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Evidence for perturbation of the carbon cycle in the Middle Frasnian *punctata* Zone (Late Devonian)

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Abstract – New carbon isotopic data from the Devonian of Ardennes (Belgium) and partly from the Holy Cross Mountains (Poland) highlight an abrupt and high-amplitude negative excursion in the *punctata* conodont Zone. Published information from Moravia and China suggests that this Middle Frasnian negative excursion, jointly with the preceding large-scale positive shift, should be used as a global chemostratigraphic marker. Causation scenarios for this negative '*punctata* Event' are correlated neither with major biota turnover nor major sea-level changes, but may be related to: (1) the Alamo Impact Event, that led to (2) the massive dissociation of methane hydrates and (3) the rapid onset of global warming.

Keywords: *punctata* Event, Frasnian, carbon isotopes, Ardennes, Belgium.

1. Introduction

Previous carbon isotope studies have been widely used to measure changes in the global carbon cycle through geological time (e.g. Joachimski & Buggisch, 1996; Prokoph & Veizer, 1999; Saltzman, Groessens & Zhuravlev, 2004), including links with major sea-level changes (e.g. Immenhauser *et al.* 2003), mass extinction episodes (e.g. Margaritz, 1989; Kump, 1991) and stratigraphic boundaries (e.g. Zachos *et al.* 2001).

Calcitic brachiopod shells have been measured in studies of Palaeozoic palaeoceanography and palaeoclimatology because of their ability to retain unaltered $\delta^{13}C$ signals and the fact that they lend themselves to diagenetic screening. In the Devonian, $\delta^{13}C$ curves, based mostly on very few reliable measurements from widely separated sections, reveal long-term (above conodont biozone stratigraphic resolution, see below) patterns only (Veizer *et al.* 1999; see http://www.science.uottawa.ca/geology/isotope_data/; van Geldern & Joachimski, 2001). Here we present new $\delta^{13}C$ curves encompassing the uppermost Emsian to the uppermost Frasnian, at high stratigraphic resolution from well-dated continuous sections in the Ardennes (Belgium) and to a lesser extent in the Holy Cross Mountains (Poland); this has allowed us to recognize a Middle Frasnian (terminology following Ziegler & Sandberg, 2001) $\delta^{13}C$ isotopic excursion on a supra-regional scale.

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2. Samples and methods

We have minimized diagenetic artefacts such as effects of burial, meteoric diagenesis and isotopic disequilibrium during crystallization ('vital-effects') by using samples from the fabric-retentive and non-luminescent 'secondary' layers of brachiopods. A thin-section (0.5 to 1 mm thick) of each brachiopod was studied under the optical microscope and under cathodoluminescence. Moreover, trace element concentrations (Sr, Mn, Fe) were measured by a CAMEBAX SX50 microprobe at the Catholic University of Louvain-la-Neuve (Belgium). The precision was better than ± 10 % for Sr and Mn measurements. Only specimens (1) with distinct and sharp microstructures, (2) which showed no luminescence, and (3) with Sr concentrations > 800 ppm and Mn concentrations < 100 ppm were used for isotopic analysis (data available from author on request, and at http://gfa.fpms.ac.be/Recherche/Publications.htm). Sr contents of non-luminescent brachiopods can reach 3280 ppm (mean value of ∼ 1280 ppm); Mn contents of non-luminescent brachiopods may be < 10 ppm (mean value of ∼ 50 ppm). Such material is routinely judged as adequate to reflect the primary isotopic record of ancient oceans (e.g. Carpenter & Lohmann, 1995; Veizer *et al.* 1999; Lee & Wan, 2000; Brand *et al.* 2003; Han *et al.* 2003). Matrices, and to a lesser extent luminescent brachiopods exhibiting dull luminescence, have Sr contents as low as 340 ppm and Mn contents up to 2230 ppm. Only 257 brachiopods of the 420 sampled specimens (about 61 %) were considered as 'well preserved' using the methodology described above.

