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

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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 $\delta^{13}C_{\text{organic}}$ 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 $\delta^{13}C_{\text{organic}}$ and total organic carbon (TOC) analyses from latest Katian to earliest Rhuddanian dark shale, siltstone, diamicite 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).
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 (N49º 55.677', E14º 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 Třebání (N49º 54.865', E14º 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 -2.93‰ (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 1. Summary of $\delta^{13}$C$_{org}$ results from Levín (lower part) and Hlásná Třebání (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).
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 diamicite” 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 diamicite 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 49° 55.359', E 14° 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...
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.

**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 (N38° 45.115', E04° 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
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 Kráľův 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 Třebán 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-Feboryje (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
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 periphery of the Gondwanan and 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 diamicites 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 Trˇebáň. Scale bar is 1 mm in length in all figures.
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 $\delta^{13}C_{\text{org}}$ 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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