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Přídolí carbon isotope trend and upper Silurian to lowermost Devonian chemostratigraphy based on sections in Podolia (Ukraine) and the East Baltic area

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Abstract. Insufficient knowledge of carbon isotope cycling in the latest Silurian initiated the study of two regions at the western and southwestern margins of Baltica in order to obtain a more complete picture about the carbon isotope trend through the Přídolí. Shallow and open shelf carbonate rocks of the Dniester River outcrops and Kotuzhiny core in Podolia and deep shelf rocks of the East Baltic area, especially the Lithuanian cores, were studied for bulk-rock isotope analysis. The data sets of both regions begin with the mid-Ludfordian excursion and include also some part of the lowermost Devonian. The data show a new minor twin positive $\delta^{13}C$ excursion (peak values 0.8–1.7‰) in the upper Ludfordian. The Přídolí carbon isotope trend begins with a low of negative $\delta^{13}C$ values, succeeded by the lower to middle Přídolí 'stability' interval (variable values below or close to 0‰ with a slight rising trend). The upper Přídolí begins with a medium to major excursion (peak values 2.3–4.5‰), which reflects the pattern of the carbon isotope trend on the west of the Baltica palaeocontinent. Its wider significance awaits confirmation from observations elsewhere. The carbon isotope excursion at the Silurian–Devonian boundary, named here the SIDE excursion (its $\delta^{13}C$ values range from 1.6‰ in deep shelf settings to 3.8‰ in shallower ones and 4.5‰ in brachiopod shells), has been traced on several continents, and now also in Baltica. This excursion can serve as a well-dated global chemostratigraphic correlation tool. The shape of the excursion indicates the completeness of the studied section. We conclude that carbon isotope chemostratigraphy may contribute to subdividing the Přídolí Series into stages and that Baltica *sensu lato* seems to be the right place for such a development.

Key words: carbon isotopes, chemostratigraphy, Přídolí, East Baltic, Podolia, lowermost Devonian.

INTRODUCTION

Carbon isotope studies in the Lower Palaeozoic, including chemostratigraphy, have been progressing notably during the last two decades. This is well marked by a series of publications of IGCP project 503 and earlier papers. Most of the Silurian papers discuss the Wenlock and Ludlow carbon isotope trends, but much less attention has been devoted to the Llandovery and the Přídolí. Insufficient knowledge of carbon isotope cycling through the latest Silurian seems a serious gap despite the shortness of that epoch. For this reason we returned to the excellent Dniester River outcrop sections in Podolia with their rich fossil content and continuous marine transition into the Devonian. Already the first comparisons of new data with those from the East Baltic showed several minor coincidences in trends (Ohesaare and Ventspils cores, Kaljo et al. 1998), but the two positive excursions noted in Podolia (Kaljo et al. 2009) were not observed in the Baltic sections. This raised several questions and we decided to check also the Baltic situation by study of more continuous drill core sections in Lithuania which penetrated deep shelf rocks of the Silurian Minija and Jura formations (Fms) and the much shallower marine Devonian Tilže Formation (Fm).

The main task of this paper is to present the results of the study of these two regions at the western and southwestern margins of Baltica in order to provide a more complete record of the carbon isotope trend through the Přídolí Epoch. These data would also enable adjustment of the generalized $\delta^{13}C_{carb}$ curve (Cramer et al. 2011), which, in part of the upper Přídolí, shows a small excursion but any reasoning is missing. Wishing to achieve firm linkage with earlier published trends, we began our study interval with the mid-Ludfordian (sometimes called the Lau) excursion and finished it at another excursion (named Klonk by Buggisch & Joachimski 2006) at the Silurian–Devonian boundary (= S/D below).

Our team at the Institute of Geology, Tallinn University of Technology, initiated carbon isotope studies in the mid-1990s. Involving colleagues from other countries, we have published $\delta^{13}C_{carb}$ curves for most of the Baltic Silurian System except for the Přídolí (see references). Recently Munnecke et al. (2010) compiled a comprehensive synopsis of the majority of those publications and thus a more detailed overview is unnecessary here. However, in addition to studies performed by our group on isotopes of the East Baltic Přídolí, papers by Azmy et al. (1998) and Žigaite et al. (2010) should also be mentioned. The former is a wider paper that documented only negative values from bioclasts collected from the rocks in the Kolka, Taurage, etc. drill cores. The latter, based on $\delta^{18}O$ analyses from the Geluva-99 core, identified a cooling episode at the junction of the Vievis and Lapes Fms (discussed further below).

The Silurian–Devonian chemostratigraphy of Podolia has been less discussed in publications. A pioneering paper by Azmy et al. (1998), mentioned above, reported results of 21 analyses of Silurian brachiopod shells from Podolia. Three of them revealed the early Wenlock $\delta^{13}C$ excursion, but eight bioclast and three rock matrix analyses from the Přídolí did not show any important isotopic shift. On the basis of 149 bulk rock analyses Kaljo et al. (2007) documented three global $\delta^{13}C$ excursions in the lower and upper Wenlock and upper Ludlow of Podolia, but the Přídolí was not studied. A recent paper by Malkowski et al. (2009), based mainly on 104 bulk-rock samples (in addition to eight brachiopod bioclasts) from the Silurian–Devonian transition interval, revealed a major positive carbon isotope excursion exactly at the systemic boundary, with the $\delta^{13}C_{carb}$ values reaching 4.1‰. This excursion has earlier been established in several localities on different continents (Andrew et al. 1994; Hladíková et al. 1997; Saltzman 2002; Buggisch & Joachimski 2006), which testifies to its value as a global marker excursion.

The above brief overview of carbon isotope studies shows that data sets concerning the Přídolí are rather scarce everywhere. Podolia seems the most promising region for improving knowledge of the latest Silurian carbon isotope trend. We started with the study of a drill core at the Kotuzhiny village, western Ukraine, and reported the preliminary results at the SSS Sardinia meeting (Kaljo et al. 2009). The current paper is an elaboration of these results that are complemented with a Baltic *sensu stricto* data set.

GEOLOGICAL SETTING

The two areas considered in this study were during the late Silurian parts of a larger sea on the western and southwestern margins of Baltica (Fig. 1). Two outcrop areas, Estonia and Gotland in the north and the Dniester River region (Podolia, Ukraine) in the south, are known as classical areas of Silurian rocks with a long study history. The subsurface areas in between (Latvia, Lithuania, east Poland, Belarus and north Ukraine) were studied in the course of different drilling projects. The youngest strata of Podolia (Skala Étage by Kozłowski 1929) were proposed in 1981 as a candidate for the fourth series of the Silurian System (Abushik et al. 1985).

The northern part of the basin embracing the East Baltic, Gotland and northeast Poland is a gulf-like pericontinental shelf sea, which at times in the early Silurian had epicontinental extensions towards the centre of the continent. Figure 1 shows the environmental situation in the early Přídolí when previously wide facies belts were considerably reduced due to late Silurian regression and step by step moved towards NE Poland. In the southern part of the basin (Podolia, Moldova), where facies distribution follows the pericontinental pattern, those territorial changes were less notable – facies belts were narrower and therefore the bathymetric and facies changes were more rapid. The environmental development of these two areas has several common features, but also differences (Einasto et al. 1986). The starting point of our study, the mid-Ludfordian sea level drop and accompanying events (e.g. extinction of several groups, $\delta^{13}C$ shift), is easily recognized in both areas, as is the following short-lived deepening episode in the latest Ludlow. The Přídolí sea level pattern is rather different in these areas – a general regression occurs in the north, but the situation is reversed in the Dniester River sections.

The section in Podolia begins with the uppermost Llandovery, ranges up to the end of the Přídolí and continues into the lower Devonian. The outcrop at the Dniester River and its tributaries was briefly described in Kaljo et al. (2007). In order to facilitate the reading of the paper, we include here a correlation chart (based mainly on biostratigraphy) presenting all needed stratigraphical terminology (Fig. 2). The terminology for the East Baltic and Gotland is rather traditional (Nestor 1997; Paškevičius 1997; Calner et al. 2004). More changes occur in the Podolian part – in general the unit names by Tsegelnyuk et al. 1983 (as in Kaljo et al. 2007) are used, but their orthography follows the recommendations by the International Stratigraphical Guide (Salvador 1994, chapter 3, B. 3). This means that the Ukrainian language is taken as a primary basis for spelling even if some cases seem arguable (e.g. Dzwinogorod by Kozłowski 1929, Abushik et al. 1985, Koren et al. 1989; Zvenigorod by Tsegelnyuk et al. 1983, Gritsenko et al. 1999; Dzv(w)enygorod by Malkowski et al. 2009). Still, in order to avoid repetition of the terminological

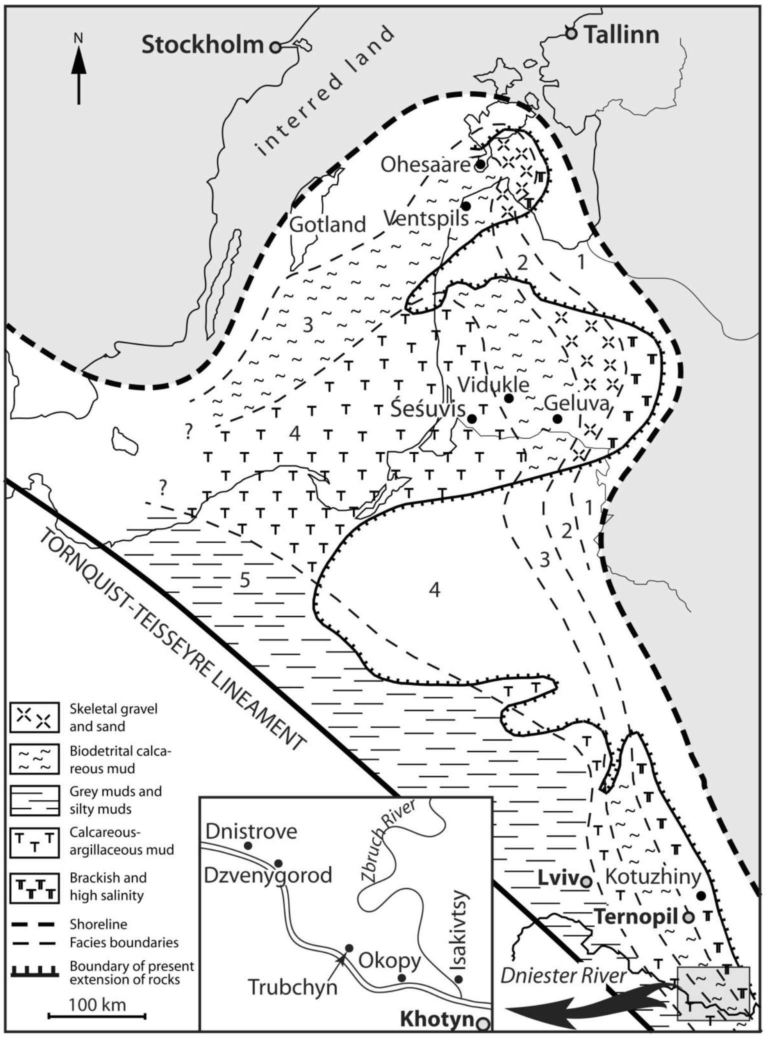

Fig. 1. Location of the studied sections and general facies zonation of the West Baltica marginal sea basin during early Přídolí time. Modified from Einasto et al. (1986) and Bassett et al. (1989). Facies belts (signature shows presence of sediments, white areas – postsedimentary erosion or no data): 1, tidal-flat–lagoonal; 2, high-energy shoal-bar; 3, open shelf, mid-ramp; 4, offshore shelf, outer ramp; 5, ramp/shelf depression.

content of the chart in Fig. 2, we show here, i.e. before the right place in the discussion chapter, the chemostratigraphical event or correlation lines. It should be noted that these lines caused only slight moving of a boundary line in the upper Přídolí. The locality numbers used in this paper follow those applied by Tsegelnyuk et al. (1983). The last paper noted also all known metabentonite beds (in the Isakivtsy – 3, Prygorodok – 6, Varnytsya – 2, Trubchyn – 2, Dzvenygorod – 1). Some of those are better studied (Huff et al. 2000; Kiipli et al. 2000) and are helpful for local correlation of sections (note several beds marked C_2 etc. in Figs 4, 5) revealing sampling gaps noted at some outcrops.