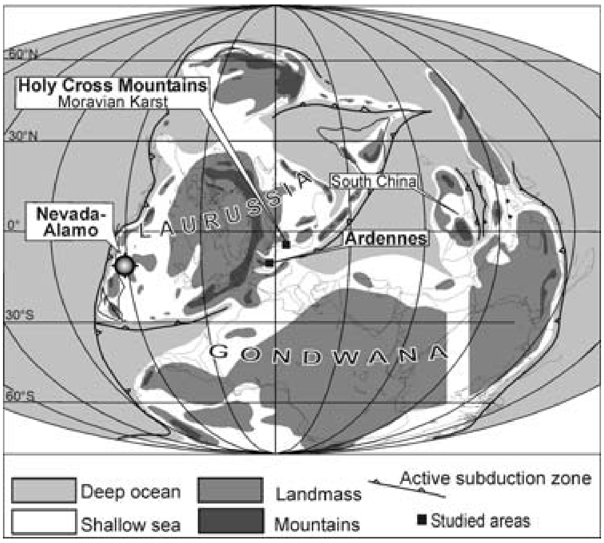

Figure 1. Location of studied sections and of the Alamo impact site against the Late Devonian palaeogeography (from Golonka, 2000, modified).

Brachiopod material was collected in biostratigraphically well-constrained (from late Emsian to late Frasnian; *patulus* to Upper *rhenana* Zones) shelf carbonates and bank-to-reef successions. The Ardennes (Belgium) and the Holy Cross Mountains (Poland) had a palaeo-location on the southeastern margin of subtropical Laurussian shelves (Fig. 1) during Devonian time. They are particularly suitable areas for studies of detailed carbon isotope change because of the relative abundance of brachiopods and well-defined stratigraphy, sedimentology and diagenesis of the Devonian rocks (Bultynck *et al.* 1991; Bultynck, 1993; Boulvain *et al.* 1999; Bultynck, Coen-Aubert & Godefroid, 2000; Gouwy & Bultynck, 2000; Han *et al.* 2000 for Ardennes; Racki, 1993; Szulczewski, 1971, 1995; Racki & Bultynck, 1993; Malec & Turnau, 1997; Sartenaer, Racki & Szulczewski, 1998; Turnau & Racki, 1999 for Holy Cross Mountains). Conodonts provide the best worldwide and high-resolution time-calibration for the Middle and Late Devonian (less than 500 000 years for each conodont Zone in the Late Devonian: Sandberg & Ziegler, 1996). Moreover, we refined the existing conodont biozone resolution by using well-constrained regional sea-level cyclicity and macrofaunal evidence in conodont-poor localities, as well as the relative positions of the samples to several marker levels in each well-dated succession.

The $\delta^{13}C$ ratios were determined for 257 brachiopod specimens, resulting in more than ten successive $\delta^{13}C$ measurements for each conodont Zone in the most densely sampled intervals of the Frasnian succession in the Ardennes. About 10 mg of powder were drilled for each sample. The powder was cleaned in 10 % hydrogen peroxide for 30 minutes to remove any organic contamination, rinsed and then dried for 30 minutes at 60 °C. The samples were analysed with a VG Isotech PRISM mass spectrometer in the Oxford laboratory by online reaction with purified orthophosphoric acid at 90 °C. Carbon isotope ratios are expressed as per mil (‰) deviation from the Peedee Belemnite (PDB) standard. Reproducibility of replicate standards was better than 0.1 ‰ (data available from author on request, and at http://gfa.fpms.ac.be/Recherche/Publications.htm)

3. Results

The carbon isotopic data from Belgium (curve A) and Poland (curve B), and the eustatic, stratigraphic and palaeoclimatic settings from the late Emsian to late Frasnian are presented in Figure 2. The new Eifelian to Frasnian high-resolution Belgian curve shows nine excursions (cycles 1 to 9 in Fig. 2). The negative shifts are more gradual than the positive ones, even in the Givetian isotopic record which is at lower resolution.

The highest $\delta^{13}C$ values (above 5 ‰) are found in the Frasnian *transitans–punctata* conodont Zones, and cycle 6 is marked by the strongest variation (see detail in Fig. 3) influenced by the abrupt negative excursion in the *punctata* Zone (negative trend of cycle 6). The amplitude of this change is especially noteworthy: from 5.85 ‰ to −1.20 ‰ (negative shift of −7.05 ‰).

