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Carbon isotope chemostratigraphy of the Llandovery in northern peri-Gondwana: new data from the Barrandian area, Czech Republic

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Abstract. The first complete $\delta^{13}C_{org}$ record of the uppermost Hirnantian to lower Telychian strata of the Barrandian area (northern peri-Gondwana) is presented based on 168 new samples. The new data from the study area reveal that the evolution of the Llandoverian organic carbon isotope reservoir was similar to that on other palaeoplates, but it differs from the development of the coeval carbonate carbon isotope reservoir in the absence of two $\delta^{13}C$ excursions (i.e. the early Aeronian positive excursion in the upper part of the *Demirastrites triangulatus* graptolite Biozone and a negative excursion occurring close to the boundary between the *Cystograptus vesiculosus* and *Coronograptus cyphus* graptolite biozones).

Key words: carbon isotope chemostratigraphy, Llandovery, Barrandian area, northern peri-Gondwana, Czech Republic.

INTRODUCTION

On-going systematic search for major $\delta^{13}C$ excursions in the Silurian strata of the Barrandian area of northern peri-Gondwana revealed five excursions: (a) a positive excursion associated with the late Aeronian *sedgwickii* Event (Štorch & Frýda 2012), (b) the early Sheinwoodian (Ireviken) positive $\delta^{13}C$ excursion (Frýda et al. 2015), (c) the late Homerian (Mulde) positive carbon isotope excursion (Frýda & Frýdová 2014), (d) the mid-Ludfordian excursion associated with the Lau and *kozlowskii* events (Lehnert et al. 2003, 2007; Frýda & Manda 2013) and (e) the Silurian–Devonian boundary (Klonk) excursion associated with several bioevents (Hladíková et al. 1997; Buggisch & Mann 2004; Manda & Frýda 2010). The present study is heading towards the compilation of a complete $\delta^{13}C$ curve across the Silurian strata of the Perunica microplate. Here we report the first $\delta^{13}C_{org}$ and total organic carbon (TOC) data from the uppermost Hirnantian to lower Telychian successions based on the study of three representative, biostratigraphically well-dated sections (Řepy, Radotín tunnel and Hlásná Třebaň) of the Barrandian area (Štorch 1994; Fig. 1).

GEOLOGICAL SETTING

Richly fossiliferous Lower Palaeozoic rocks of the Barrandian area belong to a world-class natural heritage site. Unmetamorphosed and tectonically little deformed Ordovician to Middle Devonian deposits preserved in the Barrandian area unconformably overlie the Neoproterozoic and Cambrian basement (e.g. Kříž 1992; Chlupáč et al. 1998). The Ordovician succession ends with storm sandstones deposited during the Hirnantian glacio-eustatic regression. It is overlain conformably by condensed hemipelagic, largely anoxic early Silurian black shale. During mid- and late Silurian, the black shales were gradually replaced by biodetrital limestones which first developed around active submarine volcanic centres and eventually dominated the depositional setting during the latest Silurian and Devonian.

The Hirnantian succession of the Barrandian area corresponds to the Kosov Formation. While most of its shale-sandstone alternation was deposited well above the storm-wave base, upper Hirnantian sediments witnessed substantial post-glacial rise in sea level. Light-coloured mudstones of the uppermost Kosov Formation yield the age-diagnostic *Hirnantia* fauna along with