An initial suite of samples for this study was taken from a drill core near the Kotuzhiny village ca 35 km NNE from the town of Ternopil. The drilling site lies roughly 125 km north of the Dniester River, but facies belts following the configuration of the western margins of the Baltica landmass are also directed northwards (Fig. 1). The drilling partly penetrated very shallow-water facies (uppermost Ludlow to lower Přídolí), represented by dolomitic rocks with gypsum interbeds and obvious gaps. Higher in the Přídolí, the facies became gradually more marine, as evidenced by limestones, marlstones and even argillites with graptolites (*Monograptus uniformis*) occurring in the lowermost Devonian. This indicates that after a sea level low stand in the late Ludlow and earliest Přídolí, later during the Přídolí the Podolian basin experienced a continued transgression and deepening. The same general pattern occurs also in the Dniester River

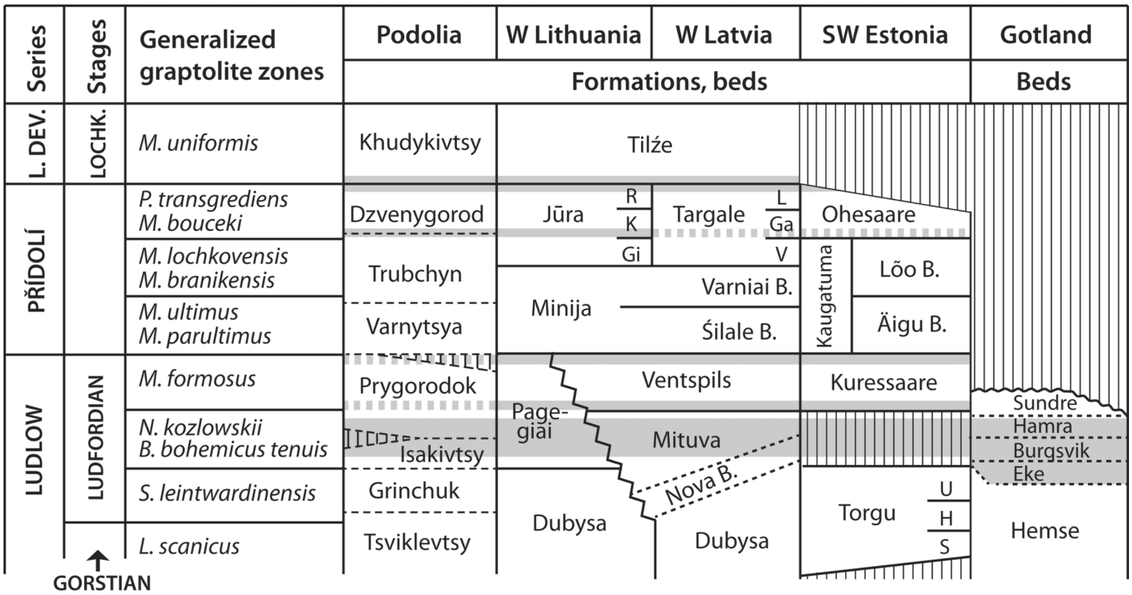

Fig. 2. Baltic–Podolian lithostratigraphical nomenclature and bio- and chemostratigraphical correlation chart. For explanations see text. Abbreviations: L. Dev. – Lower Devonian; Lochk. – Lochkovian; Beds in the Jura Fm: R – Rietavas, K – Kelme, Gi – Girdžiai; in the Targale Fm: L – Lužni, Ga – Garzde, V – Venzava; in the Torgu Fm: U – Uduvere, H – Himmiste, S – Sauvere. Generalized graptolite zones according to Koren et al. (1996). Grey lines (disruped when doubtful) are chemostratigraphic event or correlation lines, discussed in detail in the 'Discussion' section of the paper.

outcrops (Isakivtsy, Okopy, Trubchyn, Dnistrove, etc.) sampled for this study in 2010, but with one difference – the general facies situation was always slightly deeper than at Kotuzhiny, where graptolites are not found.

This is clearly demonstrated by the succession of benthic fossil communities described from the corresponding formations. As is well known, those communities are more or less depth-related, and occur alongside each other, being tied to certain facies belts (Boucot & Lawson 1999). Their temporal succession gives evidence of sea depth changes through consecutive time slices of basin history. Below, we quote some data from Gritsenko et al. (1999), indicating clearly the general trend of sea level changes in the Podolian basin during most of late Silurian time. It should be noted that such a pattern deduced from the distribution of fossil communities might be locally deformed by tectonic and basin fill processes (Munnecke et al. 2010).

The early Ludfordian Grinchuk Fm is characterized by representatives of the *Didymothyris didyma*, *Atrypoidea prunum* and *Dayia navicula* brachiopod communities, and the *Balizoma–Encrinurus macrourus* trilobite community belonging mostly to benthic assemblage (BA) 3, partly also to BA 2. The *Rhizophyllum gothlandicus* coral community, belonging to BA 2, occurs near the top of the Grinchuk Fm. The brachiopod communities may in some localities continue also into the lower part of the Isakivtsy Fm, but its upper part (containing only the trilobite *Acaste podolica*) and the Prygorodok Fm are practically barren beds. From the latter formation only stromatolites (BA 1) have been noted (Gritsenko et al. 1999). The lower Přídolí (Varnytsya Fm) has yielded brachiopods of the *Atrypoidea gigantus*, trilobites of the *Acaste podolica* and *Proetus scalicus* and cnidarians of the *Stelopora rara* communities, all belonging to BA 2. The Trubchyn Fm marks slight deepening, but is still rather shallow, as testified by the *Stegorhynchella pseudobidentata* brachiopod community (BA 2) and the *Lophiostroma schmidti* and *Endophyllum commodus* cnidarian communities (both BA 2–3). The Dzvenygorod Fm represents open shelf facies conditions, as shown by the *Dayia bohemica* brachiopod, *Calymene dnestroviana* trilobite and *Holacanthia socialis* coral communities (all BA 3, the last one also BA 4). The deepening of the basin continues also at the very beginning of the Devonian through the Khudykivtsy Fm, where besides open shelf (BA 3) brachiopods (*Ambocoelia praecox*) and corals (*Mucophyllum crateroides*) there occur deep shelf (BA 4–5) trilobites and a few graptolites (Gritsenko et al. 1999).

The Přídolí in the East Baltic area shows a general step-by-step regression and infilling of the basin with a specific complex of terrigenous–carbonate sediments. Nestor & Einasto (1997) defined this infilling dominating from the late Ludlow (the Kuressaare Age) up to the end of the Silurian, when the basin depression was filled by terrigenous material and in the open shelf area bioclastic marls replaced earlier limestones or partly even intercalate with skeletal sands in the shoal belt.

Two facies areas are represented in the East Baltic. Shallow-water belts occur in SW Estonia (Saaremaa Island) and north Kurzeme (Latvia); southwards follows a tectonic–erosional gap (Fig. 1) in distribution, but the above facies belts continue in eastern Lithuania. Deeper-shelf rocks occur mostly in western Latvia and Lithuania, continuing to the Kaliningrad region of Russia and NE Poland. For detailed stratigraphy of the Přídolí rocks and environmental zonation of the sedimentary basin different communities and biozones have been used, most efficiently microfossil ones (ostracodes, conodonts, chitinozoans and vertebrates). The corresponding papers are quoted in the text as needed, but a more detailed overview and references are available in the summarizing books by Raukas & Teedumäe (1997) for Estonia and by Paškevičius (1997) for Lithuania. Latvia is treated in both books, especially in the latter embracing the entire East Baltic.

METHODS

To achieve the goals of our study, the compilation of a general carbon isotope trend for the Přídolí in particular, analyses made at regular sampling intervals were required. For this purpose we analysed bulk-rock samples, not calcite from brachiopod shells, which are commonly considered to be better for isotope studies, but which occur too unevenly for such kind of research as our project.

Carbon and oxygen isotope analyses were performed by T. Martma in the Laboratory of Palaeoclimatology of the Institute of Geology at Tallinn University of Technology, using a standard method explained in more detail in Kaljo et al. (1997) and Martma et al. (2005). Here we note only that whole-rock samples were crushed, powdered and treated with 100% phosphoric acid at 70 °C for 2 h and analysed by the Delta V Advantage mass spectrometer with the GasBench II preparation line. All results were checked regularly against laboratory control samples and the international standard. The results are given in the usual δ-notation, as per mil deviation from the VPDB standard. Reproducibility of replicate analyses was generally better than 0.1‰.

The Silurian rocks used by us for carbon isotope analyses show very little or no late diagenetic overprint. The same observation has been made by SEM, cathodoluminescence and trace element studies (Azmy et al. 1998) and is supported by data on the conodont colour alteration index (CAI) from different parts of the East Baltic (Männik & Viira 2005) and southwest Ukraine (Drygant 1984). According to these authors, the CAI of the Silurian conodonts remains between 1 and 1.5, indicating that the rocks have been heated up to 50–60 °C or even up to 90 °C (Nowlan & Barnes 1987). In the light of the above data and earlier experience (Samtleben et al. 1996; Kaljo et al. 1997; Heath et al. 1998), showing that rocks are as a rule excellently preserved, we anticipated good results of carbon isotope analysis based on the bulk-rock samples also in our current Přídolí study. However, data from some cores show partial diagenetic alteration of rocks (Kaljo et al. 1997). Such a possibility should always be remembered.

RESULTS

The analytical data, lithology and stratigraphy of sections can be found in the figures and in Table 1 entitled ‘Carbon isotope data from the upper Silurian rocks of East Baltic and Podolia’ containing results of all 557 analyses made for this study. A great majority of these $\delta^{13}C$ values are depicted in Figures 3–7. Table 1 is available online at http://www.eap.ee/earthsciences. All localities are shown in Fig. 1.

