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NEW STABLE ISOTOPE DATA AND FOSSILS FROM THE HIRNANTIAN STAGE IN BOHEMIA AND SPAIN: IMPLICATIONS FOR CORRELATION AND PALEOCLIMATE

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INTRODUCTION

Rocks in the Late Ordovician paleotropics commonly exhibit the now well-known, positive Hirnantian Isotopic Carbon Excursion (HICE). This event is coincident with both continental scale glaciation in Gondwana and dramatic extinction across the marine realm (Delabroye and Vecoli, 2010). Both the proximate cause of the isotopic excursion and the ultimate drivers of large scale cooling remain the subject of debate. Suggestions range from tectonic effects on weathering or changes in biological productivity, through large basaltic eruptions to gamma ray bombardment. Discussion of these alternative models is beyond the scope of this short paper, however. Our intent is to briefly report the direct association of a new high resolution $\delta^{13}C_{organic}$ record from rocks at a high latitude site that also bears biostratigraphic and sequence stratigraphic data needed to link Hirnantian oceanographic changes (especially those recorded in the paleotropics) with glacial events in the peri-Gondwanan realm (Delabroye and Vecoli, 2010; Young et al., 2010).

NEW HIGH RESOLUTION HICE IN BOHEMIA

We collected 152 samples (approx. 50-100 g each) for $\delta^{13}C_{organic}$ and total organic carbon (TOC) analyses from latest Katian to earliest Rhuddanian dark shale, siltstone, diamictite and sandy mudstone. Mid Hirnantian rocks are not readily accessible in this region at present. Samples were analyzed using facilities managed by C. Holmden at the University of Saskatchewan (Fig. 1; data and methodological details available upon request).

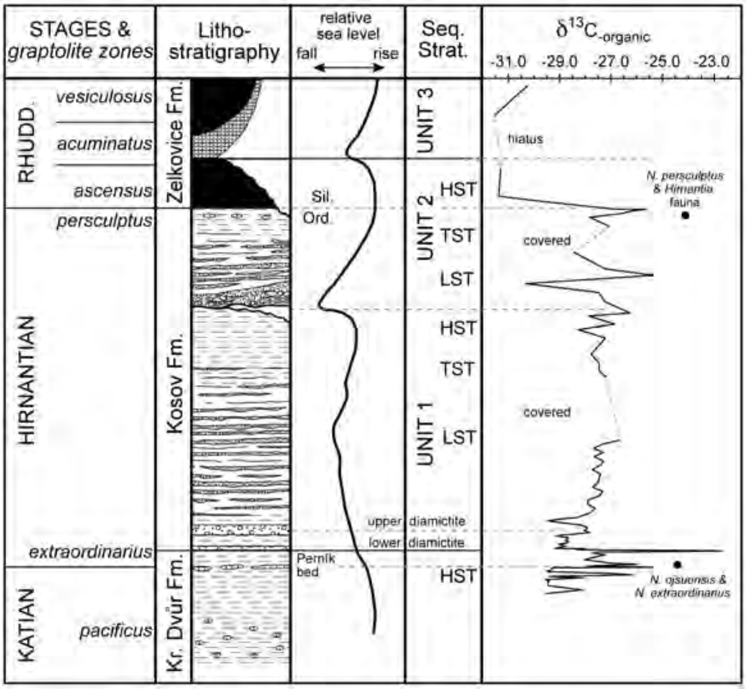

Figure 1. Summary of $\delta^{13}C_{org}$ results from Levín (lower part) and Hlásná Třebaň (upper part) plotted relative to regional stratigraphic composite through the Hirnantian based on sections in the vicinity of Praha, Czech Republic (modified from Štorch, 2006).

Early Hirnantian sections

We sampled the uppermost 4 m of the Králův Dvůr Formation (including the calcareous mudstones of the Perník Bed; Brenchley and Štorch, 1989) and 25 m of the overlying Kosov Formation in a fresh road cut (N49° 55.677', E14° 00.770') near the village of Levín (see Brenchley and Štorch, 1989, fig. 6). Samples through the lower part of this succession (including the two prominent glaciomarine "diamictite" beds at 0 and 3.5 m above the base of this unit) generally were taken at 20 cm intervals and those in the more expanded, storm-dominated succession above the diamictites at one-meter intervals (Fig. 2). The lower part of this succession was also sampled at a somewhat more weathered railway cutting at the village of Zadní Třebáň (N49° 54.865', E14° 12.299') from which Štorch (1989) reported the occurrence of *Normalograptus* cf. *ojsuensis* together with *Mucronaspis grandis* immediately above the Perník Bed (discussed further below). On the basis of that and other evidence, Štorch (2006) placed the base of the Hirnantian Stage at this graptolite-bearing level in the uppermost Králův Dvůr Formation.