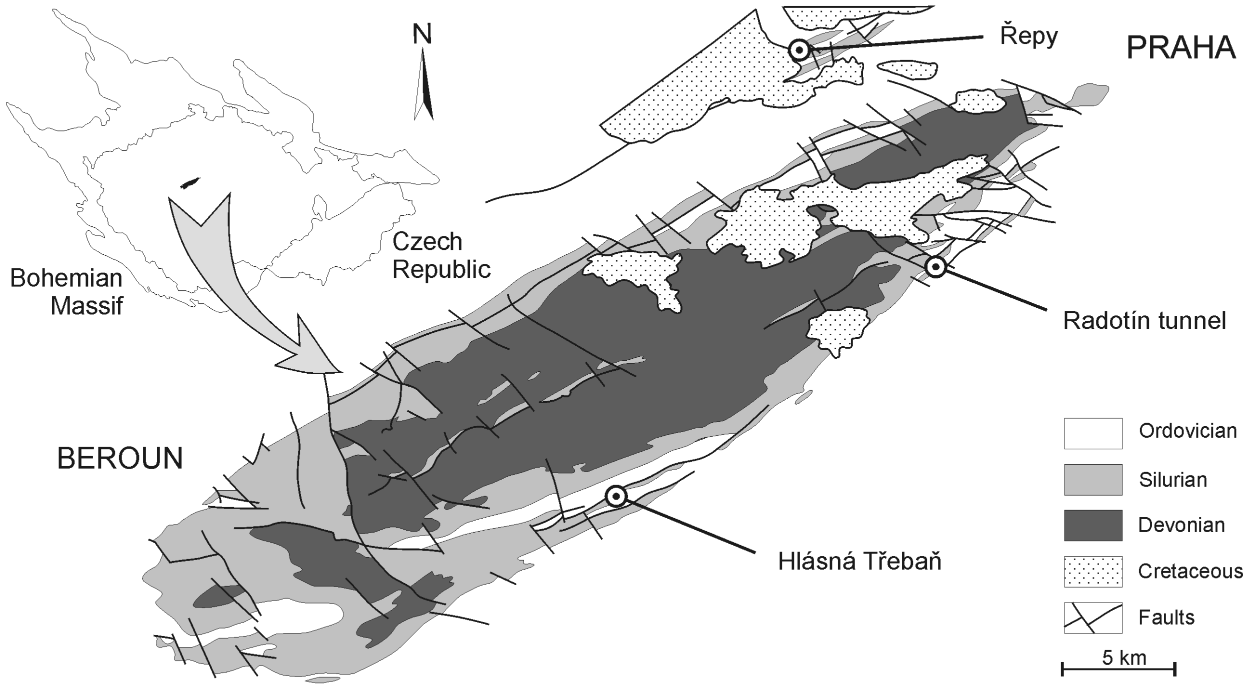

Fig. 1. Location of the sections referred to in the text.

the youngest Ordovician zonal index graptolite *Metabolograptus persculptus* (Štorch 2006). Hirnantian mudstones are abruptly but conformably overlain by anoxic black shales with abundant graptolites of the basal Silurian *Akidograptus ascensus* Biozone (Štorch 2006). Except in the northeasternmost part of the Prague Syncline (including the Prague-Řepy section), the black shale succession was interrupted by a hiatus (rather a long-term omission of sedimentation) in the upper part of the *Parakidograptus acuminatus* Biozone (Štorch 2006) which resulted in a biostratigraphically dated paraconformity in most of the sections (including the Hlásná Třebaň and Radotín tunnel sections). The hiatus is associated with a basin-wide facies of organic-rich silty-micaceous laminites which are gradually replaced by regular black shales during the upper Rhuddanian and lower Aeronian. The remaining part of the Rhuddanian and Aeronian succession, the Želkovice Formation, is composed of organic-rich black shales, siliceous shales and mudstones. Prolific graptolite fauna allows for high-resolution biostratigraphic dating and correlation of the strata. Graptolite mass-extinction and a prominent positive, stratigraphically well constrained carbon isotope excursion has been identified by Štorch & Frýda (2012) in the middle part of late Aeronian *Stimulograptus sedgwickii* Biozone in the Radotín tunnel section. The overlying Telychian succession, assigned to the Litohlavy Formation, begins with a thick bed of yellow-green mudstone, barren of graptolites. Graptolites from below and above the mudstone, indicating a correlation to the lower part of the *Spirograptus guerichi* (i.e. *Rastrites linnaei*) Biozone, suggest its earliest Telychian age (Štorch & Frýda 2012). The remaining succession of the early and middle Telychian Litohlavy Formation is formed by rhythmically bedded black shales and pale-coloured mudstones.