Podolia

Kotuzhiny core

The $\delta^{13}C$ curve of the Kotuzhiny core (Fig. 3 and Table 1) begins with an early Ludfordian plateau of the $\delta^{13}C$ values (around 0‰) in the Grinchuk Fm. Such a dating is based on lithostratigraphy and similarity to the curve with the same plateau of values that was observed earlier in the Dniester outcrops just below the mid-Ludfordian positive excursion (Kaljo et al. 2007). However, the mid-Ludfordian excursion itself is missing in the Isakivtsy Fm and lower Prygorodok Fm of the core. Instead there occurs a negative shift, which is followed by a much larger negative excursion (called here the post-Prygorodok low; Fig. 3) embracing the upper half of the Prygorodok Fm and the first dolomite bed of the lower Varnytsya Fm. A maximum negative value of the low (–5‰) was measured within that bed. The biostratigraphical data available from the core section are too poor for precise dating of the negative excursion, but it seems obvious that the upper Isakivtsy Fm and the lower Prygorodok Fm (which elsewhere contain a major $\delta^{13}C$ excursion) are not represented due to a gap. The following intercalation of dolomitic and gypsum-bearing rocks demonstrates a highly variable negative $\delta^{13}C$ curve that in its lower part might be referred to the uppermost

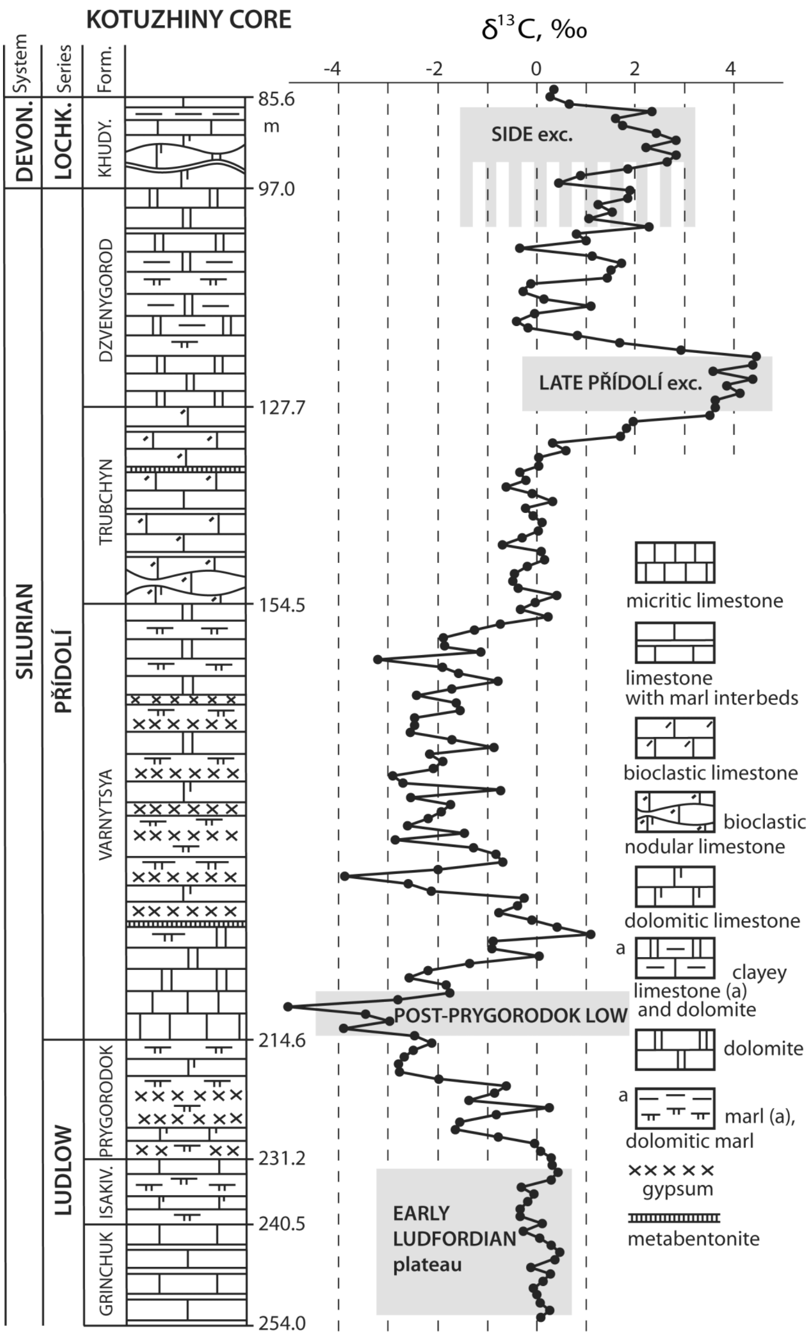

Fig. 3. Carbon isotope trend in the Kotuzhiny drill core: log and lithostratigraphy by V. Grytsenko and L. Konstantinenko (Geological Institute, National Academy of Sciences, Ukraine). For explanations see text. Abbreviations: Devon. – Devonian; Lochk. – Lochkovian; Khudy. – Khudykivtsy; Isakiv. – Isakivtsy. Grey belts mark isotope events, the striped belt is a questionable part of the SIDE.

Ludlow (see the 'Discussion' section). However, the current position of the lower boundary of the Přídolí, here tentatively identified on the basis of lithologies, is not confirmed either bio- and chemostratigraphically.

Higher in the section the $\delta^{13}C$ trend shows two 'plateaus' (based on a median trendline) of values. The lower 'plateau' in the Varnytsya Fm comprises highly variable values, mostly between –1‰ and –3‰ (mean value for the 'plateau' is –1.8‰). In the higher 'plateau', in the Trubchyn Fm, the values become more stable around 0 with a mean of –0.3‰, except in a few samples towards the top of the formation (Fig. 3). In these last samples a new $\delta^{13}C$ excursion begins with the highest value of 4.5‰ in the lowermost Dzvenygorod Fm. The falling limb of this excursion is rather steep and warrants attention. The following new recovery of the trend is rather variable, but shows a steady increase in the running mean values from about 0.3‰ to 1.6‰ just below the next more distinct shift (of 2.8‰) in the lowermost Devonian (Khudykivtsy Fm). An approximate distance between these two peaks (measured roughly between medians of the peaks) corresponds to the thickness of the Dzvenygorod Fm, i.e. about 30 m in this section. However, the exact beginning of the excursion at the S/D in the Kotuzhiny core remains somewhat debatable (see 'Discussion' below) because of the rising values of the $\delta^{13}C$ curve in the uppermost Silurian.

Dniester outcrops

The sampling for the $\delta^{13}C$ analyses was performed at the Isakivtsy-45, Okopy-46, Trubchyn-65, Dzvenygorod-West (located slightly west of Dzvenygorod; GPS: 48°32.471′N; 26°16.224′E) and Dnistrove-West (= Volkovtsy) outcrops. The last outcrop was recently studied also by Malkowski et al. (2009) (for comparisons see the 'Discussion' section).

The new data set (Figs 4, 5 and Table 1) begins with the mid-Ludfordian excursion (6‰) in the lower

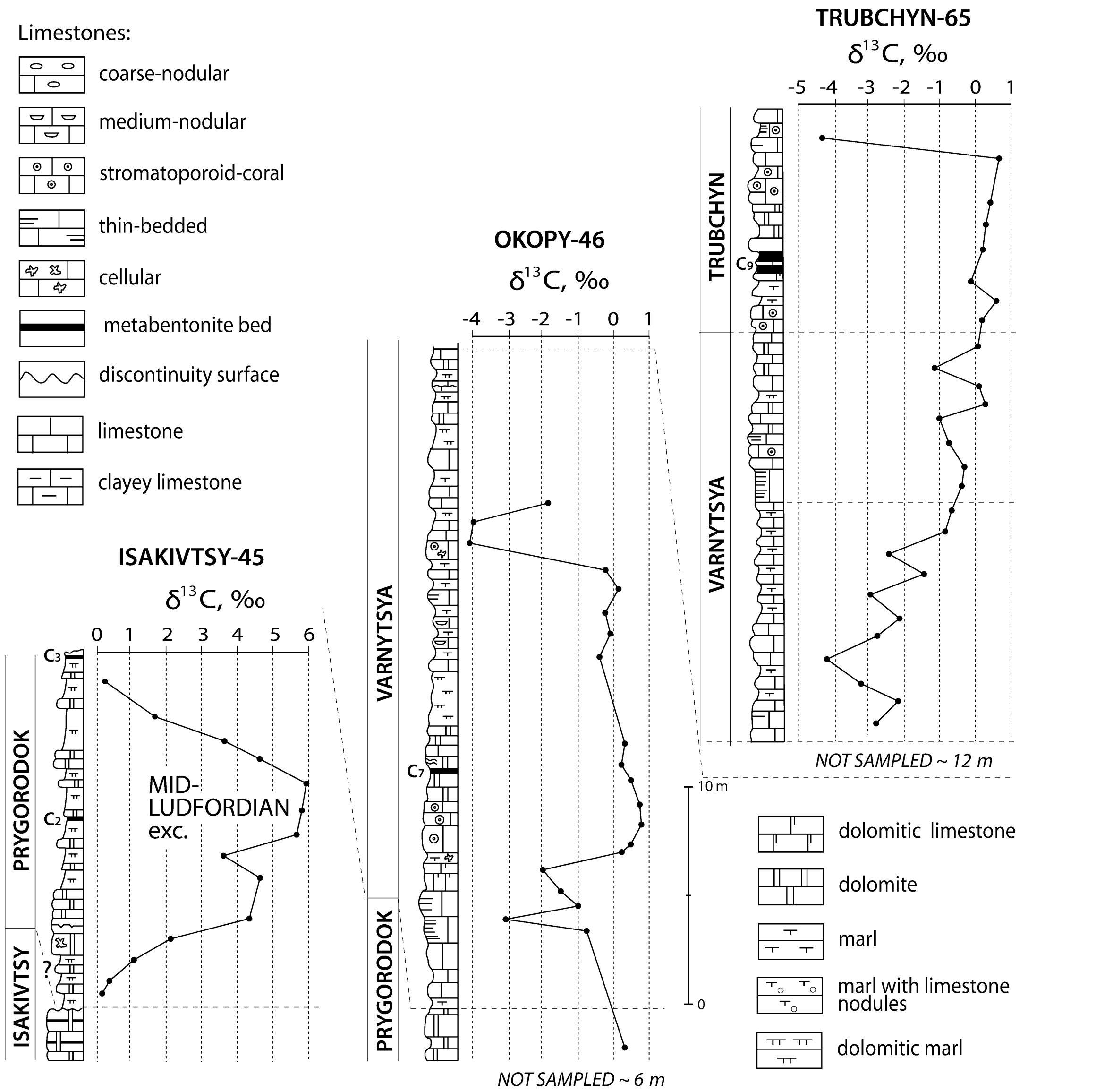

Fig. 4. Upper Ludlow and lower Přídolí $\delta^{13}C$ curves from the Dniester area. Log and lithostratigraphy from Tsegelnyuk et al. (1983). Note sampling gaps in the upper Prygorodok and within the Varnytsya Fms. For explanations see text.