The sampling in Belgium has a resolution three times better than in Poland (respectively 190 and 67) and is more tightly constrained biostratigraphically. The less precisely dated dataset from Poland is arranged in intra-zonal time intervals, because several single brachiopod samples have been taken from sections difficult to correlate and/or some sampled successions are not very accurately biostratigraphically constrained (data available from author on request, and at http://gfa.fpms.ac.be/Recherche/Publications.htm). Despite this lower Polish sampling resolution, the highest values above 5 ‰ are again observed in cycle 6, and proved undoubtedly by the organic carbon isotopic secular trend (Racki *et al.* 2004). The abrupt shift in the *punctata* Zone may be obscured by inadequate time constraints of the Polish samples but is deduced from the wide scatter of $\delta^{13}C$ (from 5.47 ‰ to −0.72 ‰, that is, a probable negative shift of −6.19 ‰) in six samples from the *punctata* interval.

4. Discussion

4.a. The whole curve

Where data are numerous, Belgian and Polish secular curves show a similar secular variation. Six excursions (from the base of the *kockelianus* to the base of the Lower *rhenana* Zones) are observed in both areas and minor differences reflect only the coarser resolution of the Polish samples.

In both areas, the episodes of sea-level rise are clearly correlated with the positive shifts (Fig. 2). The negative shifts are more gradual than the positive ones and correspond to the main regressive pulses. Only the

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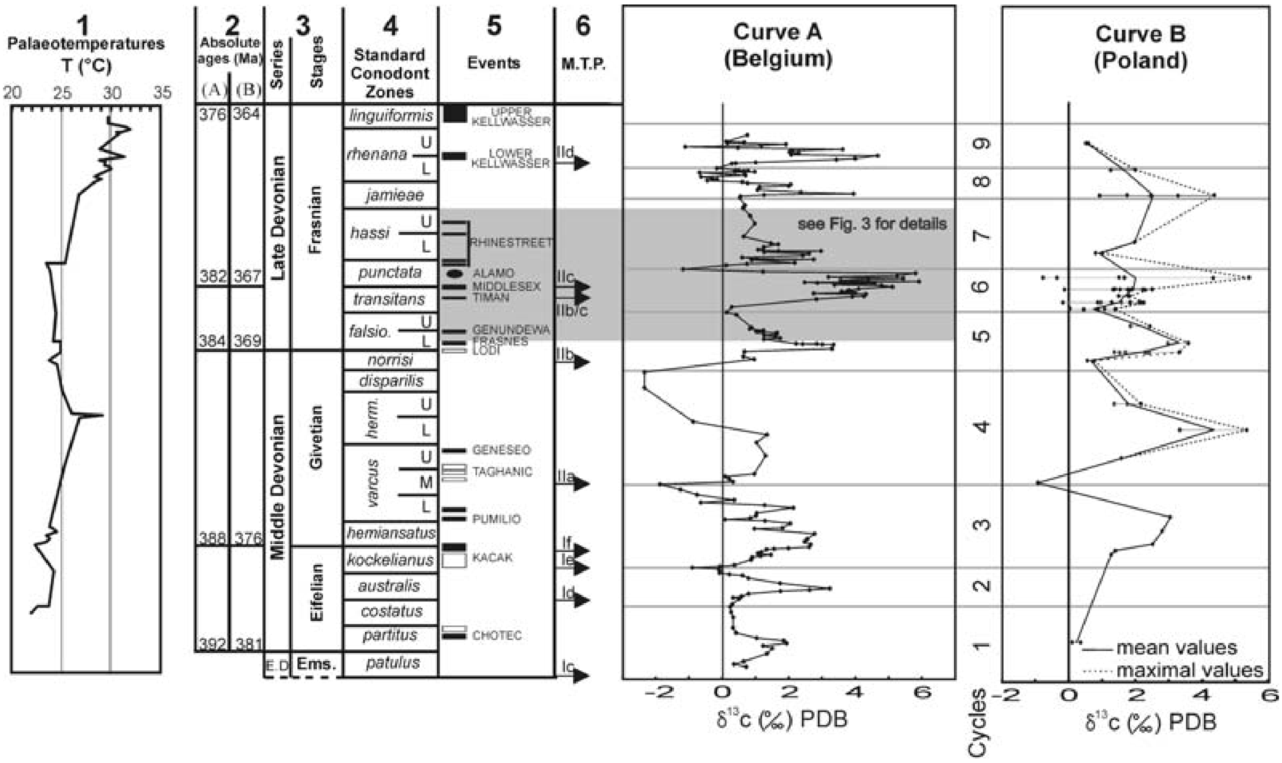