LOCALITIES

Radotín tunnel section

The sedimentary succession temporarily exposed in the highway tunnel north of Radotín, near Prague (Fig. 1), provided unique, unweathered material for detailed multidisciplinary studies. The black shale succession begins with the basal Silurian *A. ascensus* graptolite Biozone (Štorch & Frýda 2012; Fig. 2). A major part of the Rhuddanian record is missing due to a gap in sedimentation, but robust evidence based upon the rich graptolite fauna and excellent samples for TOC and carbon isotope analyses was obtained for the Aeronian and early Telychian part of the succession (Štorch & Frýda 2012; Fig. 2). A thrust fault terminated this subsurface section in the early Telychian *Spirograptus turriculatus* Biozone.

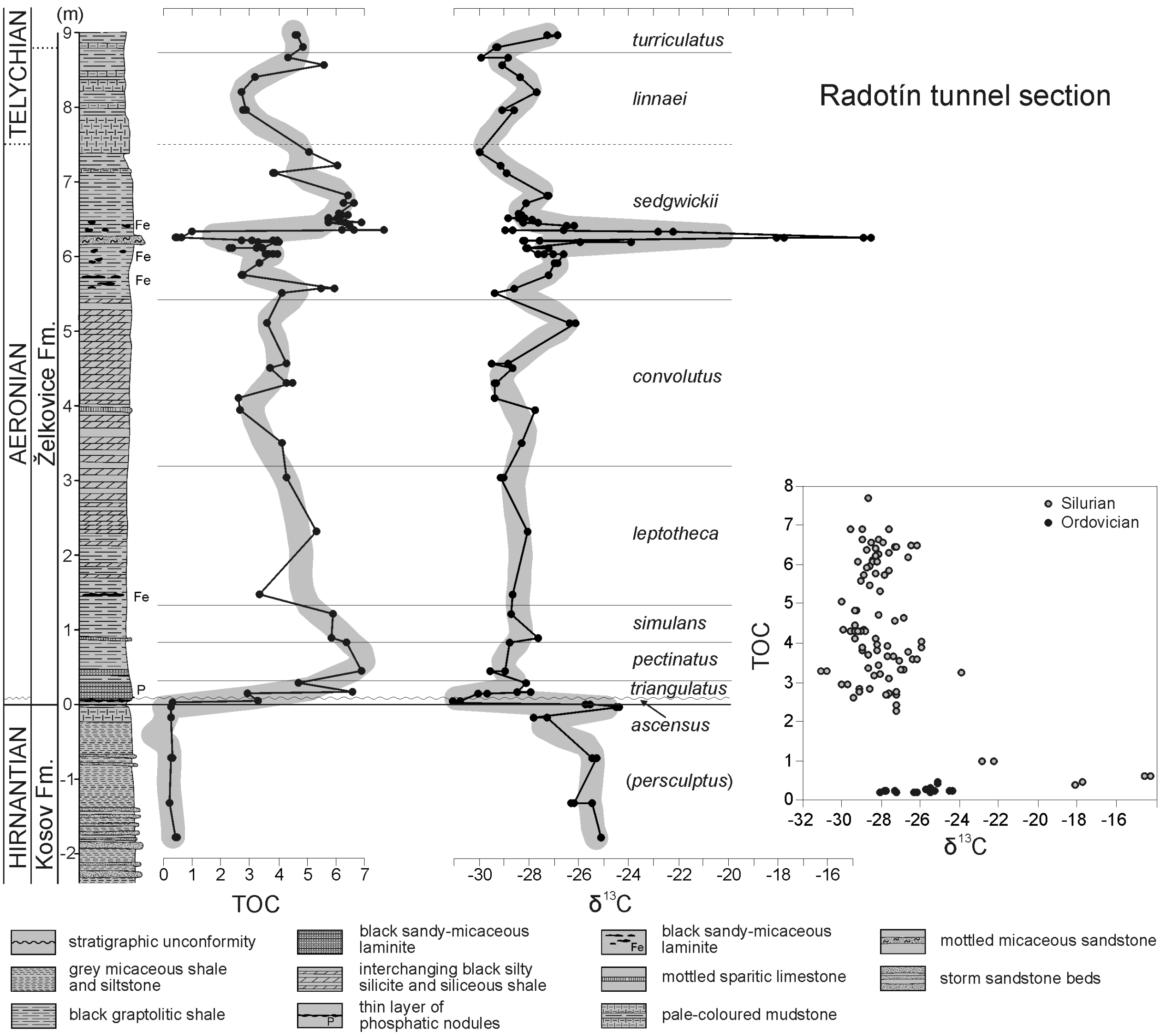

Fig. 2. The $\delta^{13}C_{org}$ record across the Radotín tunnel section of the Kosov and Želkovice formations (Barrandian area; northern peri-Gondwana) and relationship of $\delta^{13}C_{org}$ (‰ VPDB) and TOC (%) values. The grey line represents locfit regression.

