increase in microbial activity is inferred from post-extinction sedimentary rocks (Schubert and Bottjer, 1992; Kershaw et al., 1999; Lehrmann et al., 2003; Pruss and Bottjer, 2004; Baud et al., 2005, 2007; Kershaw et al., 2007; Mary and Woods, 2008; Woods and Baud, 2008). Detailed studies using cyanobacterial biomarkers across the P/Tr boundary revealed variations in the microbial community structure with cyanobacteria expansion after the P/Tr mass extinction event (Xie et al., 2005, 2007; Wang, 2007), recently associated with volcanic activity (Xie et al., 2010). Surprisingly, much less is known about microbial activity after other mass extinction events. Reports on the Late Ordovician extinction event revealed microbialite resurgence (Sheehan and Harris, 2004). Similar work showed expansion of opportunistic stromatolites, oncoids, and large-scale microbial thrombolites after the Frasnian–Famennian (F/F) mass extinction (Becker et al., 1991; Whalen et al., 2002; see also Racki et al., 2002). Finally, elevated concentrations of cyanobacteria biomarkers have been reported across the Triassic/Jurassic extinction boundary (Jiao et al., 2009).

Kowala, Poland is one of the best documented high-resolution sections that includes the F/F transition (see e.g. Racki et al., 2002) and has been investigated using paleontological (Racki and Baliński, 1998; Sartenaer et al., 1998; Dzik, 2002; Filipiak, 2002; Ginter, 2002; Vishnevskaya et al., 2002; Bond, 2006), petrographic (Bond et al., 2004), organic and inorganic geochemical (Joachimski et al., 2001; Girard and Lécuyer, 2002; Racki et al., 2002; Bond and Zatoń, 2003; Bond et al., 2004) and isotopic (Joachimski et al., 2001, 2002) techniques. Although the F/F stratigraphic boundary in Kowala is well studied, little has been written about microbial communities in the Early Famennian, particularly regarding any hypothetical increase in microbial activity after the F/F biotic crisis.

Here we report the presence of cyanobacteria biomarkers in the Early Famennian portion of the Kowala section, as confirmed by scanning electron microscope observations of fossil cyanobacterial colonies. In addition, we detail the biogeochemical characteristics of redox conditions using a combination of organic-biomarker and

* Corresponding author.
E-mail address: leszek.marynowski@us.edu.pl (L. Marynowski).

0031-0182/$ – see front matter
doi:10.1016/j.palaeo.2011.03.018

pyrite petrographic data. The data confirmed the common expansion of cyanobacterial communities after global mass extinctions also in the basinal environments with low light intensity and described detailed characteristic of the post-extinction water column structure.

2. Geological background and previous geochemical studies

The Kowala quarry is located in the southern limb of the Gałęzie-Kowala syncline, within the southern part of the Kielce region of the Holy Cross Mountains (HCM), approximately 10 km SW of Kielce, Poland (Fig. 1a and b) (see e.g., Racki et al., 2002). Many papers have characterized the Famennian section in the Kowala quarry, including Racki and Szulczewski (1996), Berkowski (2002), Racki et al. (2002), Bond and Zatoń (2003), Dzik (2006), Marynowski and Filipiak (2007), Marynowski et al. (2007, 2010) and Halamski and Baliński (2009). During the Late Devonian the Holy Cross Mountains were part of a ≤600 km wide carbonate shelf. This region comprised a portion of the pericratonic basin extending along the southern margin of Laurussia (e.g. Narkiewicz, 1988; Racki and Baliński, 1998; Joachimski et al., 2001; Racki et al., 2002). The Devonian paleogeography of the HCM is characterized by two major distinct tectonic regions: the Kielce paleohigh in the south and the Łysogóry paleolow to the north. These subsymmetric facies occur in the center of the Frasnian Dyminy reef and the Famennian remnant pelagic ridge (see Szulczewski, 1971, 1995; Racki and Baliński, 1998; Racki et al., 2002). These features were surrounded by two intrashelf basins: the Chęciny–Zbrza to the south and the Łysogóry–Kostomłoty to the north. The study area is located within in the Chęciny–Zbrza intra-shelf basin. Lower Famennian successions are represented by a monotonous series of thin- and rhythmically-bedded marly limestones and shales which are poor in fossils (Racki and Szulczewski, 1996). The depositional environment is interpreted as poorly oxygenated and open-marine, and deep-water below storm wave-base; there is also an expanded base of slope to basinal succession (see e.g. Racki et al., 2002; Bond and Zatoń, 2003; Bond et al., 2004; Filipiak, 2009).