TOC in the Králův Dvůr and Kosov formation samples is generally quite low (0.1 to 0.5 weight percent), with the highest TOC occurring in the lowermost Kosov Fm. diamictites. The $\delta^{13}C_{org}$ values are uncorrelated with TOC. In both of the basal Hirnantian sections, $\delta^{13}C_{org}$ values obtained in the upper Králův Dvůr Formation rise rapidly from a baseline value of about -29.3‰ (defined by the lowest 7 samples) and display initially fluctuating values in the lower part of the record before transitioning to a strong positive excursion

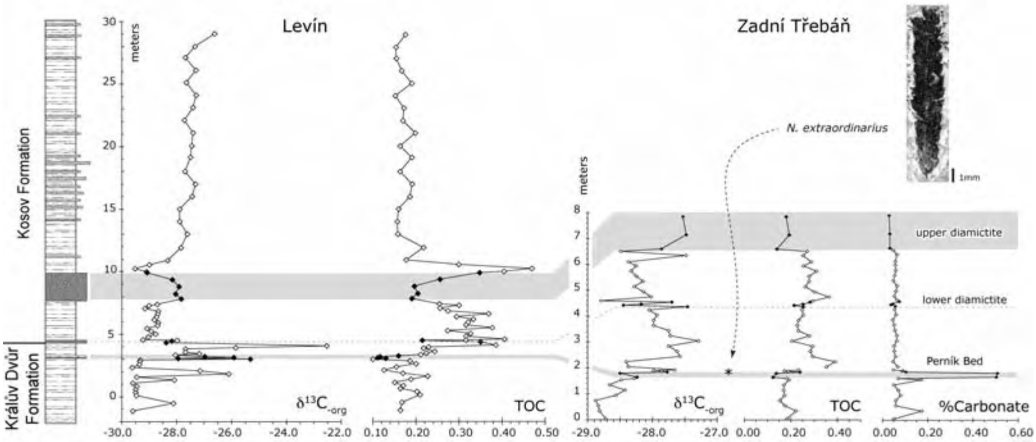

Figure 2. Organic carbon isotope data, total organic carbon (TOC) and carbonate concentration through the upper Králův Dvůr and lower Kosov formations at Levín and Zadní Třebáň.

in the lowermost Kosov Formation with peak values of about -27.5 to -26.5‰. These values are comparable to the 2-3‰ shift commonly seen in oceanic sites in the basal Hirnantian (Melchin and Holmden, 2006; Fan et al., 2009). A dark gray shale sample from immediately below the basal Kosov "lower diamictite" yields a much higher value of -22.53‰. The resulting 7‰ shift from baseline calculated using that sample is of the same scale as shifts observed in more on-shore sections in the paleotropics during the early Hirnantian (Melchin and Holmden, 2006; LaPorte et al., 2009). It is unclear whether this particularly heavy value has paleoenvironmental significance or is merely an artifact of local mixing or selective preservation of organic matter (or both) at this level in the stratigraphy.

The Perník Bed and the first appearance of Hirnantian graptolites both lie within the rising lower limb of the early HICE isotopic peak in these sections. From the lowermost Kosov Formation peak, $\delta^{13}C_{org}$ values decline somewhat toward the upper diamictite in both sections and then, at Levín where our samples continue for another 15 m, $\delta^{13}C_{org}$ values climb slowly to a maximum of about -27.0‰.