Prague-Řepy section

This section, which consists of light-coloured uppermost Hirnantian mudstones with *Hirnantia* fauna and *M. persculptus*, mostly complete, graptolite-rich Rhuddanian black shales and a lower part of the Aeronian succession, was temporarily exposed due to building excavations in the 1980s (Figs 1, 3). The TOC and carbon isotope data were obtained from archived samples.

Hlásná Třebaň section

A Hirnantian, Rhuddanian and Aeronian sedimentary succession crops out on the hill side above the Berounka River (Fig. 1). Sampling covered the Rhuddanian black shales and sandy-micaceous laminites, lower Aeronian shales and middle Aeronian siliceous black shales and silty silicites up to the *Lituigraptus convolutus* Biozone. A Rhuddanian gap in sedimentation corresponds in age to the upper *P. acuminatus* and lower *Cystograptus vesiculosus* biozones (Štorch 2006; Fig. 4).

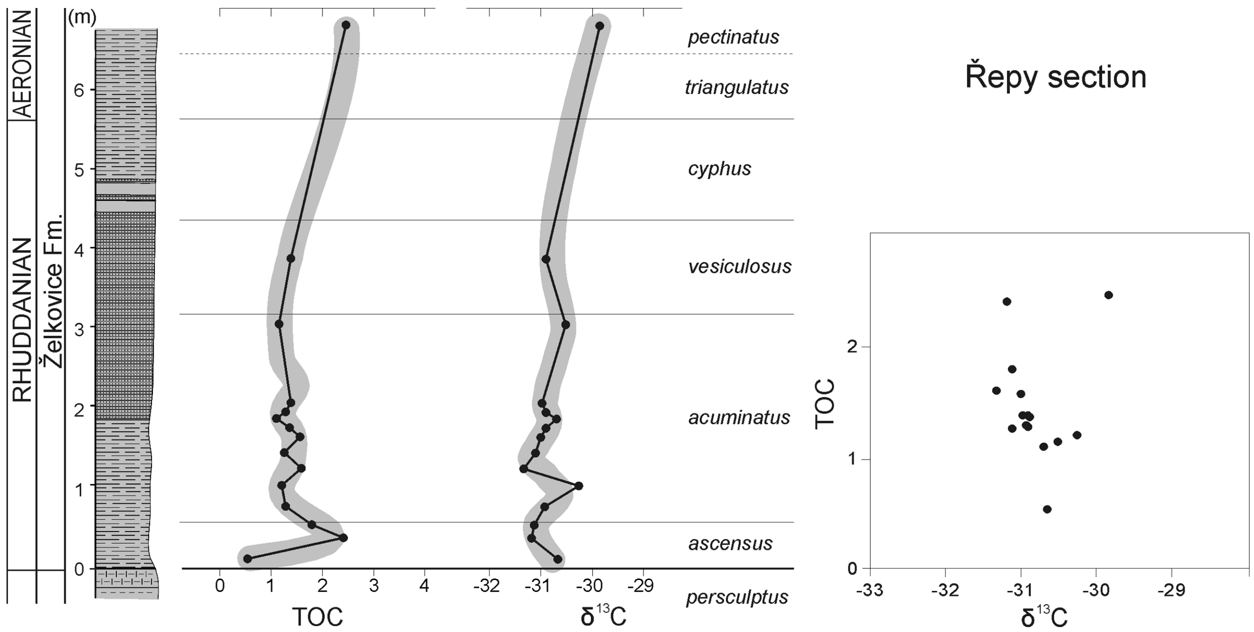

Fig. 3. The $\delta^{13}C_{org}$ record across the Řepy section of the Želkovice Formation (Barrandian area; northern peri-Gondwana) and relationship of $\delta^{13}C_{org}$ (‰ VPDB) and TOC (%) values. The grey line represents locfit regression. See Fig. 2 for legend.

