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Isotopic chemostratigraphy across the Early–Middle Frasnian transition (Late Devonian) on the South Polish carbonate shelf: A reference for the global *punctata* Event

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ABSTRACT

The coupled high-resolution carbon isotope data from whole-rock limestone and organic matter samples of the *transitans* (Early Frasnian), *punctata* and the earliest *hassi* Zones (Middle Frasnian) from the South Polish carbonate shelf successions reveal the presence of a large, multi-part $\delta^{13}C$ excursion, one of the largest known carbon cycle disturbance of Devonian period. This Early–Middle Frasnian (E–MF) $\delta^{13}C$ perturbation consists of two positive excursions (a minor event I and a major event III) and two negative shifts (events II and IV). The major positive excursion, up to 5‰, begins near the E–MF boundary and the onset of Middlesex transgressive–anoxic event. The latter broader-scale positive $\delta^{13}C$ perturbation correlates with the worldwide *punctata* Event documented across eastern and western Laurussia as well as northern Gondwana. The large magnitude of the *punctata* Isotopic Event, paired with negligible biotic effects, is similar to the Silurian biogeochemical perturbations but contrasts markedly with the younger Kellwasser Events. The distinctive protracted (about 1 Ma) E–MF $\delta^{13}C$ variations may be only partly explained by escalated sea water exchange between epeiric seas and the anoxic open ocean during successive transgressive pulses. Very high $\delta^{13}C$ plateau values of the *punctata* Event correspond to a positive $^{87}Sr/^{86}Sr$ shift, as well as elevated clastic input proxies and magnetic susceptibility, suggesting altogether that delivery of tectonically-promoted land-derived nutrients to marine basins was a key factor stimulating the biogeochemical perturbation. Extreme increases in primary productivity and enhanced organic matter burial in restricted deeper basinal settings would promote a gradual drawdown in surface-water as well as atmospheric pCO_2, and consequently a climatic cooling by 5 °C, as indicated by the high-resolution $\delta^{18}O_{phosphate}$ record.

1. Introduction

The Devonian was a period of significant changes in marine and terrestrial ecosystems. This Middle Paleozoic interval is characterized by increasing tectonic activity, continental deformation and uplift related to the incipient collision of the major continental crustal blocks of Laurussia, Gondwana, Kazakhstan and Siberia (Averbuch et al., 2005). Throughout the Devonian, changes in weathering processes and soil development had taken place due to the evolution of vascular land plants (Algeo et al., 1995; Walliser, 1996; Algeo and Scheckler, 1998). A warm climate predominated, although the Paleozoic greenhouse climate declined during the Givetian to Famennian time interval (Scotese and McKerrow, 1990; Joachimski et al., 2009). Based on these premises the Devonian was considered as a time period of elevated atmospheric CO_2 levels (Berner, 1990, 2006) and intensive organic carbon burial (Berner and Raiswell, 1983; Berner, 2006). Further, a stepwise marine faunal crisis is well documented throughout Late Devonian time and culminated in the Frasnian-Famennian (F–F) biodiversity crisis (see review in McGhee, 1996; Walliser, 1996; Hallam and Wignall, 1997; House, 2002; Becker et al., 2012). A causal relationship thus existed between these fundamental ecosystem transformations, ecological turnovers and distinct geochemical anomalies in the marine sedimentary record, especially the short-term global carbon cycle perturbations (Buggisch and Joachimski, 2006).

Most of the previous research has been concerned with the F–F mass extinction, recognized as one of the most severe ecological catastrophes of the Phanerozoic (e.g. McGhee, 1996; Sandberg et al., 2002), although more recently viewed as a massive biodiversity depletion (Bambach, 2006; Stigall, 2012). However, significant geochemical anomalies are not always associated with documented global events (Racki, 2005) and can still be found during 'background' intervals and during most minor biotic turnovers (e.g. Holser et al., 1996; Veizer et al., 1999), as for example at the Silurian–Devonian boundary and its large-scale $\delta^{13}C$ anomaly (Małkowski and Racki, 2009).