Late Hirnantian section

We collected 27 samples from an approximately 42 m-thick interval through the upper part of the Kosov Fm. and the base of the Želkovice Fm. in a natural bluff exposure above the village of Hlásná Třebaň (N 49º 55.359', E 14º 12.761'; see Štorch 2006, fig. 4). This section contains the upper part of the Kosov Fm. Sequence 1 of Štorch (2006) and the entire succession of Sequence 2 (the base of which lies at 18.5 m in our measured section; Fig. 3) as well as the lower part of the Rhuddanian-Aeronian Želkovice Formation (base at 41.5 m). Once again, TOC in the Kosov Formation samples are generally quite low (0.1-0.2 weight percent) with the exception of the lowermost Želkovice Formation strata where TOC rises abruptly to 2 to 7 weight percent. Samples through most of the upper Kosov at Hlásná Třebaň yielded $\delta^{13}C_{org}$ values that hover around -27.4‰, corresponding closely to those from the top of the lower Kosov Fm. at Levín; however, the uppermost samples show a slight positive shift to a peak value of -25.61‰. Elsewhere in the region these uppermost Kosov beds produce a shelly *Hirnantia* fauna as well as specimens

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of *Normalograptus persculptus* (Štorch, 2006 and references cited therein). The black shale succession in the overlying Želkovice Formation begins with an *c*. 15 cm thick *Akidograptus ascensus* Zone and, after a disconformity (Štorch, 2006, fig. 4), sedimentation continues from *C. vesiculosus* Zone through middle Aeronian in this outcrop. Two samples each from the *Akidograptus ascensus* and *Cystograptus vesiculosus* zones exhibit $\delta^{13}C_{org}$ values of about -31‰, as is common in the early Rhuddanian.

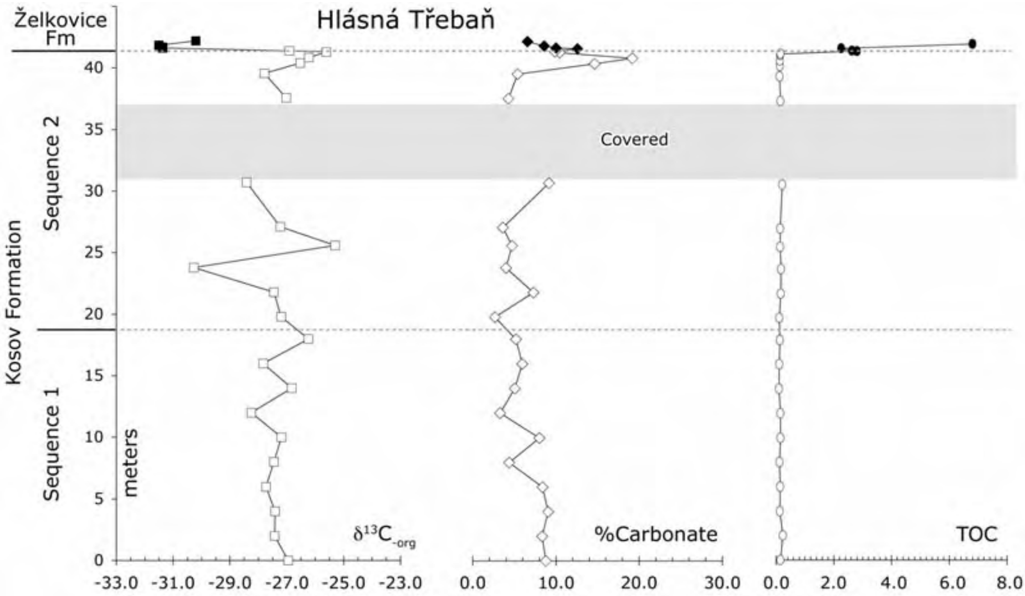

Figure 3. Organic carbon isotope data, total organic carbon (TOC) and carbonate concentration through the upper Kosov and lower Želkovice formations at Hlásná Třebaň.

NEW EARLY HIRNANTIAN GRAPTOLITES IN BOHEMIA AND SPAIN

Štorch (1989, 2006) reported specimens of *Normalograptus ojsuensis* from a thin band of shales immediately above the Perník Bed in the uppermost Králův Dvůr Formation at four sites in the study region, including Zadní Třebáň. We have now recovered *N. extraordinarius* at this site in addition to the more abundant *N. ojsuensis*. We have also recovered these two species from the basal part of the tempestite and diamictite dominated, Hirnantian Rio San Marco Fm. in Sardinia (Štorch and Leone, 2003; Leone et al., 2009). *N. ojsuensis* is also present in Niger (Legrand, 1993), but occurs there in transgressive strata deposited *between* the two major Hirnantian glacial advances (Ghienne et al., 2007). Accordingly, it may be a somewhat younger occurrence than that in the Králův Dvůr Formation.