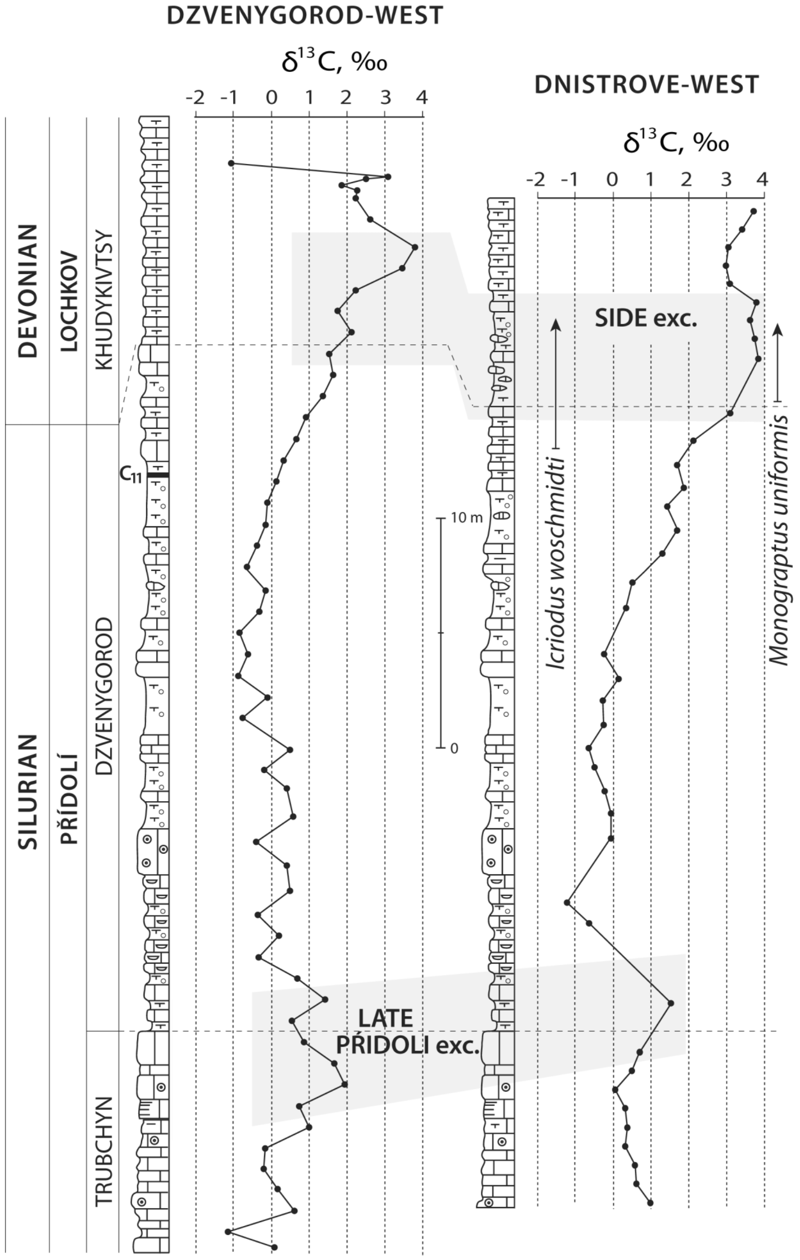

Fig. 5. Upper Přídolí $\delta^{13}C$ curves from the Dniester area. Log and lithostratigraphy from Tsegelnyuk et al. (1983). For legend see Figs 2 and 4.

Prygorodok Fm in the Isakivtsy-45 section (Fig. 4) and ranges upwards through the Varnytsya, Trubchyn and Dzvenygorod Fms, i.e. the entire Přídolí Series. Unfortunately there are three sampling gaps. The first one, embracing the upper Prygorodok Fm, is really significant, because it overshadows a transition from Ludlow to Přídolí (note the sampling gap in the bottom of the Okopy-46 section, Fig. 4). The other two (in the middle parts of the Varnytsya and Trubchyn Fms) seem not so disturbing thanks to data available from the Kotuzhiny core.

The carbon isotope data obtained from the Isakivtsy section (Fig. 4) display well the wide peak of the mid-Ludfordian excursion with its typically steep rising limb, occurring entirely within the limits of the Prygorodok Fm. This is at least half the formation higher than we expected on the basis of our earlier observations in the Dniester area (Kaljo et al. 2007), where the peak values of the mid-Ludfordian excursion were reached in the top of the Isakivtsy Fm or in the base of the overlying Prygorodok Fm. Surely this excursion cannot be diachronous; more likely such could be the litho-stratigraphical boundary or, even more likely, we can have here a dating error due to extreme muddy conditions of field work in a rainy June of 2010. Anyway, the peak is followed by a sampling gap (above the C_2 bentonite, Fig. 4) embracing the upper Ludfordian part of the Prygorodok Fm.

The $\delta^{13}C$ values identified through most of the Přídolí are generally low (close to 0‰) with a negative excursion (down to –3‰ in the lower Varnytsya Fm in the Okopy section, Fig. 4) and two positive excursions in the upper part of the succession. A minor peak (1.9‰) occurs (Fig. 5) close to the junction of the Trubchyn and Dzvenygorod Fms and a more prominent peak (3.8‰) ca 30 m higher (depending on the thickness of the Dzvenygorod Fm) at the S/D, which in the Dnistrove-West section is marked by the first appearance of *Monograptus uniformis*. As in the Kotuzhiny core, the carbon isotope excursion clearly begins within the upper Dzvenygorod Fm and has a rather long (ca 10 m) and steadily rising slope before the peak (Fig. 5).

In addition to the samples discussed above, we analysed 12 palaeontological samples collected previously from the Dzvenygorod-47 (= Zvenigorod-47 of Tsegelnyuk et al. 1983) locality where the ca 20 m boundary interval of the Trubchyn and Dzvenygorod Fms crops out. These samples were not exactly dated, but we were interested to see if the late Přídolí excursion is traceable also by random analysis. The result was positive – besides values typical of this interval (–1.5‰ to +0.9‰), two analyses gave the values 1.7‰ and 2.3‰ indicating the late Přídolí excursion. The latter is a peak value for this excursion in the Dniester area, but we cannot be sure about its exact place in the section.

Although the minor and major peaks have changed positions, their occurrence in the Dniester area confirms the findings in the Kotuzhiny core. The late Přídolí excursion was documented for the first time in Podolia. Biostratigraphically it is dated in the Dniester outcrops by the first appearance of new brachiopod (*Delthyris magna*, *Isorthis ovalis*), ostracode (*Kloedenia* aff. *leptosoma*), trilobite (*Calymene dnestroviana*) etc. associations (Gritsenko et al. 1999). The position of the S/D is well marked by the occurrences of *Monograptus uniformis* and *Icriodus woschmidti* in the Dnistrove-West section (Fig. 5), as well as by different fossils in several outcrops of the same age (Nikiforova & Predtechensky 1972; Tsegelnyuk et al. 1983; Abushik et al. 1985; Koren et al. 1989; Gritsenko et al. 1999).

East Baltic

Vidukle core

The late Silurian $\delta^{13}C$ trend is best seen and dated in the Vidukle-61 core (Fig. 6, Table 1), the Wenlock and Ludlow chemostratigraphy of which was described by Martma et al. (2005). The following intervals could be noted above the mid-Ludfordian peak (local stratigraphy in Fig. 2). The Ventspils Fm shows a rather unstable trend with two minor positive shifts at the bottom (1.4–1.7‰) and in the upper part (0.8‰). The Minija Fm is divided into two nearly equal parts: a wide negative excursion of $\delta^{13}C$ values (reaching –1.5‰) in the lower part (provisionally we call it the Šilale low) and a wide slightly rising plateau of values beginning some 10 m higher in the Varniai Beds. Within the Minija Fm the values remain mostly just below 0‰, in the Jura Fm, up to the middle of the Kelme Beds, mostly just above 0‰. The $\delta^{13}C$ trend ends in the Vidukle core with two minor excursions – the first in the upper Kelme Beds (max value 1.3‰) and the other 15–20 m higher at the S/D (in the Rietavas Beds 1.3‰ and in the Tilže Fm 1.6‰, see also the Discussion section). The most important biostratigraphical information is presented in Fig. 6, especially occurrences of *Ozarkodina crispa* in the Ventspils Fm and *O. remscheidensis* in the upper Jura Fm, defining the positions of the both minor carbon isotope excursions reported above.

Šešuvis and Ventspils cores

The Šešuvis curve (embracing the succession beginning with the uppermost part of the Minija Fm) was analysed to check the results from the upper Přídolí in the Vidukle core. As is obvious from Fig. 6, both $\delta^{13}C$ curves are in general rather similar – they show a long plateau in the main part of the upper Minija and Jura Fms and slightly raised values in the uppermost part of the latter. Differences are observed only in some details, partly caused by insufficient sampling. A general difference is that the $\delta^{13}C$ values in the Šešuvis curve are at least 0.5‰ lower than those in the Vidukle curve (see Table 1) which is in harmony with the known pattern (discussed in the last chapter).

The Ventspils $\delta^{13}C$ curve was first published by Kaljo et al. (1998). Its mid-Ludfordian excursion and two minor shifts in the Ventspils Fm repeat well the trend known from the Vidukle core (Martma et al. 2005), but the trend through the Přídolí is highly monotonous up to the very end of the Silurian (Fig. 6). The values remain close to 0‰, most of them on the negative side. Only the last sample from the Tilže Fm shows a rising trend (1.7‰). The negative values in the