Figure 2. High-resolution carbon isotope record from the late Emsian to late Frasnian. Column 1 – palaeotemperatures calculated from the oxygen isotope record of conodont apatite from Joachimski *et al.* (2004); column 2 – absolute ages from (A) Kaufmann (2006), (B) Sandberg & Ziegler (1996); column 3 – stratigraphy; column 4 – standard conodont zonation from Klapper & Becker (1999), column 5 – Events from House (2002) except Alamo event (this study); events characterized by short-term dysoxic or anoxic facies in their name areas are shown as black rectangles; column 6 – M.T.P. (= Major Transgressive Pulses) from Johnson, Klapper & Sandberg, 1985; Boulvain & Herbosch, 1996; Racki, 1997; Gouwy & Bultynck, 2000. Curve A from sampling in Belgium (190 samples). Curve B from sampling in Poland (67 samples). Less precisely dated data set from Poland is arranged in intra-zonal time intervals, because several single brachiopod samples have been taken from sections difficult to correlate and/or some sampled successions are not very accurately biostratigraphically constrained (see http://gfa.fpms.ac.be/Recherche/Publications.htm); the two graphs are presented to reflect mean and maximal values for the particular stratigraphic intervals. Grey lines are located at the base of each cycle in relation with sea-level changes. The main object of our study (grey-filled segment) is detailed in Figure 3. U – Upper, M – Middle, L – Lower; E.D. – Early Devonian; Fam. – Famennian; Ems. – Emsian; *herm.* – *hermanni*; *falsio*. – *falsiovalis*.

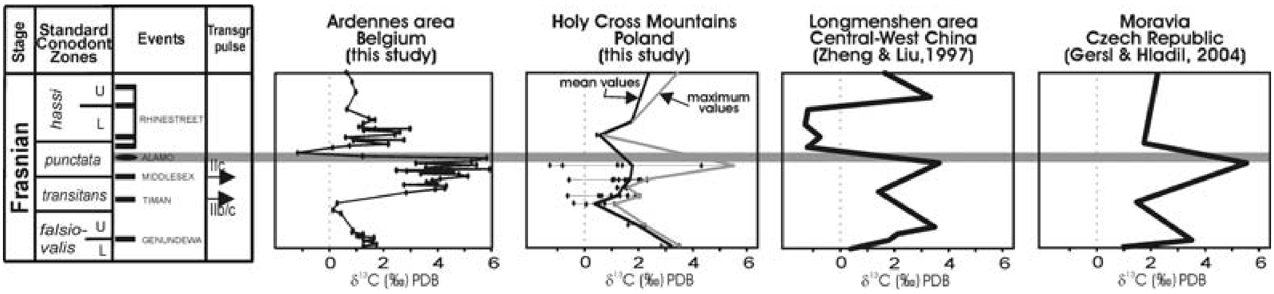

Figure 3. High-resolution carbon isotope record of the Early–Middle Frasnian (upper part of cycle 5 to lower part of cycle 7 in Fig. 2) in Belgium (this study), Poland (this study), China (Zheng & Liu, 1997) and Moravia (Hladikova, Hladil & Zuskowa, 1997, followed by Geršl & Hladil, 2004). For explanation see Figure 2.

negative shift in the *punctata* Zone is abrupt and not related to a gradual sea-level fall.

4.b. The *punctata* excursion as a global biogeochemical perturbation

The Early–Middle Frasnian interval had previously been considered as a homogeneous interval in terms of carbon isotope change superimposed on a longer-term increase in δ^{13}C (Holser, Margaritz & Ripperdan, 1996; Prokoph & Veizer, 1999). Any δ^{13}C perturbations were assumed to be of a regional extent. The most reliable test for a global versus regional control of isotope signals is comparative analysis of secular curves from separate sedimentary basins (Fig. 3).

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Early–Middle Frasnian data by Hladikova, Hladil & Zuskowa (1997) on stromatoporoids, rugose corals and carbonate matrices in Moravia document $\delta^{13}C$ shifts up to 5.3 ‰ and a drop in Frasnian 'background' $\delta^{13}C$ values of 1.5–2 ‰ (Joachimski & Buggisch, 1996). The prominent anomaly remained crudely dated as *?transitans* Zone, but its probable middle–upper *punctata* assignment has been recently stressed by Geršl & Hladil (2004).