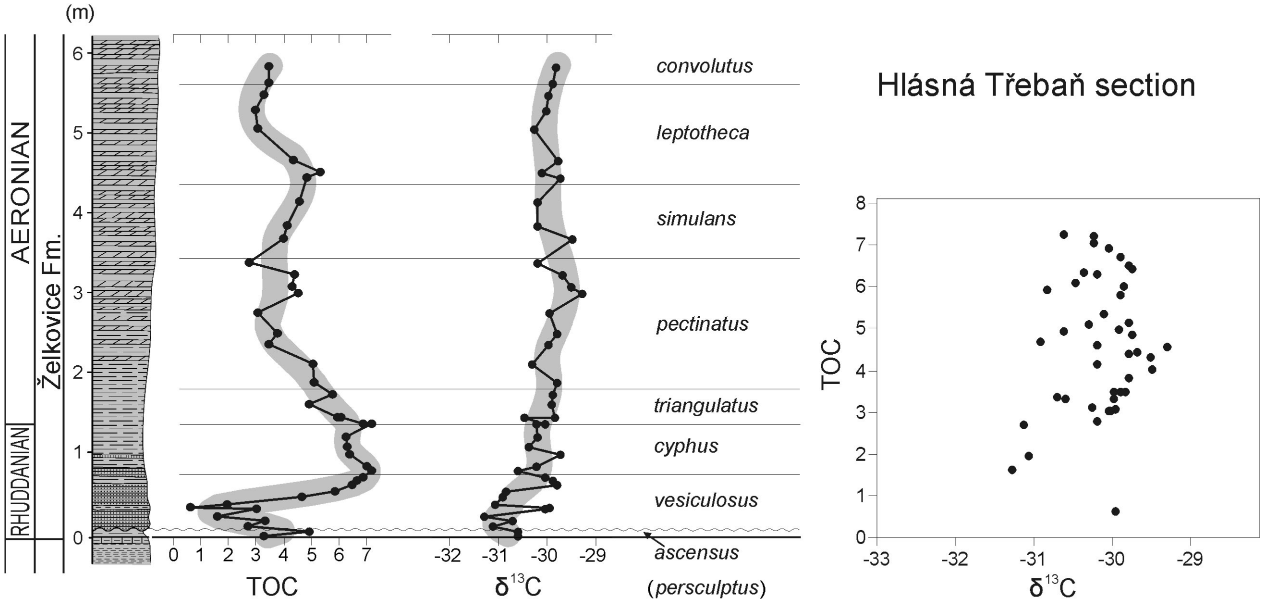

Fig. 4. The $\delta^{13}C_{org}$ record across the Hlasná Třeban section of the Želkovice Formation (Barrandian area; northern peri-Gondwana) and relationship of $\delta^{13}C_{org}$ (‰ VPDB) and TOC (%) values. The grey line represents locfit regression. See Fig. 2 for legend.

METHOD

A total of 168 samples were analysed for organic carbon isotopes and TOC, whereas 44 samples originated from the Hlásná Třebaň section, 15 samples from the Řepy section and 109 samples from the Radotín tunnel section. Hand specimens were cut and rock powder was prepared from a few grams of a fresh sample. A few milligrams of rock powder were taken for TOC and organic carbon isotope analyses. Before analyses, rock powders were decarbonatized with 10% HCl at 40 °C for several hours, then washed and dried. About 20 mg of rock powder was used for TOC and about 10 mg for isotope analyses. Samples were combusted in a Fisons 1108 elemental analyser coupled on-line to a Finnigan Mat 251 mass spectrometer via a ConFlo interface. As reference material, NBS 22 (Gulf oil, with $\delta^{13}C$ value –29.75‰ VPDB) and acetanilid (Analytical Microanalysis, UK) were measured. Accuracy and precision were controlled by replicate measurements of laboratory standards and were better than ±0.1‰ (1σ) for total carbon isotope analyses and better than ±0.02% (1σ) for TOC content. All $\delta^{13}C$ values were measured against Vienna Pee Dee Belemnite (‰ VPDB). Isotope trend lines were calculated using the nonparametric locally weighted regression method 'Locfit' (Loader 1999) which produces a 'smoothed' curve retaining the local minima and maxima.