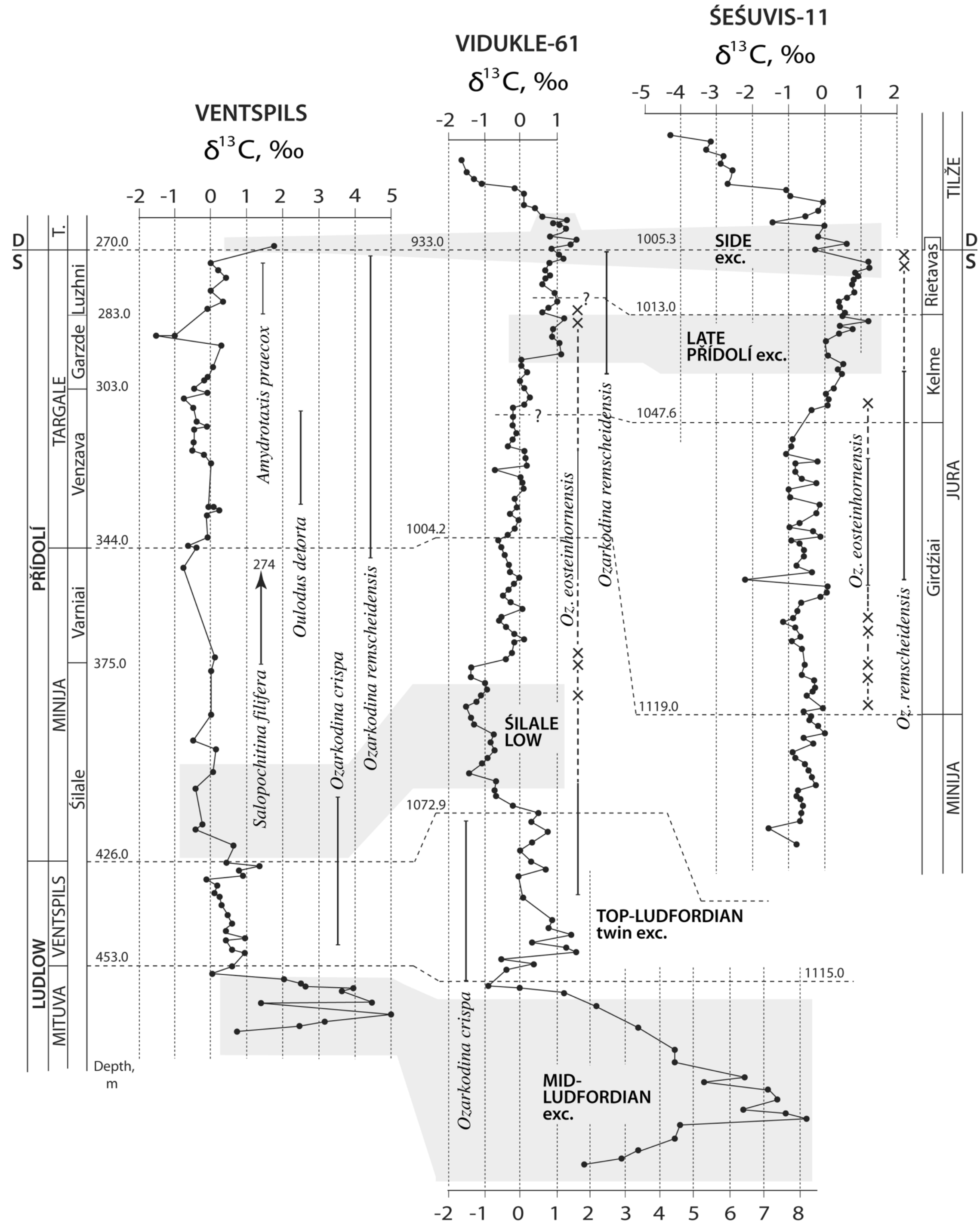

Fig. 6. Correlation of the Vidukle, Šešuvis and Ventspils $\delta^{13}C$ curves between the mid-Ludfordian and the Silurian–Devonian boundary (SIDE) excursions. Conodont information in Vidukle and Šešuvis is from Brazauskas (1993) and in Ventspils from Viira (1999, 2000). Note that binary nomenclature is used for economy of space. Chitinozoan data from Nestor (2011). The steady line shows continual occurrences, the broken line with x – single occurrences. Number 274 in the Ventspils part means that *S. filifera* continues up to this depth.

lower Minija Fm could represent some similarity with the Šilale low in the Vidukle core and elsewhere. The Ventspils section is well studied biostratigraphically (Gailite et al. 1987; Märss 1986, 1997; Viira 1999, 2000; Nestor 2009, 2011), but the δ^{13}C curve shows only parts of expected excursions. Despite of that correlation of sections within the Targale–Jura Fm is rather complicated and some additional biostratigraphical work is needed for more firm conclusions. Still, the facies position of the Ventspils drilling site is clearly shallower than that of the Vidukle site and some gaps could occur in the upper part, in the Garzde Beds in particular. This might be an explanation, but having *Oulodus detorta* in the Venzava Beds, it keeps a possible gap (and assumed excursion) very high in the Přídolí (cf. Viira 2000).

Ohesaare core, outcrop sections at Ohesaare and Loode

Ohesaare was the first drill core studied for carbon isotopes by the Tallinn team (Kaljo et al. 1997), but the Ohesaare Stage was not cored. A major δ^{13}C excursion was revealed in the upper Homerian, a negative one at the Wenlock–Ludlow boundary (known also in Wales, Corfield et al. 1992), and two gaps were detected in the Ludlow, among them one omitting the mid-Ludfordian excursion. Still, two minor shifts that could be called the top-Ludfordian or Ventspils twins are well expressed in the Kuressaare Fm (Fig. 7). The lower Přídolí Šilale low is also easily recognizable in the Kaugatuma Fm. New data from the Ohesaare stratotypic cliff section and a small exposure at Loode do not report anything new but complement the chemostratigraphic interpretation of the composite Ohesaare δ^{13}C curve (Fig. 7) with its wealth of biostratigraphical data (see references concerning the Ventspils section above; also, e.g. Sarv 1982). Values typical of the Přídolí low, measured in the cliff section and in the Loode outcrop, have an upward rising trend analogous to that in the Kotuzhiny core above the late Přídolí excursion. Based on this similarity, we locate the Ohesaare cliff in the composite section slightly above that excursion (Fig. 2). Biostratigraphical and chemostratigraphical correlations with the Ventspils curve (Fig. 6) seem relatively easy, but face the same difficulties as noted at this section.

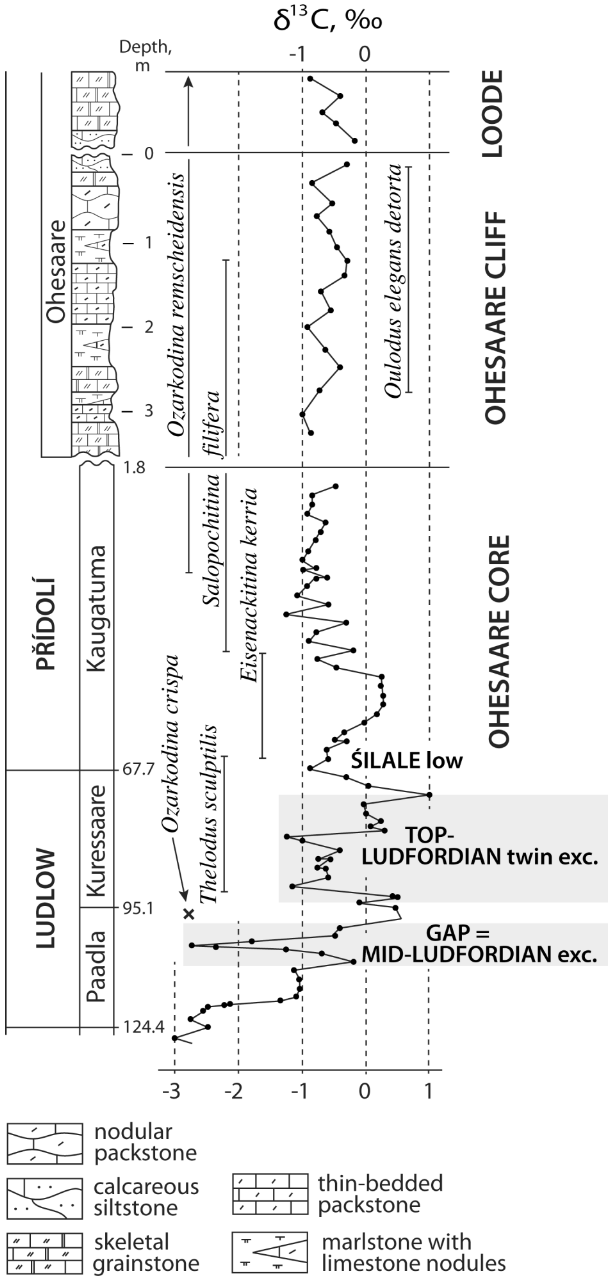

Fig. 7. Ludlow and Přídolí δ^{13}C curve from the Ohesaare drill core, Ohesaare cliff section and Loode outcrop south of the cliff on the Sõrve Peninsula. Note that calcareous siltstone beds in the top of the cliff and in the bottom of the outcrop are very similar. Conodont data from Viira (1999, 2000), chitinozoans from Nestor (2011) and vertebrates from Märss (1986).

DISCUSSION

The Ludlow carbon isotope trend above the mid-Ludfordian excursion

The uppermost Ludfordian in the East Baltic comprises the Kuressaare (a gap underlies it in parts of SW Estonia), Ventspils and part of the Pagegiai Fms (listed in the order of increasing water depth, Fig. 2), containing rather rich and distinctive shelly and microfaunal assemblages (see also Gailite et al. 1987). For example, those of the ostracodes *Plicibeyrichia numerosa–Undulirete baltica* (Sarv 1982; Gailite 1986); the thelodont *Thelodus sculptilis* (Märss 1997); the conodont *Ozarkodina crispa*

(Brazauskas 1993; Viira 1999); and the chitinozoan *Eisenackitina barrandei* (Nestor 2009). This interval has not attracted much attention in chemostratigraphy, although its position just above the mid-Ludfordian excursion is well defined. Moreover, a new revision of the East Baltic curves from this interval has revealed (Figs 6, 7) a variable $\delta^{13}C$ curve with two minor positive excursions. These top-Ludfordian carbon isotope twin peaks located within the Kuressaare–Ventspils interval just above the mid-Ludfordian excursion are rather specific in the actual context of the general carbon isotope trend and as such deserves to be identified as a separate chemostratigraphic unit.

Unfortunately the corresponding interval in Podolia (upper part of the Prygorodok Fm) was insufficiently sampled in the Dniester outcrops (Fig. 4) and the above pattern was not traced. In the Kotuzhiny core (Fig. 3) the Prygorodok–Varnytsya transition, where the mid-Ludfordian peak is missing, seems significantly affected by specific shallow-water conditions (occurrence of gypsum) that have resulted in the negative post-Prygorodok $\delta^{13}C$ excursion (–5‰). Another explanation might be that the above low should be considered wider – falling between a small positive shift in the lower Prygorodok Fm (depth 225 m, 0.3‰) and the one (depth 201 m, 1.1‰) just below a metabentonite interbed in the lowermost Varnytsya Fm (Fig. 4). This guess is based on the similarity of general configuration of the isotope curve in the Kotuzhiny and Ventspils cores above the mid-Ludfordian excursion (Fig. 6). The Kotuzhiny core provides also a good possibility for testing this suggestion – sanidine and other XRF analyses (Kiipli et al. 2008) should define whether the bentonite bed mentioned is No. 6 (at the Prygorodok–Varnytsya boundary) or No. 7 occurring slightly higher. Such a test will be performed as soon as possible.

On the other hand, the Okopy isotope curve (Fig. 4) shows a negative excursion at the bottom of the Varnytsya Fm and in this respect is similar to the Kotuzhiny curve – perhaps the 'top-Ludfordian' twin peak excursion is in the lower Varnytsya Fm of the Okopy-46 section. Some similarities of the trend could be seen even in the Vidukle core, where at the bottom of the Minija Fm the Šilale low is trending in the same way. Those observations make the interpretation of the Prygorodok–Varnytsya transition in the Kotuzhiny core highly doubtful and it is possible that there are two successive negative excursions of different origin.

Parameters of the Přídolí excursions

The late Přídolí excursion was first described by Kaljo et al. (2009) in the Kotuzhiny core (Fig. 3). The $\delta^{13}C$ value 4.5‰ measured at the junction of the Trubchyn and Dzvenygorod Fms remains the highest among those obtained from the samples analysed for checking the same level in the Dniester area outcrops (Fig. 5; max value 2.3‰) and in Lithuania, in the Kelme Beds of the Minija Fm (Fig. 6; max value 1.5‰). The corresponding rocks analysed in the Kotuzhiny core represented the shallow to open shelf, and the Lithuanian ones deep shelf facies. Rock samples of the Dniester area are somewhere in between, but closer to the deep shelf. A pattern of decreasing values from inshore to open sea area is obvious and expected based on earlier Silurian experience (see the next section).