Restudy of collections made in Spain by JCGM from the northern flank of the Guadalmez Syncline, Central Iberian Zone (N38º 45.115', E04º 58.565') reveals yet another occurrence of pre-glacial, Hirnantian graptolites (Pl. 1), in this case abundant specimens that we refer to *Neodiplograptus charis* (Mu and Ni, 1983). They occur in a laminated shale that lies stratigraphically between the top of the Bancos Mixtos and the glaciomarine Chavera Shales. The Urbana Limestone, which in many places occurs between these units, is not present at this locality. At present we are uncertain whether the graptolite-bearing beds

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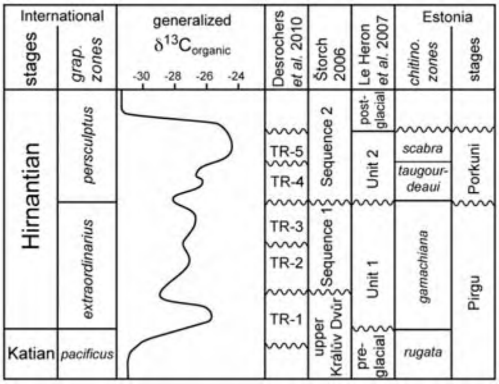

Figure 4. Summary correlation of cycles from Desrochers et al. (2010), Štorch (2006) and Le Heron et al. (2007).

are part of the depositional sequence that contains the Chavera Shale or not. In Tibet and SE China, however, *N. charis* appears to be restricted to the uppermost part of the *Paraorthograptus pacificus* Zone (upper *Diceratograptus mirus* Subzone) and the *N. extraordinarius* Zone, where it is commonly associated with *N. ojsuensis* (Chen et al., 2005). A calcareous coquina present immediately above the Bancos Mixtos at this locality (Gutiérrez-Marco, 1995) yields conodonts indicative of the *Amorphognathus ordovicicus* Conodont Biozone, which spans the Katian-Hirnantian boundary everywhere (Del Moral and Sarmiento, 2008).

REINTERPRETATION OF THE PERNÍK BED

As noted above, the Perník Bed of the uppermost Králův Dvůr Formation lies within the rising limb of the large $\delta^{13}C_{org}$ positive excursion that is present in the Bohemian succession. This unique bed is more calcareous than the other units in the predominantly clastic Late Ordovician succession in this region. It contains a moderately diverse, shelly fauna dominated by brachiopods of the to *Proboscisambon* Community of the *Foliomena* Fauna (Havlíček, 1982). The main Perník Bed fauna has been interpreted as containing warm water immigrants suggestive of a connection to the Boda Event (Fortey and Cocks, 2005). On the other hand, the Perník Bed grades both laterally and vertically into shales. Towards the top of the Perník Bed the shelly faunal assemblage becomes less diverse and is dominated by mucronaspid trilobites and varied ostracods. It is *within* these transitional layers at Zadní Třebáň that *N. ojsuensis* and *N. extraordinarius* first appear (Fig. 2; Pl. 1, fig. 6). Finally, some brachiopod index taxa of the *Hirnantia* fauna (*Hirnantia sagittifera* and *Kinella kielanae kielanae*) have been found immediately above the Perník Bed in a temporary outcrop at Praha-řeporyje (Mergl, in press). The Hirnantian age of the shale overlying Perník Bed is, thus, well dated by both graptolites and shelly fauna.

Vertical change in the faunal composition of the Perník Bed and lateral changes in its lithology suggest condensed sedimentation in a siliciclastic-starved setting. Considering the association of the Perník Bed with the onset of the HICE, we suggest that this bed may reflect cooling and increased aridity associated with ice cap growth, which in turn reduced clastic input and permitted a temporary development of conditions conducive to deposition of cool water carbonate. If that is so, then it may also be the case that the Urbana Limestone and its equivalents in Spain as well as the marly limestones of the uppermost Domusnovas Fm. in Sardinia may reflect a similar genesis.