A carbon isotope stratigraphy for the Devonian was initially based primarily on analyses of well-preserved brachiopod calcite (e.g. Popp

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et al., 1986; Brand, 1989; Veizer et al., 1999). Palaeozoic brachiopods preferentially occurred in shallow-water environments and mostly reveal only long-term $\delta^{13}C$ trends with a time resolution less than that provided by conodont biochronology (but see an exception in Yans et al., 2007). The analysis of whole-rock samples from continuous carbonate successions, however, proves to be a powerful method of compiling high-resolution $\delta^{13}C$ records (Buggisch and Mann, 2004; Buggisch and Joachimski, 2006) and has brought to light previously unknown yet significant short-term carbon isotope changes, exemplified by the *falsiovalis* Event at the beginning of the Frasnian age (Buggisch and Joachimski, 2006). Remarkable changes in the carbon cycle were also discovered by Yans et al. (2007) in the Early–Middle Frasnian transition at the well-dated and biostratigraphically continuous stratigraphic sections in the Ardennes of Belgium, and are supported by data from the Holy Cross Mountains (Pisarzowska et al., 2006).

According to the standard conodont biozonation of Ziegler and Sandberg (1990), the Early–Middle Frasnian (E–MF) transition corresponds to the *Palmatolepis transitans*–*Palmatolepis punctata* conodont zonal boundary (Becker and House, 1998). High-resolution carbon isotope data generated from recovered brachiopods allowed Yans's (et al., 2007) research group to identify a positive $\delta^{13}C$ excursion that began in the *transitans* Zone and continued throughout much of the *punctata* Zone to eventually be followed by an abrupt negative $\delta^{13}C$ shift of approximately 5‰ (from 5.85‰ to −1.20‰ in the Ardennes and from 5‰ to −0.72‰ in the Holy Cross Mountains). The *punctata* Event carbon isotope anomaly (*sensu*; see Saltzman and Thomas, 2012; Yans et al., 2007) is thus considered as a major, broad positive $\delta^{13}C$ excursion within the *punctata* Zone and a principal component of a larger, composite E–MF geochemical perturbation (see Saltzman and Thomas, 2012) that is recognizable worldwide (Ma et al., 2008; Morrow et al., 2009; Śliwiński et al., 2011). Aspects of the shelf ecosystem evolution were presented in the thematic issue of *Acta Palaeontologica Polonica* edited by Baliński et al. (2006), whereas diverse geochemical results were included in a special issue of *Palaeogeography, Palaeoclimatology, Palaeoecology* edited by Racki et al. (2008).

This contribution focuses on providing high-resolution accounts of carbon and oxygen isotopic variability in several southeastern Laurussian successions across the E–MF transition (based on the doctoral dissertation of Pisarzowska, 2008). We present here for the first time a parallel set of isotopic $\delta^{13}C$ records for both organic and inorganic carbon, as well as oxygen isotope ratios measured in coeval carbonates and conodont apatite. We document carbon isotope excursions on the South Polish carbonate shelf that coincided with the Timan, Middlesex and the first step of the Rhinestreet global events (*sensu* House, 2002), and comprehensively discuss the causes of these worldwide biogeochemical perturbations in the context of sea-level and climate changes, tectonic activity and concomitant bio-events.

2. Facies settings and stratigraphy

During the Devonian Period, Poland was situated on the epicontinental shelf of the Laurussian landmass at paleolatitudes of 5–10° S of the equator (Golonka, 2000). The southern part of the Laurussian shelf, situated between the SW margin of the East European Craton and Variscan deformation front, included the Holy Cross Mountains (HCMts) regions and the environs of Silesia–Cracow, and extended to the Moravian Karst and the Sub-Carpathian area (Fig. 1). The regional structural and palaeogeographic setting of the Upper Devonian strata was summarised by Pisarzowska et al. (2006) and Narkiewicz (2007).