The carbon isotope excursion at the S/D seems to demonstrate the same pattern as above. The following values were recorded: Kotuzhiny core 2.8‰, Dniester outcrops (Fig. 5) max value 3.8‰ (from Dnistrove-West also data by Malkowski et al. 2009 max $\delta^{13}C_{carb}$ value 4.1‰, $\delta^{13}C_{brach}$ 4.5‰) and Lithuanian cores – max 1.6‰ just below the S/D in the Rietavas Beds (Fig. 6, Šešuvis) and above it in the Tilže Beds in the Vidukle core. Two aspects are surprising here. The first is the only ca 0.5‰ difference of values measured from bulk-rock and brachiopod valves. Baltic Ordovician and Silurian data have shown a much greater difference (e.g. 2.3–3.3‰ in the Stirnas core, Hints et al. 2010). Another unexpected result is the relatively low value in the Kotuzhiny core, which, according to the trend highlighted above, as the shallowest locality should have the highest $\delta^{13}C_{carb}$ values.

The carbon isotope excursion at the S/D has been named differently. Several authors use the above long name, which is surely an exact, but a rather long expression. Some have taken the Klonk Bioevent as a basis and formed a new term – the Klonk isotope event and/or excursion (Buggisch & Joachimski 2006). Such a method of naming $\delta^{13}C$ excursions has been in use in the Silurian, but some discords or inaccuracies have lessened this practice (Kaljo et al. 2003; Loydell 2007). The names based on stratigraphy are more rational and if these are not too long, we prefer this method. In the case of longer names Bergström et al. (2006) suggested HICE and similar terms that are rather convenient for use. Applying this model, we suggest to use 'the positive $\delta^{13}C$ excursion at the Silurian–Devonian boundary' or 'the SIDE excursion' in acronym form.

The shape of the studied carbon isotope excursions

The general shape of the Přídolí $\delta^{13}C$ curve, especially that of the two positive excursions of the Kotuzhiny section, is rather different from those of the Dniester outcrops and also the Lithuanian ones. The Kotuzhiny curve has rapidly rising peaks with steep slopes and excursions are therefore easy to define. The same excursions in the Dniester sections are of considerably smoother configuration with long slowly rising (or falling) slopes and lower peak values. Therefore the Dniester excursions are much less distinct. This may become a problem when one wishes to use the carbon isotope signal as a correlation marker.

As mentioned above, the Kotuzhiny core represents shallow-water facies conditions even if the Podolian basin experienced a deepening episode during the late Přídolí. The presence of lower $\delta^{13}C$ values in deeper-water facies is a well-known pattern discussed in several papers (e.g. in the early Wenlock by Kaljo et al. 1998; Munnecke et al. 2003; Loydell 2007), even if not fully understood, but the steep slopes of excursions in near-shore facies seem to be of different origin. Many high peaks are linked to shallow-water rocks or mark wider eustatic events, e.g. the mid-Ludfordian excursion (Wigforss-Lange 1999; Martma et al. 2005; Munnecke et al. 2010). However, this huge excursion may be missing in the section due to a gap created by too deep regression of the shoreline, e.g. in the Ohesaare core in Estonia (Kaljo et al. 1997) and in the Kotuzhiny core, described here. It is logical to think that sea level oscillations in the nearshore area, causing big gaps in sections that eliminate long intervals of $\delta^{13}C$ curves, can also modify the peak configuration by making it steeper.

From this point of view smooth carbon isotope curves (like the Dniester and Lithuanian ones) should be considered to be the most continuous, with a good chance of providing a full account of a global (or smaller) carbon isotope event. Steep-sided peaks are or might be in this sense less representative, though more distinctly limited. Correlation of the boundaries of different types of peaks seems complicated, but some details of the curve may be helpful.

General pattern and peaks of the Přídolí $\delta^{13}C$ curve extending into the Devonian

The previous paragraphs highlighted the main characteristics of the carbon isotope trend through the Přídolí of Podolia and the East Baltic area. In order to get a clear idea about the most common aspects, these are summarized here.

In Podolia (Figs 3–5) the $\delta^{13}C$ trend begins with a post-Prygorodok deep low of values, which apparently marks a gap and may be complicated by a smaller negative excursion at the bottom of the Varnytsya Fm. The following two thirds of the Přídolí shows a long line of variable but generally low values. Considering the trendline, it can be described as a two-stepped rising plateau of low values through the Varnytsya (mean –1.8‰ in Kotuzhiny) and Trubchyn (–0.3‰) Fms. The upper third of the section displays two solid peaks: the first at the junction of the Trubchyn and Dzvenygorod Fms and the second at the top of the latter formation, continuing into the Devonian (Fig. 5). New data from the Dniester basin show that the upper Přídolí $\delta^{13}C$ peaks are considerably lower (~2‰) in deeper-water settings than in the shallower Kotuzhiny area.

Baltic data reveal very much the same situation. The lower Přídolí (Kaugatuma, Minija and lower Jura/Targale Fms) shows mostly a stable plateau-like trend of values varying within 0.5–1‰ and having an upward rising trend. The Šilale low (near to –1‰) occurs in the lowermost part. Values are higher in the upper Minija Fm and slightly higher also in the Jura/Targale Fms, but still remain close to 0‰. Two minor excursions occur in the uppermost Přídolí (upper Jura Fm) – one in the Kelme Beds and another at the top of the Jura Fm (see a comment at the very end of this chapter), continuing into the bottom of the Tilže Fm and so marking the S/D.

Summarizing these new data from the Přídolí of the East Baltic and Podolia, despite some local differences in values and trends, it is possible to define the general pattern of carbon isotope changes. This process was rather stable (partly variable but low-level values were close to 0‰ or below) during most of the first two thirds of Přídolí time. Two minor to medium-size (exceptionally major) positive $\delta^{13}C$ excursions followed at the beginning and top of the late Přídolí with a continuation into the Devonian, evidencing that the carbon cyclic development had become labile again by the end of the Silurian Period.

Such a pattern of carbon isotope changes in the Přídolí – a secular beginning and a brief cyclic end – is in principle similar (when not considering time differences) to analogous processes in the Ordovician and earlier Silurian. The duration of the Přídolí was usually given as 2 Ma, nowadays 2.7 Ma (International Stratigraphic chart 2010 available on the IUGS ICS website) which is a rather short time interval, commonly more suitable for a stage. In shallow and mid-shelf areas (SW Estonia, Podolia) the thickness of the Přídolí rocks remains below 150 m, whereas deep shelf rocks are 250 m and more thick in SW Lithuania in the limits of the Baltic–Polish depression and even 500 m close to Kaliningrad (Paškevičius 1997). The last figures are reliable and allow recognition also of some smaller details on the isotope curve, which are hardly visible in the case of condensation of a section.

These remarks were needed in order to introduce another aspect of Přídolí chemostratigraphy. Figure 5 demonstrates a relatively long stratigraphical distance between the late Přídolí and SIDE excursions in the Dniester outcrops, even if defining the exact boundary level may be problematic. In the Kotuzhiny core (Fig. 3) the lower boundary of the SIDE is even more debatable and the stratigraphical difference might be even smaller. And finally, in Lithuanian sections (Fig. 6) the distance between the two named excursions is nearly missing or, more correctly said, overshadowed to such an extent that it might be better to treat them as one wide excursion embracing the latest Přídolí and earliest Lochkovian. This seems a good idea, when one is studying only the Vidukle and Šešuvis trends, but having seen the Podolian sections with the separately placed late Přídolí and SIDE excursions, we prefer to keep them apart and to look for explanations of their proximity in some sections.

Some correlations within the western margins of Baltica

The main idea of including chemostratigraphic time lines in Fig. 2 was to demonstrate the possible use of $\delta^{13}C$ correlation of detailed time slices or datum planes. Our data show that this method can work well in the upper Ludlow and Přídolí. However, this correlation chart is far from being exact, e.g., concerning the positions of some Baltic unit boundaries (the topmost ones in particular) as related to those of graptolite biozones, the position and extent of gaps, the age of the Sundre Beds, etc. Biostratigraphy should be widely applied to get a trustworthy chart, at least more reliable than was possible in our case.

In terms of the East Baltic Silurian, the late Přídolí excursion might occur somewhere at the bottom of the Ohesaare Stage, as indicated by biostratigraphical correlations of the Dzvenygorod Fm (Abushik 1983; Abushik et al. 1985; Kaljo 1987; Koren et al. 1989; Nestor 2011). New $\delta^{13}C$ data from the Ohesaare cliff section (see above) seem to support this conclusion, but some additional studies are needed to enhance its reliability.

Žigaite et al. (2010) observed an interesting $\delta^{18}O$ shift (–19.2‰) in the Geluva-99 core (location in Fig. 1) at the junction of the Vievis and Lapes Fms of Lithuania. It is not yet clear how this might be correlated with the $\delta^{13}C$ excursion discussed here, but some considerations could be noted. Several earlier authors described a parallel development of carbon and oxygen isotope curves (Samtleben et al. 1996; Brenchley et al. 2003), but opposite statements are also common and wider analysis shows that both scenarios are possible (Munnecke et al. 2010). So, a positive $\delta^{13}C$ shift might (but should not) be expected.

According to common views (Paškevičius et al. 1994; Paškevičius 1997), the Vievis and Lapes Fms occupy in the Přídolí correlation charts the same position in the shallow shelf area in central Lithuania as do the Minija and Jura Fms in deeper environments in the west. Their boundaries are considered to coincide; only the uppermost Silurian beds are missing at the top of the Lapes Fm (Karatajute-Talimaa & Brazauskas 1994). Based on this correlation, we should conclude that the $\delta^{18}O$ shift described by Žigaite et al. (2010) cannot be linked to the late Přídolí $\delta^{13}C$ excursion identified high in the Jura Fm (Kelme Beds). This conclusion is supported by conodont occurrences recognized in the Vidukle and Šešuvis cores (Fig. 6) – the excursion in the Kelme Beds occurs within the *Ozarkodina remscheidensis* Biozone, not clearly below it as does the oxygen excursion in the Geluva-99 core. Lower down, including the Minija–Jura boundary interval, the $\delta^{13}C$ curve is variable but low-level plateau-like in the named west Lithuanian core sections, making it impossible to identify any small variation that could be connected with an oxygen isotope shift.

Correlations with excursions observed elsewhere and possible links to some environmental agents

Beginning with papers by Andrew et al. (1994) from Australia and by Schönlaub et al. (1994) from Europe, a medium to major $\delta^{13}C$ excursion at the S/D (here named the SIDE) became well known from several areas of the world, in particular those of Europe (Hladíková et al. 1997; Buggisch & Joachimski 2006; Malkowski et al. 2009) and North America (Saltzman 2002; Kleffner et al. 2009). Even such a limited list of selected publications indicates that the SIDE is a global event occurring exactly at a major chronostratigraphic boundary and testifying to the isochroneity of this boundary but also that it is itself isochronous as proved by biostratigraphy. In general terms the results are trustworthy, and only a couple of details should be noted below, but it would be more important to ask why such a global event in carbon cycling occurred at a level at which a biozonal index graptolite species appeared (www.stratigraphy.org/GSSPs).