IMPLICATIONS FOR CORRELATION OF THE BASE OF THE HIRNANTIAN STAGE

The brief 3-5‰ $\delta^{13}C_{org}$ positive excursion documented here in association with the local occurrence of *N. ojsuensis* and *N. extraordinarius* confirms the location of the base of the Hirnantian Stage previously identified by Štorch (2006). This is followed by a sharp return to lower $\delta^{13}C_{org}$ values and then by a long

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steady climb to a second positive excursion of between 4 and 5‰ above the late Katian and early Rhuddanian baseline (Fig. 1). That the HICE is a multiple isotope carbon excursion has now been documented in several sites around Laurentia (Melchin et al., 2003; Melchin and Holmden, 2006; LaPorte et al., 2009), including Anticosti Island (Desrochers et al., 2010), as well as in SE China (Fan et al., 2009). Our new data support the correlation between the paleotropics and the Gondwanan margin proposed by Desrochers et al. (2010), which they derived from their recent sequence stratigraphic interpretation of Hirnantian rocks at Anticosti Island and contradict the correlation advocated by Young et al. (2010). Our data suggest that the first HICE peak occurred during the early part of the *N. extraordinarius* Zone (Fig. 4), associated with a modest eustatic sea level rise (TR-1 of Desrochers et al., 2010), which brought early Hirnantian graptolites onto the peri-Gondwanan massifs in Spain, Sardinia, and Bohemia, and culminated in declining $\delta^{13}C_{org}$ values across the following sequence boundary. The first major Hirnantian ice sheet advance is recorded in the basal Kosov diamictites and overlying storm bed succession of Sequence 1 of Štorch (2006) and the Unit 1 synglacial and interglacial sediments of Ghienne et al. (2007) and Le Heron et al. (2007). This advance is reflected by a very modest tropical sea surface temperature decline as recorded in the Anticosti Island succession (Finnegan et al., 2011) and was evidently considerably smaller that the main later Hirnantian advance (Desrochers et al., 2010; Moreau, 2011). We suggest that this whole interval is represented by the *N. extraordinarius* Graptolite Zone and the *Belonechitina gamachiana* Chitinozoan Zone of Anticosti Island and Estonia. In most of the Estonian sections studied for carbon isotopes, however, the *B. gamachiana* Zone is absent or extremely condensed – at its thickest (at Kaugatuma – Brenchley et al.,

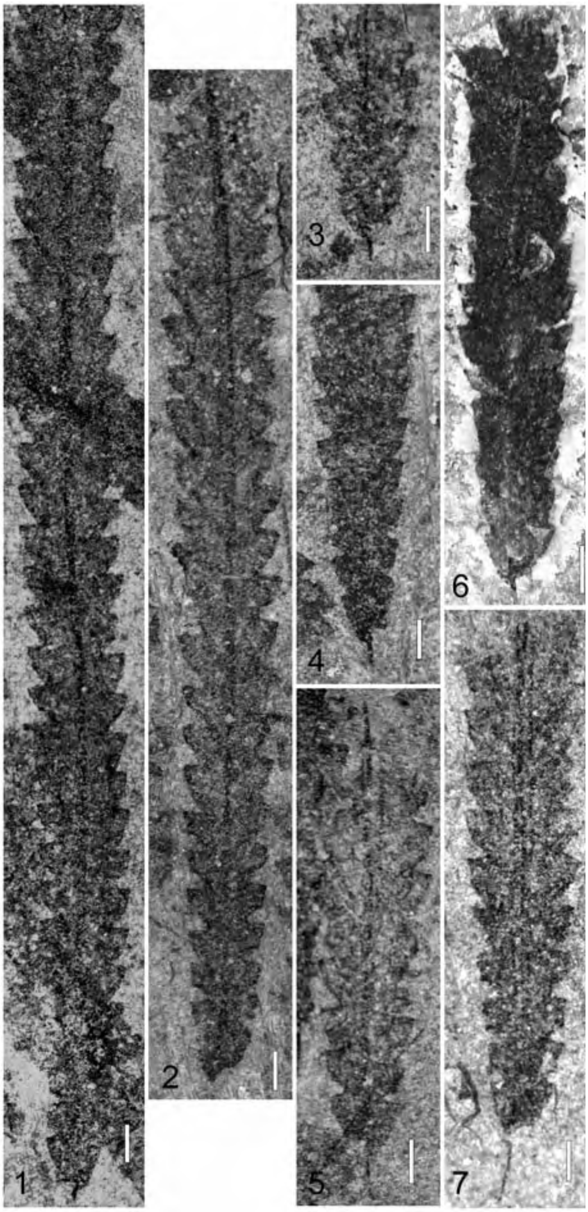

Plate 1. 1-5, 7: *Neodiplograptus charis* (Mu and Ni, 1983) from 3 km NW of Guadalmez, central Spain; 6: *Normalograptus extraordinarius* from uppermost layers of the Perník Bed at Zadní Třebáň. Scale bar is 1 mm in length in all figures.