Relevant isotopic patterns are seen in the Givetian–Frasnian carbonate sequences of China. Bai *et al.* (1994) indicated a starting $\delta^{13}C$ excursion towards more positive values in the basal *transitans* Zone. Zheng & Liu (1997) show that this significant change, up to 3.54 ‰, correlated with the IIb/IIc T-R sea-level cycle (their sequence S15; a broadly timed *transitans* to *punctata* Zone transition) is followed by a rapid negative shift to −0.61 ‰. This scenario is similar to the one observed in Belgium and Poland.

High-quality brachiopod data from six disparate regions of four Devonian continents have been compiled into a global curve by van Geldern & Joachimski (2001), but the secular trend is established only in inter-zonal time windows and for averaged $\delta^{13}C$ values from individual biozones. Nonetheless, the Early–Middle Frasnian smoothed positive–negative couplets are similar to our cycles 5–6. In addition, the scatter of seven $\delta^{13}C$ measurements for the 367 Ma time horizon (= *punctata* Zone: Sandberg & Ziegler, 1996) is remarkably wide, from ~0.6 ‰ to 3.4 ‰. This pattern can be explained by high-amplitude secular variations recognized in the Ardennes succession, and implied from the Polish, Czech and Chinese data.

The variability of several per mil, recorded in different carbonate shelves during the *punctata* positive and negative $\delta^{13}C$ shifts (Fig. 3), likely reflects locally elevated biological pumping (Saltzman, Groessens & Zhuravlev, 2004) and/or highly reduced impact of isotopically light meteoric fluids on the epeiric carbonates during sea-level rise (Immenhauser *et al.* 2003) and/or regional-scale processes of ^{13}C-depleted delivery, such as from terrestrial domains, and/or local oxidation of organic matter in a shallow water column (Saltzman, Groessens & Zhuravlev, 2004; Panchuk, Holmden & Kump, 2005). Therefore, the global negative signal in the *punctata* Zone might be partly biased by these localized influences.

In summary, chemostratigraphic studies from different epeiric sedimentary basins and continents during the Early–Middle Frasnian transition (see Fig. 1) support the primary character and supraregional extent of the geochemical signals exhibited by the Ardennes succession (see also Racki *et al.* 2004). Altogether, the intercontinental positive and negative carbon isotope shifts in the *punctata* Zone probably correspond to a worldwide perturbation in the earth-ocean system rather than a diagenetic overprint and/or a random set of local oceanographic phenomena. Therefore, both excursions can be regarded jointly as a 'global isotopic event' (*sensu* Holser, Margaritz & Ripperdan, 1996), and used as a potentially worldwide chemostratigraphic datum tool.

The two relatively depleted $\delta^{13}C$ values (−1.20 ‰ and 0.11 ‰) observed in the negative shift of the *punctata* Event correspond to brachiopods taken from the dark shales of the Ermitage Member in two different locations of the Ardennes. Although the Mn contents of the latter brachiopods are relatively high (80 and 90 ppm), no intense diagenesis overprint has been deciphered under cathodoluminescence and with Sr analyses. Nevertheless, the ^{13}C-depleted values of these two samples could be related to potential alteration due to the stabilization of the sediments in an open system for CO_2 derived from a remineralization of the organic carbon in the shaly sediments of the Ermitage Member (e.g. Sageman *et al.* 2003). In consequence, minimal $\delta^{13}C$ values of 1–2 ‰ are probably more appropriate to characterize the negative shift of the *punctata* Event. However, Zheng & Liu (1997) observed $\delta^{13}C$ values < 0 ‰ in the negative shift of China (Fig. 3). Further detailed study is required to determine precisely the amplitude of the negative shift of the *punctata* Event.

4.c. Potential causes and consequences of the perturbation

The high-amplitude $\delta^{13}C$ negative excursion in the *punctata* Zone is recorded globally and reflects changes in the carbon isotopic composition of the oceanic reservoir. In order to evaluate the cause(s) of this change, the duration of the event must be roughly estimated. The relative duration of the *punctata* Zone is estimated at about 0.5 Ma (Sandberg & Ziegler, 1996), 0.8 Ma (Gouwy & Bultynck, 2000), and less than 1 Ma (Kaufmann, 2006). The $\delta^{13}C$ negative excursion is abrupt and less than the zone duration, probably around several hundred thousand to several million years.