RESULTS

The Ordovician–Silurian boundary

The Ordovician–Silurian boundary interval was studied in the Radotín tunnel section. It is characterized by a distinct change in $\delta^{13}C_{org}$ as well as in TOC values. Typical uppermost Hirnantian $\delta^{13}C_{org}$ values, about –26‰, decrease by about 6‰ to –31‰ in the lowermost Rhuddanian strata (*A. ascensus* Biozone). Similar $\delta^{13}C_{org}$ values from the *A. ascensus* Biozone were recorded in the Řepy and Hlásná Třebaň sections (Figs 3, 4). In the Radotín tunnel section this significant negative shift in $\delta^{13}C_{org}$ values across the Ordovician–Silurian boundary is linked to a rapid increase in TOC values, from about 0.25% in the uppermost Ordovician strata through about 2% TOC in graptolite-rich black shales just above the base of the Silurian, to ca 6% TOC in the lowermost Aeronian strata. Similar TOC values as in the Radotín tunnel section were recorded in the *A. ascensus* Biozone in the Řepy and Hlásná Třebaň sections, 0.7–2.4% and 3.3–4.9%, respectively.

Rhuddanian

The $\delta^{13}C_{org}$ values in the Řepy and Hlásná Třebaň sections rise slowly, from the *A. ascensus* Biozone to the end of the Rhuddanian, reaching $\delta^{13}C_{org}$ values of about –30‰ in the *Coronograptus cyphus* Biozone (Figs 3, 4). The TOC values in both sections are more variable. Starting from the *A. ascensus* Biozone, the TOC values vary about 1.5% for most of the Rhuddanian strata in the Řepy section (Fig. 3). On the other hand, the TOC values decrease from the *A. ascensus* Biozone to the middle of the *C. vesiculosus* Biozone (*P. acuminatus* Biozone is missing), and later a strong increase to values about 7% is maintained from the end of the *C. vesiculosus* Biozone through the entire *Cor. cyphus* Biozone in the Hlásná Třebaň section (Fig. 4).

Aeronian–early Telychian

Both $\delta^{13}C_{org}$ and TOC values in Aeronian to lower Telychian strata are more variable than those in the Rhuddanian. The $\delta^{13}C_{org}$ values fluctuate between –30‰ and –27‰ and the TOC values between 4% and 7%, with an exception of the late Aeronian *S. sedgwickii* Biozone where a distinct positive excursion in $\delta^{13}C_{org}$ was documented (Fig. 2). It is noteworthy that the $\delta^{13}C_{org}$ values from the *Demirastrites triangulatus* to *L. convolutus* biozones in the Hlásná Třebaň section are systematically about 1‰ lower than those in the Radotín tunnel section. The $\delta^{13}C_{org}$ values rapidly increase in about the middle of the *S. sedgwickii* Biozone, forming a strong positive $\delta^{13}C_{org}$ excursion with a peak shift, whereas TOC values drop temporarily (Fig. 2).

DISCUSSION

Analysis of TOC and $\delta^{13}C_{org}$ values did not reveal any statistically significant correlation between these two variables. This fact suggests no or very weak post-depositional overprinting of the $\delta^{13}C_{org}$ values which, therefore, could be interpreted as values of primary marine organic matter. Only two samples from the Aeronian *S. sedgwickii* Biozone with extremely high $\delta^{13}C_{org}$ values may represent an exception. These samples come from sandstones that have rather low TOC values (less than 1%) and much higher porosities than the surrounding graptolitic shales, which could make the alternation of carbon isotopic composition of primary organic matter easier. On the other hand, all Ordovician samples from the same section, having much lower TOC values than the above-mentioned Aeronian samples, have similar $\delta^{13}C_{org}$ values as the Silurian samples with high TOC values (Fig. 2).