Some of the authors mentioned above answer this question in a manner referred to below, but still having in mind only their own object of study. For example, having studied the S/D stratotype (GSSP) section at Klonk in the Barrandian (Czech Republic), Hladíková et al. (1997) compiled a detailed $\delta^{13}C$ curve for the 12.5 m interval of transitional beds from the uppermost Přídolí to the lower Lochkovian. The values increased up to 2.4‰ in bed No. 19 just below the GSSP level (bed No. 20) in the Přídolí part of the excursion, a maximum (3.6‰) was reached ca 7 m higher in the Devonian, but the falling limb was not reached. The authors suggest that this $\delta^{13}C$ excursion was caused by a combination of higher productivity, increased deposition of organic matter and shallowing of the basin (Hladíková et al. 1997).

Saltzman (2002) discussed three $\delta^{13}C$ curves from North America representing the sections in the central Appalachian Mountains (West Virginia), Great Basin (Nevada) and the Mid-continent (Oklahoma). In Virginia a much thicker interval of Silurian–Devonian transition was studied; thus a rather wide excursion occupies ca 50 m of the section. The peak value (5.1‰) is reached ca 10 m below the S/D. In Nevada the excursion ranges for ca 40+ m (upper part is covered), and the peak value is reached ca 10 m above the S/D level. The Oklahoma curve is partly truncated (Saltzman 2002) and therefore not discussed here. In all cases the S/D position is well constrained by occurrences of *Icriodus woschmidti*, the *Ozarkodina remscheidensis* group and *Monograptus uniformis*. Saltzman (2002) links seawater $\delta^{13}C$ enrichment to a eustatic drop during the Silurian–Devonian transition, due to enhanced carbonate weathering during exposure of platform areas, as well as to an increased burial of organic carbon in the same time interval in Gondwana basins (Flügel et al. 1977; Hladil 1991).

Buggisch & Joachimski (2006) discussed the SIDE excursion in a general manner, based on data sets from the Barrandian and the Carnic Alps (Schönlaub et al. 1994; Hladíková et al. 1997). They noted a faunal change at the S/D and two *Scyphocrinites* blooming events just before it, all of which could be correlated with the major SIDE excursion at the boundary. Deposition of organic carbon-rich sediments, occurring in the S/D interval, took place in deeper shelf settings (Hladil 1992). However, Buggisch & Joachimski (2006) support those authors (Hladíková et al. 1997; Saltzman 2002), indicating a sea level low stand for the latest Silurian on Laurentia and Baltica, leading to the enhanced erosion of carbonate platforms. Summarizing all Silurian–Devonian transition and Devonian data, they underline that the combination of sea level changes, weathering intensity, nutrient supply, organic carbon production and climate is assumed to be a driving force of the carbon isotope excursions.

The work by Malkowski et al. (2009) was based on the same outcrop at the Dniester River banks as our study and some comments were provided above. Here we quote only their summarizing statement about environmental aspects as follows: 'The global biogeochemical perturbation across the Silurian–Devonian transition reflects a complex combination of palaeogeographical, biogeochemical and evolutionary processes in the late Caledonian geodynamic setting, with a likely undervalued role of the expanding vegetation …' (*op. cit.*, p. 674). This point of view is the most general one among those presented above and without doubt correct. However, turning to more detailed approaches, we are obviously rather far from a generally accepted understanding of processes of global carbon cycling and its driving forces. All mentioned authors list sea level dynamics resulting from a complex of environmental processes. This is a commonly accepted point of view; however, let us test it at the S/D.

In the text above we quoted several localities where a major global $\delta^{13}C$ excursion has been established, which in most cases begins in the uppermost Silurian and continues to some extent into the lowest Devonian (see also below). In some areas of Laurentia Saltzman (2002) reported a eustatic sea level drop at the S/D. In the East Baltic the Přídolí shows a long-lasting step by step regression, which most likely is not a eustatic process that peaked at the S/D (Nestor & Einasto 1997). In Podolia, on the other hand, the second half of the Přídolí is transgressive, with maximum flooding noted in the lowermost Devonian (Predtechensky et al. 1983). The same tendency was well documented in the Kotuzhiny core by Kaljo et al. (2009) (Fig. 3) and noted also by Skompski et al. (2008). Walliser (1995) discussed the S/D Event among the Devonian global events and classified it as a minor but globally traceable event. In the boundary type section (Klonk, Barrandian) the S/D lies within a monotonous sequence without any serious facies change (Hladil 1992). Still, Walliser (1995) mentions several localities of the Bohemian facies realm (Carnic Alps, Sardinia, Moroccan Meseta) and European Variscides where some lithological changes mark a sea level rise. The transgressive beginning of the Devonian has been noted also in Australia and SW Siberia.

The above citations give surprisingly different interpretations of the Klonk section, but in general it seems that both rise and fall of sea level in the Silurian–Devonian transition interval are possible. Most likely rather different agents cause sea level dynamics. Podolia and the East Baltic are good examples of those differences. There is no need to explain all events by a single agent, but a question remains as to why an event is global.

As to the chronostratigraphic aspect, it was striking that there are two types of relations of the $\delta^{13}C$ excursion with the S/D: one as described by Hladíková et al. (1997) at Klonk, where a slowly rising limb of the excursion occupies some interval of the Přídolí section before passing the boundary level and another, where the excursion begins close to the boundary and rises very rapidly through the S/D (Saltzman 2002). Our data set contains both types: the Vidukle, Šešuvis and Dnistrove sections belong to the first type, the Kotuzhiny section represents the second one. However, when drawing any conclusions we should bear in mind that the above types of relations are based on trusting the correctness of stratigraphy applied by the authors cited above. If the stratigraphy is not reliable, the pattern identified above should be revised.

Proceeding from a general idea of such chronostratigraphical boundaries (Salvador 1994), we consider the first type of relations normal. This trend shows that the succession of beds is complete (= entire time interval is represented by rocks) at a boundary. In this sense the actual trend is complete e.g. at Klonk and Vidukle, but not at Kotuzhiny, possibly due to some kind of gap.

CONCLUSIONS

1. Summarizing the $\delta^{13}C$ data from the East Baltic and Podolia, we are convinced that an early to middle Přídolí 'stability' interval and the late Přídolí excursion are reliable patterns of the carbon isotope trend on the Baltica palaeocontinent. Their wider significance awaits confirmation by observations elsewhere, as do several excursions in the Llandovery.
2. The carbon isotope excursion at the Silurian–Devonian boundary (SIDE) has been traced on several continents, now also in Baltica. Although this excursion begins either in the uppermost Silurian or at the bottom of the Devonian, it can serve as a well-dated global chemostratigraphical correlation tool. The details and causes of the noted differences in the stratigraphical level of this excursion definitely need to be clarified.
3. Carbon isotope chemostratigraphy has proved its efficiency when applied together with high-resolution biostratigraphy. It helps to overcome ecologically (= facies dependence) caused cases of diachroneity of fossil occurrences or their absence (so-called barren beds).
4. Having established a series of carbon isotope excursions in the Silurian, we can use those seven levels as markers for tracing certain time planes through different facies belts over the whole basin.
5. However, at least one difficulty still exists – excursions are often linked to sea level low stands, meaning that these event levels may be missing in certain sections, in peripheral ones in particular.

In summary, we think that carbon isotope chemostratigraphy may contribute to subdividing the Přídolí into stages in the nearest future and that Baltica *sensu lato* seems to be the right place for such a development. However, different decisions are possible, but anyway an undivided series in the Silurian stratigraphy needs reconsideration.

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Süsinikisotoopide suhte arengutrend Pridolis ja Ülem-Siluri ning Devoni alguse kemostratigraafia Podoolia (Ukraina) ja Baltikumi andmetel

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Seni maailmas äärmiselt vähe uuritud Pridoli süsinikisotoopide suhte arengutrendi selgitamiseks uuriti Podoolias viit Dnestri jõe paljandit ja Kotuzhiny puursüdamikku ning nelja puurläbilõiget (Vidukle, Šešuvis, Ventspils, Ohesaare) Baltimaades. Neile lisaks ka Ohesaare ja Loode pangal avanevaid kivimeid. Kindla seose tagamiseks varasemate uurimustega alustati Kesk-Ludfordi suurest hälbest, hõlmati kogu Pridol ja ka Devoni allosa, mida markeerib varem tuntud Siluri–Devoni piiril olev $\delta^{13}C$ hälve (akronüümina SIDE). Uued andmed näitavad väikest positiivset kaksikhälvet Hilis-Ludfordis (kõrgeimad väärtused 0,8–1,7‰), Pridol algab madala negatiivse trendiga, millele järgneb suhteliselt stabiilne madalate $\delta^{13}C$ väärtustega intervall, mis hõlmab umbes 2/3 ladestiku mahust. Ülem-Pridol algab keskmise suurusega hälbega (2,3–4,5‰), milles $\delta^{13}C$ suurus on sõltuv kivimi tekkekoha veesügavusest. Sama reeglipära on jälgitav ka SIDE hälbe puhul: sügavaveelistes kivimites on väärtus väikseim (1,6‰), madalamerelistes suurem (3,8‰) ja käsijalgsete kaantes veelgi enam (4,5‰). SIDE on jälgitud enamikul praeguse maailma kontinentidel ja sellisena on see kujunenud geoloogias oluliseks kronostratigraafiliseks tööriistaks. Ülem-Pridoli hälbe väärtus jääb ootama kinnitust teistelt aladelt. Uuritud süsiniku isotoophälvete kuju võimaldab otsustada läbilõigete täielikkuse üle. Uurimistulemused näitavad, et Baltika mandri lääneosa geoloogiliste läbilõigete hea biostratigraafiline tagapõhi koos isotoopandmetega annab Pridoli ladestiku liigestamiseks senisest parema võimaluse.