The magnitude, timing, and global nature of the negative $\delta^{13}C$ event in the *punctata* Zone imply that an immense quantity of ^{12}C-enriched carbon was rapidly added to the ocean reservoir (see discussion in Berner, 2002). Comparison with other well-documented rapid and high-amplitude negative excursions suggest that the best explanation for the *punctata* Event is a catastrophic release of oceanic methane hydrate (see e.g. Dickens *et al.* 1995 for the approximately 100 kyr long carbon isotope excursion at the Paleocene–Eocene boundary; Hesselbo *et al.* 2000 in the Toarcian; Jiang, Kennedy & Christie-Blick, 2003 in the Neoproterozoic). Nevertheless, bolide impact (e.g. Bodiselitsch *et al.* 2004) or rapid and high-amplitude sea-level changes (e.g. Joachimski *et al.* 2002), among other factors, may also have contributed to the biogeochemical turnover.

Massive deliveries of methane from the seafloor are increasingly being implicated in drastic greenhouse perturbation because raised atmospheric CO_2 levels were caused by oxidation of methane, as estimated for the initial Eocene thermal maximum (Dickens *et al.* 1995) and earliest Triassic post-apocalyptic climate (Berner, 2002). Interestingly, Joachimski *et al.* (2004) deciphered a warming of the palaeotemperatures of about 9 °C, from ∼23 °C in the *punctata* Zone to ∼32 °C in the Upper *rhenana* conodont Zone, by analysing the oxygen isotope evolution of conodont apatite (Fig. 2). Greenhouse conditions in the Middle–Late Frasnian are also supported by palaeontological data (see Joachimski *et al.* 2004 for details). Thus, after a period of relative climatic stability, the rapid (impact-induced?) start of an intense warming in the *punctata* Zone may have led to a significant change in sediment thermal gradient, further dissociation of oceanic hydrate and release of ^{12}C-enriched methane to the ocean/atmosphere reservoir. The methane release, however, cannot solely explain the long-term greenhouse conditions during the whole Middle–Late Frasnian period but only their transient interruption, and the intra-zonal climatic trends are only crudely documented (fig. 2 in Joachimski *et al.* 2004).

An impact origin for the Alamo Breccia, located in southern Nevada, USA, during the *punctata* Zone (Fig. 3), is well-established by several lines of supporting evidence (including shocked quartz grains and an iridium anomaly; see Sandberg, Morrow & Ziegler, 2002 for complete reference). According to McGhee (2001), the interval from middle *transitans* to Lower *hassi* Zones was a period of multiple impacts (Alamo, Siljan and Flynn Creek impacts), although more detailed work is required to improve the geochronology of these impacts (Reimold *et al.* 2005). The release of methane hydrate after an impact in a continental shelf or seafloor, or impacts of ^{12}C-rich comets during a comet shower have produced a negative $\delta^{13}C$ excursion at the late Eocene (Bodiselitsch *et al.* 2004). A similar scenario may be suggested for the *punctata* Zone. A Frasnian marine ecosystem gradually destabilized by a series of comet showers has been hypothesized (Sandberg, Morrow & Ziegler, 2002). However, a link of the *punctata* Event with the well-documented Alamo Impact Event is still speculative and requires temporal correlation in sections proximal to the impact site(s).

Conversely, negative $\delta^{13}C$ excursions have been interpreted to represent decreases in global organic-carbon burial rates either by declined marine productivity or reduced preservation under less anoxic waters (Kump, 1991; Kump & Arthur, 1999; Joachimski *et al.* 2002; Sageman *et al.* 2003). So a large amplitude (above 5 ‰) cannot be easily explained, however, exclusively by a collapse in oceanic primary production (Bickert *et al.* 1997, p. 2727; Kump, 1991; Kump & Arthur, 1999). As previously mentioned, no sea-level fall has been detected in the *punctata* Zone (Fig. 3); instead, a eustatic sea-level rise is observed at the commencement of this time interval (Johnson, Klapper & Sandberg, 1985; Racki, 1993, 1997; Sandberg, Morrow & Ziegler, 2002).