A distinct negative shift in $\delta^{13}C_{org}$ values of about 6‰ was recorded between the last Ordovician (*M. persculptus*) Biozone and the first Silurian (*A. ascensus*) Biozone in the Radotín tunnel section (Fig. 2). Such a distinct negative shift in $\delta^{13}C_{org}$ values of about 4–6‰ has been recorded within the *M. persculptus* Biozone in several areas (Arctic Canada, South China and Scotland), well below the Ordovician–Silurian boundary (e.g. Melchin & Holmden 2006; Fan et al. 2009; LaPorte et al. 2009; Yan et al. 2009; Gorjan et al. 2012). This fact, along with firmground developed at the interface between the topmost Ordovician mudstone and black shale of the *A. ascensus* Biozone, may suggest that non-deposition occurred, which included the upper part of the *M. persculptus* Biozone in the Radotín tunnel section.

Our new data from the Barrandian area (northen peri-Gondwana) represent the first complete $\delta^{13}C_{org}$ record from the base of the Rhuddanian to early Telychian from this area. The $\delta^{13}C_{org}$ values from the Rhuddanian strata (Řepy and Hlásná Třebaň sections) show a small but statistically significant positive shift of about 1‰. The same trend has already been recorded from Arctic Canada (Cornwallis Island; Melchin & Holmden 2006), Scotland (Dob's Linn; Underwood et al. 1997) and northern Gondwana (Loydell et al. 2009, 2013) (see also Gouldey et al. 2010). On the other hand, new data confirm the absence of a distinct negative shift in the $\delta^{13}C_{org}$ record, which was found in the $\delta^{13}C_{carb}$ record close to the boundary between the *C. vesiculosus* and *Cor. cyphus* biozones in Baltica (Kaljo & Martma 2000) and Laurentia (Azmy et al. 1998). Therefore, the new data from northern peri-Gondwana, as well as published data from Laurentia (Arctic Canada), suggest that a distinct negative perturbance in $\delta^{13}C$ was restricted to shallow-water carbonate environments and did not affect the deeper-water organic carbon reservoir. The absence of the above-mentioned negative perturbance in deeper-water environments could also be explained by a gap in sedimentation, however, there are no lithological markers for it in the studied sections. In addition, such a gap should be rather long because of the residence time of carbon in the global ocean reservoir.

The $\delta^{13}C_{org}$ values from the Aeronian to lower Telychian strata show only one statistically significant $\delta^{13}C_{org}$ excursion at about the middle of the *S. sedgwickii* Biozone. This excursion is restricted to a period of distinct shallowing in the Barrandian area when also the first deposition of carbonates occurred in Silurian strata (Hýskov area; Havlíček & Kříž 1973; Šnajdr 1978; Kraft 1982; Štorch 2001). The late Aeronian $\delta^{13}C_{org}$ excursion as well as the associated *sedgwickii* Event in the Radotín tunnel section was recently analysed by Štorch & Frýda (2012).

It should be pointed out that two additional $\delta^{13}C$ excursions known from the Aeronian to lower Telychian interval (i.e. the early Aeronian positive $\delta^{13}C$ excursion and the early Telychian negative $\delta^{13}C$ excursion) were not recorded in the Barrandian area. Both $\delta^{13}C$ excursions are known from the carbonate reservoir (Baltica and Laurentia; Kaljo & Martma 2000; Põldvere 2003; Melchin & Holmden 2006), although a weak increase in $\delta^{13}C_{org}$ values recorded in the Cape Manning section (Arctic Canada; Melchin & Holmden 2006) may correspond to the early Aeronian $\delta^{13}C$ excursion.

CONCLUSIONS

1. The first complete $\delta^{13}C_{org}$ record from the uppermost Hirnantian to lower Telychian strata of the Barrandian area presented in this study revealed a similar evolution of the organic carbon isotope reservoir as recorded from other palaeoplates.
2. The lack of two Llandovery $\delta^{13}C$ excursions (i.e. the early Aeronian positive $\delta^{13}C$ and the early Telychian negative $\delta^{13}C$ excursions known from the carbonate carbon isotope reservoir) in the $\delta^{13}C_{org}$ record from the Barrandian area suggests a partially independent evolution of carbonate and organic carbon isotopic reservoirs.

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