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2003; Kaljo et al., 2008) that zone is less than 5 m thick and is bounded both below and above by discontinuity surfaces. Therefore, it is not surprising that the lower HICE peak has not been sampled in Estonia.

The main late Hirnantian ice advance appears to correspond to the interval of the hiatus and overlying low-stand in Sequence 2 within the upper Kosov Formation. The upper part of Sequence 2 succession, still within the interval of high $\delta^{13}C$ values, clearly deepens upward. If this deepening reflects eustatic sea level change rather than local subsidence, then this association suggests that high $\delta^{13}C_{org}$ values persisted into the early part of the post-glacial interval and that this pattern is obscured on Anticosti Island and in the Estonian succession by condensation or omission as result of rapid sea level rise during deglaciation. Conversely, it may be that the end of the HICE is slightly diachronous - younger in Bohemia than in the paleotropics in relation to the post-glacial transgression as a result of regional differences in carbon cycling processes. Testing of these competing hypotheses will require additional, high-resolution data sets, especially in a high-latitude site, with precise biostratigraphic and sedimentological control.

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REFERENCES

Brenchley, P.J. and Štorch, P. 1989. Environmental changes in the Hirnantian (upper Ordovician) of the Prague Basin, Czechoslovakia. *Geological Journal*, 24 (3), 165-181.

Brenchley, P.J., Carden, G.A., Hints, L., Kaljo, D., Marshall, J.D., Martma, T., Meidla, T., and Nõlvak, J. 2003. High resolution isotope stratigraphy of Late Ordovician sequences: constraints on the timing of bio-events and environmental changes associated with mass extinction and glaciation. *Geological Society of America Bulletin*, 115, 89-104.

Chen, Xu, Fan, Jun-xuan, Melchin, M.J. and Mitchell, C.E. 2005. Hirnantian (Latest Ordovician) Graptolites from the Upper Yantze Region, China. *Palaeontology*, 48 (2), 235-280.

Delabroye, A. and Vecoli, M. 2010. The end-Ordovician glaciation and the Hirnantian Stage: A global review and questions about Late Ordovician event stratigraphy. *Earth-Science Reviews*, 98 (3-4), 269-282.

Del Moral, B. and Sarmiento, G.N. 2008. Conodontos del Katiense (Ordovícico Superior) del sector meridional de la Zona Centroibérica (España). *Revista Española de Micropaleontología*, 40 (3), 169-245.

Desrochers, A., Farley, C., Achab, A., Asselin, E. and Riva, J.F. 2010. A far-field record of the end Ordovician glaciation: The Ellis Bay Formation, Anticosti Island, Eastern Canada. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 296 (3-4), 248-263.

Fan, J., Peng, P-a. and Melchin, M.J. 2009. Carbon isotopes and event stratigraphy near the Ordovician-Silurian boundary, Yichang, South China. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 276 (1-4), 160-169.

Finnegan, S., Bergmann, K., Eiler, J.M., Jones, D.S., Fike, D.A., Eisenman, I., Hughes, N.C., Tripati, A.K., and Fischer, W.W. 2011. The Magnitude and Duration of Late Ordovician-Early Silurian Glaciation. *Science*, 331, 903-906.

Fortey, R.A. and Cocks, L.R.M. 2005. Late Ordovician global warming. The Boda event. *Geology*, 33 (5), 405-408.

Ghienne, J.-F., Le Heron, D.P., Moreau, J., Denis, M. and Deynoux, M. 2007. The Late Ordovician glacial sedimentary system of the North Gondwana platform. In Hambrey, M., Christoffersen, P., Glasser, N., Janssen, P., Hubbard, B. and Siegert, M. (eds.), *Glacial Sedimentary Processes and Products*. Special Publication. International Association of Sedimentologists. Blackwells, Oxford, 295-319.