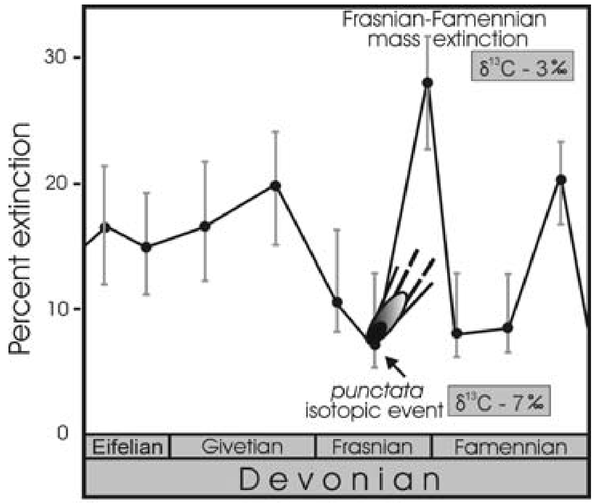

Figure 4. Impact events plotted against percent extinctions of 'well-preserved' marine genera through Eifelian to Famennian stages (Devonian), from Sepkoski (1996, fig. 6), modified; with kind permission of Springer Science and Business Media. The major *punctata* isotopic event is definitely not related to a mass extinction, despite the large scale of this carbon cycling perturbation.

Even if a link with the start of the Middle–Late Frasnian warming is suspected, further detailed multidisciplinary work is necessary to improve our knowledge of the mechanisms involved in the *punctata* negative $\delta^{13}C$ excursion. Nevertheless, the $\delta^{13}C$ fluctuations of the *punctata* Zone are among the highest $\delta^{13}C$ oscillations known in the Phanerozoic (Holser, Margaritz & Ripperdan, 1996; Veizer *et al.* 1999; van Geldern & Joachimski, 2001; Munnecke, Samtleben & Bickert, 2003) and represent higher-amplitude than biogeochemical events related to the Frasnian–Famennian and Devonian–Carboniferous mass extinction boundaries (Joachimski & Buggisch, 1996; Joachimski *et al.* 2001; Brand, Legrand-Blain & Streel, 2004).

Although the *punctata* Zone coincides with a regional reef crisis in Central Europe, well documented in a decline of diverse mud-mound biota (Arche Member in the Ardennes and Kadzielnia Member in the Holy Cross Mts; Johnson, Klapper & Sandberg, 1985; Racki, 1993; Copper, 2002), the Early to Middle Frasnian interval is marked by very low extinction intensity in the world ocean (Fig. 4; Sepkoski, 1996; McGhee, 1996, 2001). So, despite at least one proved impact event, and the onset of a global warming in the *punctata* Zone, the positive and negative $\delta^{13}C$ excursions are not connected with a major breakdown of carbonate production, analogous to pronounced Silurian perturbations (up to 12 ‰; Munnecke, Samtleben & Bickert, 2003). This lends support to the earlier discussed hypothesis that principal extrinsic environmental stimuli such as impacts and climate change may not have a major effect on biota (e.g. Reimold & Koeberl, 2002; Prothero, 2004).

5. Conclusions

The high-resolution carbon isotopic data of brachiopods of *patulus* (late Emsian) to Upper *rhenana* Zones (Late Frasnian) from Belgium (Ardennes) show nine δ^{13}C excursions. Less precisely dated data from Poland (Holy Cross Mountains) confirm a supra-regional extent of these geochemical signals.

Only the negative excursion in the *punctata* Zone is abrupt. Similar-range isotopic positive-to-negative signals are reported also from Poland, Moravia and China. This two-step major C-isotopic event has the potential to be a worldwide chemostratigraphic tool across the Early–Middle Frasnian transition.

The *punctata* Event may be partly linked with the bioproductivity collapse after the Alamo Impact Event (Nevada, USA), but probably with massive dissociation of isotopically light methane hydrate triggered by Alamo (or other) impact and/or sudden initiation of the proven global warming of the Middle–Late Frasnian.

The *punctata* biogeochemical perturbation is correlated neither with biodiversity crisis nor major biotic change (such as collapse of carbonate factory) nor major sea-level changes (*sensu* Johnson, Klapper & Sandberg, 1985), suggesting that the triggers of one of the biggest Phanerozoic perturbations were not sufficient to cause larger-scale environmental degradation.

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