The Famennian sequence has been divided into informal lithological sets H to L (in Racki and Szulczewski, 1996; see also Berkowski, 2002); however, here we describe only the lithology of the currently analyzed part of the section (Fig. 1c). Our investigated sections belong to the set H-4 (*sensu* Racki and Szulczewski, 1996) and were assigned to the Upper *Palmatolepis triangularis* zone and the lower part of the *Palmatolepis crepida* zone (see Section 4.1). This dating corresponds to palynostratigraphic data provided by Filipiak (2009), which particularly distinguished the Pw acritarch zone. The upper part of the section is notable for its rare *Guerichia* and inarticulate brachiopods including the lingulid *Barroisella* and *Orbiculoidea* (see also Berkowski, 2002; Racki et al., 2002; Bond and Zatoń, 2003), and rare undeterminable orthoconic nautiloids. In addition, Filipiak (2009) described rich and well-preserved phytoplankton assemblages containing mainly acritarchs and prasinophytes, as well as a low-diversity miospore microflora.

Until now geochemical studies of the Frasnian and Famennian portions of the Kowala section have concentrated on describing potentially global phenomena (Fig. 2), during either the F/F transition climate change (Joachimski et al., 2001, 2002; Girard and Lécuyer, 2002; Racki et al., 2002; Bond and Zatoń, 2003; Bond et al., 2004), or the Hangenberg event (Marynowski and Filipiak, 2007), or the Dasberg event (Marynowski et al., 2010). Other works focused upon specific subsections of the Kowala section, such as the Middle Famennian interval with its pyritized fauna (Marynowski et al., 2007) or the Early–Middle Frasnian transition (Marynowski et al., 2008). Here we present multi-proxy studies of the sequences belonging to the Upper *P. triangularis* zone and the lower part of the *P. crepida* zone as the first such studies of this critical portion of the post-F/F transition into the Early Famennian (Fig. 2).

3. Materials and methods

Fifteen samples were collected from the trench of the central part of the active Kowala Quarry (Fig. 1a and b). The investigated strata consisted of rhythmic successions of dark gray micritic limestones and dark gray or black marly shales; the thickness of the section investigated was approximately 4 m. Micritic limestones and marly shales were sampled and studied for geochemistry and petrography. Nine samples were studied for conodont biostratigraphy.

3.1. Micropaleontological preparation

Nine samples were used to obtain conodont elements. The samples of 800–1000 g weight were dissolved in 15% formic acid or in 20% acetic acid. The resultant sediment was rinsed using a sieve with 0.1 mm diameter meshes. Conodonts in marl samples were separated via sodium polytungstate solution with 2.78–2.84 g/ml specific weight. Isolated conodont samples were examined using binocular microscopy.

3.2. Cyanobacterial mat microscopic observations

All petrographic thin sections were polished to 0.25 μm using diamond paste, etched with 5% and 8% formic acid, rinsed in DI water, dried, and gold-coated to facilitate conductivity. Prior to scanning electron microscopy, all petrographic thin sections were scrutinized and mapped by conventional optical microscopy. The SEM investigations used either a Zeiss DSM 960A equipped with an EDS detector (Bruker-AXS) at Ludwig Maximillian University (Munich, Germany) and a JEOL JEM-3010 equipped with a Gatan slow scan CCD camera at Philipps University (Marburg, Germany).

3.3. Pyrite framboid diameter analysis

Thirteen samples were used for the pyrite framboid analysis. Samples in the form of small chips were polished, and framboid diameters were measured using the Philips Environmental Scanning Electron Microscope in a back-scattered electron mode at University of Silesia (Sosnowiec, Poland). Framboid diameters were measured using the ESEM internal measuring device (given in μm). In seven of the ten samples, at least 100 framboids were measured; in three samples this was not possible. For each sample, such statistical parameters (see Wignall and Newton, 1998) as minimum and maximum values, mean value and standard deviation have been calculated, and then shown in the form of box-and-whisker plots.

3.4. Isotope analysis

Stable isotope determinations were performed upon samples KcIII/1, 3, 4, 7, 9, 10, 11, 13, 16, 17 and 19 (Fig. 1c). Organic carbon was extracted from rock samples by digestion in 1 M HCl for 24 h at 25 °C. The remaining organic fraction was homogenized and combusted in triplicate using a Eurovector EA in conjunction with an Isoprime IRMS to obtain $\delta^{13}C$ values (Boutton, 1991). The $\delta^{13}C$ and $\delta^{18}O$ values of carbonate were obtained through classical methods, which involve reaction of sample carbonate with phosphoric acid and the purification of resultant CO_2 gas for measurement on dual inlet (McCrea, 1950). All measurements were performed using the IRMS facility of the University of Hawaii, and are reported using standard "delta-notation" relative to VSMOW and VPBD standards (Sharp, 2006).

3.5. Organic geochemistry

Abundances of total carbon and total inorganic carbon were determined using an Eltra CS-500 IR-analyzer with a total inorganic carbon module. Total organic carbon (TOC) was calculated as the difference between total carbon and total inorganic carbon. Calibration