Gutiérrez-Marco, J.C. 1995. *Informe Paleontológico (Ordovícico-Silúrico) de la Hoja nº 807 (Chillón) del Mapa Geológico Nacional esc. 1:50.000 (Segunda Serie).* Unpublished report, Instituto Geológico y Minero de España, Madrid, 32 pp.

Havlíček, V. 1982. Ordovician in Bohemia: development of the Prague Basin and its benthic communities. *Sborník geologických v d, Geologie*, 37, 103-136.

Kaljo, D., Hints, L., Männik, P., and Nõlvak, J. 2008. The succession of Hirnantian events based on data from Baltica: brachiopods, chitinozoans, conodonts, and carbon isotopes. *Estonian Journal of Earth Sciences*, 57, 197-218.

LaPorte, D.F., Holmden, C., Patterson, W.P., Loxton, J.D., Melchin, M.J., Mitchell, C.E., Finney, S.C. and Sheets, H.D. 2009. Local and global perspectives on carbon and nitrogen cycling during the Hirnantian glaciation. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 276 (1-4), 182-195.

Le Heron, D.P., Ghienne, J.-F., El Houicha, M., Khoukhi, Y. and Rubino, J.-L. 2007. Maximum extent of ice sheets in Morocco during the Late Ordovician glaciation. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 245 (1-2), 200-226.

Legrand, P. 1993. Graptolites d'âge ashgillien dans la région de Chifra (Djado, République du Niger) - Ashgillian graptolites of the Chifra Region (Djado, Republic of Niger). *Bulletin des Centres de Recherche, Exploration et Production Elf Aquitaine*, 17 (2), 435-442.

Leone, F., Loi, A., Pillola, G.L., and Štorch, P. 2009. The Late Ordovician (Hirnantian) deposits in the Domusnovas area, SW Sardinia. In Corradini, C., Ferretti, A., Štorch, P. (eds.), Silurian of Sardinia. *Rendiconti della Società Paleontologica Italiana,* 3 (2), 227-237.

Melchin, M.J. and Holmden, C. 2006. Carbon isotope chemostratigraphy in Arctic Canada: Sea-level forcing of carbonate platform weathering and implications for Hirnantian global correlation. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 234 (2-4), 186-200.

Melchin, M. J., Holmden, C. and Williams, S. H. 2003. Correlation of graptolite biozones, chitinozoan biozones, and carbon isotope curves through the Hirnantian. In Albanesi, G. L., Beresi, M. S. and Peralta, S. H. (eds.), *Ordovician from Andes.* INSUGEO, Serie Correlación Geológica, 17, 101-104.

Mergl, M. (in press). Earliest occurrence of the Hirnantia Fauna in the Prague Basin (Czech Republic). *Bulletin of Geosciences*, 86, (2011).

Mu En-zhi and Ni Yu-nan. 1983. Uppermost Ordovician and Lowermost Silurian graptolites from the Xainza area of Xizang (Tibet) with discussion on the Ordovician-Silurian boundary. *Palaeontologica Cathayana*, 1, 151-179.

Moreau, J., 2011. The Late Ordovician deglaciation sequence of the SW Murzuq Basin (Libya). *Basin Research*, pub. on line Jan 19, 2011 (doi: 10.1111/j.1365-2117.2010.00499.x).

Štorch, P. 1989. Late Ordovician graptolites from the upper part of the Králův Dvůr Formation of the Prague Basin (Barrandian, Bohemia). *Věstník Ústředního ústavu geologického,* 64 (3), 173-186.

Štorch, P. 2006. Facies development, depositional settings and sequence stratigraphy across the Ordovician–Silurian boundary: a new perspective from the Barrandian area of the Czech Republic. *Geological Journal*, 41 (2),163-192.

Štorch, P. and Leone, F. 2003. Occurrence of the late Ordovician (Hirnantian) graptolite Normalograptus ojsuensis (Koren and Michaylova, 1980) in south-western Sardinia, Italy. *Bolletino della Società Paleontologica Italiana*, 42 (1-2), 31-38.

Young, S.A., Saltzman, M.R., Ausich, W.I., Desrochers, A. and Kaljo, D. 2010. Did changes in atmospheric CO2 coincide with latest Ordovician glacial-interglacial cycles? *Palaeogeography, Palaeoclimatology, Palaeoecology*, 296 (3-4), 376-388.