The Kielce paleo-high and the Łysogóry paleo-low represent two distinct paleotectonic regions of the Holy Cross Mountains (Fig. 1). The centrally located Frasnian Dyminy Reef (Szulczewski, 1971, 1995; Racki, 1993) was surrounded by the Chęciny–Zbrza (southern) and Łysogóry–Kostomłoty (northern) intrashelf basins. Depositional data indicate that the region was affected by early Variscan block tilting throughout the E–MF time interval (Szulczewski, 1971, 1989; Racki, 1993, p. 132; Racki and Narkiewicz, 2000; Lamarche et al., 2003; Nawrocki et al., 2008), as evidenced by rapid lithological and lateral thickness changes of conglomerate and breccia layers (Vierek, 2007), mixed conodont biofacies (Sobstel et al., 2006; Vierek and Racki, 2011) and, above all, localized synsedimentary block movements (Szulczewski, 1989; Lamarche et al., 2003).

The continuous carbonate successions of HCMts and Silesia-Cracow region include a record of global and regional geochemical events in a variety of different facies deposited in the deeper-water intrashelf basin, reef foreslope and reefal environments (Figs. 2–6; see detailed descriptions of studied localities in Pisarzowska et al., 2006). Many previous studies have characterized various aspects of the deposits spanning the E–MF transition in this region, including their high-resolution conodont-based stratigraphy and sedimentology, paleontology and geochemical variability (e.g. Sobstel, 2003; Racki et al., 2004; Jagt-Yazykova et al., 2006; Krawczyński, 2006; Pisarzowska et al., 2006; Sobstel et al., 2006; Vierek, 2007; John et al., 2008; Marynowski, et al., 2008; Vierek and Racki, 2011).

2.1. Reef slope facies

The middle to upper Wietrznia Beds (Wietrznia Ie and Wietrznia Id–W outcrops; N50° 51.359′, E20° 38.514′ and N50° 51.347′, E20° 38.417′, respectively; Figs. 2–3) are the most thoroughly studied stratigraphic sections of the E–MF transition (Pisarzowska et al., 2006), and are mostly composed of thick layers of calcirudites (including flat-pebble conglomerates) that intercalate with deep-slope mud facies composed of nodular and wavy-bedded bituminous micrites and marly shales. The uppermost portion of the middle Wietrznia Beds is distinguished by rhythmically stratified, thin-bedded micrites and marly shales (Śluchowice Marly Level). The middle Wietrznia Beds were episodically deposited on the northern, storm-affected flank of the Dyminy Reef (Szulczewski, 1971; Racki, 1993; Vierek, 2007). The unit includes both coarse-grained, proximal tempestites (i.e., mostly episodic, storm-generated sediment-gravity flows from the reef margin) that laterally grade into bioclastic, crinoid-rich and coquinoid layers, and micritic-marly (basinal) sediments (Szulczewski, 1971; Vierek, 2007; Vierek and Racki, 2011).

The upper Wietrznia Beds are largely characterized by thin-bedded, laminated calcilutites and calcarenites, as well as massive detrital limestones with many intraclasts and fragmented reef-builders that form talus-like deposits in upper foreslope settings. At Śluchowice, this unit is composed of alternating marly limestones and shales that are overlain by coarse-bedded intraformational conglomerates with calcarenite interbeds, both with abundant reef-derived skeletal debris (Fig. 3).

The lowermost portion of the Kowala beds (set B and C, Kowala–railroad cut and Kowala quarry; N50° 47.512′, E20° 33.313′ and N50° 47.553′, E20° 33.835′, respectively; Fig. 4) is composed of wavy-bedded and coral-rich biostromal limestones with shaly intercalations as well as bindstone-type biohermal limestones with stromatoporoid-coral associations (Kadzielnia-type mud-mounds; see Szulczewski, 1971; Szulczewski and Racki, 1981; Racki, 1993; Łuczyński, 2009). Thick micritic and diverse grained limestones, occur in the upper portion of the middle slope successions and contain reworked reef builders and slump structures (set E, see Szulczewski, 1968, 1971; Marynowski et al., 2008).

2.2. Intrashelf basin

Deeper-water facies (Szydłówek Beds and Kostomłoty Beds) are well exposed in Kostomłoty–Mogiłki (N50° 55.427′, E20° 34.830′) and Kostomłoty–Małe Górki (N50° 55.552′, E20° 32.285′) quarries, and also partly in the outcrops at Śluchowice and Kowala (Szulczewski, 1971; Racki and Bultynck, 1993; Figs. 3–5). The upper portion of the