Table 1. Carbon isotope data from the upper Silurian rocks of the East Baltic and Podolia (available online)

Sample No.	Formation	Distance from the bottom, m	$\delta^{13}C$, ‰
Isakivtsy-45 section			
1	Prygorodok	0.0	0.1
2	Prygorodok	0.5	0.3
3	Prygorodok	1.5	1.0
4	Prygorodok	2.5	2.1
5	Prygorodok	3.5	4.3
6	Prygorodok	5.5	4.6
7	Prygorodok	6.3	3.6
8	Prygorodok	7.3	5.7
9	Prygorodok	8.3	5.8
10	Prygorodok	9.9	6.0
11	Prygorodok	10.9	4.6
12	Prygorodok	11.9	3.6
13	Prygorodok	12.9	1.7
14	Prygorodok	14.4	0.2
Okopy-46 section			
1	Prygorodok	0.0	0.3
2	Varnytsya	5.0	–0.8
3	Varnytsya	5.8	–3.0
4	Varnytsya	6.5	–1.0
5	Varnytsya	7.0	–1.5
6	Varnytsya	8.0	–2.0
7	Varnytsya	9.0	0.3
8	Varnytsya	9.9	0.5
9	Varnytsya	10.9	0.8
10	Varnytsya	11.9	0.8
11	Varnytsya	13.9	0.5
12	Varnytsya	14.9	0.2
13	Varnytsya	15.9	0.3
14	Varnytsya	19.9	–0.4
15	Varnytsya	20.9	0.0
16	Varnytsya	21.9	–0.2
17	Varnytsya	22.9	0.1
18	Varnytsya	23.9	–0.2
19	Varnytsya	24.9	–4.1
20	Varnytsya	25.9	–4.0
21	Varnytsya	26.9	–1.8
Trubchyn-65 section			
1	Varnytsya	0.0	–2.8
2	Varnytsya	1.0	–2.1
3	Varnytsya	2.0	–3.2
4	Varnytsya	3.0	–4.2
5	Varnytsya	4.0	–2.7
6	Varnytsya	5.0	–2.1
7	Varnytsya	6.0	–2.9
8	Varnytsya	8.0	–1.4
9	Varnytsya	9.0	–2.4
10	Varnytsya	10.0	–0.9
11	Varnytsya	11.0	–0.6
12	Varnytsya	12.0	–0.3
13	Varnytsya	13.0	–0.2
14	Varnytsya	14.5	–0.7
15	Varnytsya	15.3	–1.0
16	Varnytsya	16.3	0.3
17	Varnytsya	17.3	0.1
18	Varnytsya	18.3	–1.1
19	Varnytsya	19.3	0.0
20	Varnytsya	20.3	0.2
21	Varnytsya	21.3	0.7
22	Varnytsya	22.3	0.0
23	Trubchyn	23.3	0.2
24	Trubchyn	24.3	0.3
25	Trubchyn	25.3	0.4
26	Trubchyn	27.3	0.6
27	Trubchyn	28.3	–4.4
Dnistrove-West section			
1	Trubchyn	0.0	1.0
2	Trubchyn	1.0	0.6
3	Trubchyn	2.0	0.6
4	Trubchyn	3.0	0.3
5	Trubchyn	4.0	0.4
6	Trubchyn	5.0	0.3
7	Trubchyn	6.0	0.0
8	Trubchyn	7.0	0.5
9	Trubchyn	8.0	0.7
10	Dzvenygorod	10.5	1.5
11	Dzvenygorod	14.0	–0.7
12	Dzvenygorod	14.8	–1.2
13	Dzvenygorod	17.6	–0.1
14	Dzvenygorod	18.6	–0.1
15	Dzvenygorod	19.6	–0.3
16	Dzvenygorod	20.6	–0.5
17	Dzvenygorod	21.4	–0.7
18	Dzvenygorod	22.4	–0.3
19	Dzvenygorod	23.4	–0.3
20	Dzvenygorod	24.4	0.2
21	Dzvenygorod	25.4	–0.2
22	Dzvenygorod	27.4	0.3
23	Dzvenygorod	28.4	0.5
24	Dzvenygorod	28.9	0.8
25	Dzvenygorod	29.7	1.3
26	Dzvenygorod	30.7	1.7
27	Dzvenygorod	31.7	1.4
28	Dzvenygorod	32.5	1.9
29	Dzvenygorod	33.5	1.7
30	Dzvenygorod	34.5	2.1
31	Dzvenygorod	35.5	3.1
32	Khudykivtsy	38.5	3.9
33	Khudykivtsy	39.6	3.8
34	Khudykivtsy	40.6	3.6
35	Khudykivtsy	41.6	3.8
36	Khudykivtsy	42.6	3.1
37	Khudykivtsy	43.6	3.0
38	Khudykivtsy	44.6	3.1
39	Khudykivtsy	45.6	3.4
40	Khudykivtsy	46.6	3.7

Sample No.	Formation	Distance from the top, m	δ[13]C, ‰
	Dzvenygorod-West section		
22	Khudykivtsy	0.0	–1.0
23	Khudykivtsy	0.7	3.1
21	Khudykivtsy	1.1	1.9
20	Khudykivtsy	1.3	2.3
19	Khudykivtsy	1.7	2.3
18	Khudykivtsy	2.7	2.6
17	Khudykivtsy	4.0	3.8
16	Khudykivtsy	5.0	3.5
15	Khudykivtsy	6.0	2.2
14	Khudykivtsy	7.0	1.8
13	Khudykivtsy	8.0	2.1
12	Dzvenygorod	9.0	1.5
11	Dzvenygorod	10.0	1.6
10	Dzvenygorod	11.0	1.4
9	Dzvenygorod	12.0	0.9
8	Dzvenygorod	13.0	0.7
7	Dzvenygorod	14.0	0.3
6	Dzvenygorod	15.0	0.1
5	Dzvenygorod	16.0	–0.1
4	Dzvenygorod	17.0	–0.1
3	Dzvenygorod	18.0	–0.4
2	Dzvenygorod	19.0	–0.6
1	Dzvenygorod	20.0	–0.2
24	Dzvenygorod	21.0	–0.3
25	Dzvenygorod	22.0	–0.8
26	Dzvenygorod	23.0	–0.6
27	Dzvenygorod	24.0	–0.9
28	Dzvenygorod	25.0	–0.1
29	Dzvenygorod	26.0	–0.5
57	Dzvenygorod	27.0	–0.2
56	Dzvenygorod	28.0	0.1
55	Dzvenygorod	29.0	0.0
54	Dzvenygorod	30.0	0.4
53	Dzvenygorod	31.0	–0.1
52	Dzvenygorod	32.0	0.4
51	Dzvenygorod	33.0	0.6
50	Dzvenygorod	34.0	–0.4
49	Dzvenygorod	35.0	0.4
48	Dzvenygorod	36.0	0.4
47	Dzvenygorod	37.0	–0.4
46	Dzvenygorod	38.0	0.2
45	Dzvenygorod	39.0	–0.4
44	Dzvenygorod	40.0	0.7
43	Dzvenygorod	41.0	1.4
42	Dzvenygorod	42.0	0.5
41	Dzvenygorod	43.0	0.8
40	Dzvenygorod	43.6	1.6
39	Dzvenygorod	44.6	1.9
38	Trubchyn	45.6	0.7
37	Trubchyn	46.6	1.0
36	Trubchyn	47.6	–0.2
35	Trubchyn	48.6	–0.3
34	Trubchyn	49.6	0.1
33	Trubchyn	50.6	0.5
32	Trubchyn	51.6	–1.2
31	Trubchyn	52.6	0.0

Sample No.	Formation	Depth from the top, m	δ[13]C, ‰
	Vidukle-61 section		
1	Tilže	911.0	–1.6
2	Tilže	913.3	–1.5
3	Tilže	914.0	–1.4
4	Tilže	915.0	–1.3
5	Tilže	916.1	–1.1
6	Tilže	917.0	–0.1
7	Tilže	918.1	0.0
8	Tilže	919.0	0.2
9	Tilže	920.2	0.1
10	Tilže	921.2	0.1
11	Tilže	922.1	0.5
12	Tilže	924.0	0.6
13	Tilže	925.1	1.3
14	Tilže	925.6	1.0
15	Tilže	926.1	1.0
16	Tilže	926.4	1.3
17	Tilže	927.3	1.1
18	Tilže	927.9	1.3
19	Tilže	928.6	1.2
20	Tilže	929.3	0.9
21	Tilže	930.0	1.6
22	Tilže	931.1	1.5
23	Tilže	932.2	0.9
24	Jura	933.6	1.1
25	Jura	934.2	1.3
26	Jura	935.0	1.2
27	Jura	936.0	0.8
28	Jura	937.0	0.8
29	Jura	938.0	0.7
30	Jura	939.0	0.9
31	Jura	939.8	0.7
32	Jura	941.0	0.7
33	Jura	943.0	1.0
34	Jura	945.5	1.1
35	Jura	947.0	0.9
36	Jura	948.0	0.7
37	Jura	950.0	1.3
38	Jura	952.2	1.0
39	Jura	954.0	0.9
40	Jura	956.0	1.1
41	Jura	958.4	1.2
42	Jura	959.9	0.0
43	Jura	961.0	0.1
44	Jura	963.0	0.2
45	Jura	965.0	0.0
46	Jura	966.9	0.1
47	Jura	969.0	0.3
48	Jura	971.0	0.1
49	Jura	972.0	–0.2
50	Jura	973.4	–0.2
51	Jura	975.0	–0.3
52	Jura	976.0	–0.2
53	Jura	978.0	–0.1
54	Jura	980.0	–0.2
55	Jura	981.4	–0.3
56	Jura	982.1	0.1
57	Jura	984.0	0.1

Sample No.	Formation	Depth from the top, m	$\delta^{13}C$, ‰
58	Jura	986.0	0.2
59	Jura	987.1	–0.6
60	Jura	989.0	0.0
61	Jura	990.5	0.0
62	Jura	992.0	0.1
63	Jura	994.0	–0.1
64	Jura	996.0	–0.1
65	Jura	998.0	–0.3
66	Jura	999.5	0.0
67	Jura	1001.8	–0.1
68	Jura	1002.8	–0.3
69	Jura	1003.5	–0.3
70	Minija	1004.5	–0.6
71	Minija	1006.6	–0.5
72	Minija	1007.6	–0.5
73	Minija	1009.0	–0.3
74	Minija	1010.5	–0.4
75	Minija	1012.0	–0.3
76	Minija	1014.0	0.0
77	Minija	1015.4	–0.2
78	Minija	1017.0	–0.4
79	Minija	1018.3	–0.5
80	Minija	1020.0	–0.3
81	Minija	1021.5	0.1
82	Minija	1023.0	–0.4
83	Minija	1024.5	–0.6
84	Minija	1026.0	–0.3
85	Minija	1027.6	–0.2
86	Minija	1029.0	0.1
87	Minija	1030.0	–0.2
88	Minija	1032.0	–0.2
89	Minija	1034.0	–0.4
90	Minija	1036.0	–1.3
91	Minija	1037.0	–1.2
92	Minija	1038.2	–1.4
93	Minija	1040.0	–1.0
94	Minija	1041.5	–0.9
95	Minija	1042.9	–1.1
96	Minija	1044.5	–1.2
97	Minija	1046.4	–1.5
98	Minija	1048.4	–1.4
99	Minija	1050.0	–1.3
100	Minija	1052.5	–0.7
101	Minija	1054.5	–0.8
102	Minija	1056.5	–0.7
103	Minija	1058.5	–0.9
104	Minija	1060.0	–1.0
105	Minija	1062.0	–1.4
106	Minija	1064.1	–0.6
107	Minija	1065.8	–0.7
108	Minija	1067.8	–0.6
109	Minija	1069.9	–0.2
110	Minija	1071.9	0.5
111	Ventspils	1074.4	0.3
112	Ventspils	1076.5	0.8
113	Ventspils	1078.5	0.4
114	Ventspils	1081.0	0.1
115	Ventspils	1082.5	0.3
116	Ventspils	1083.5	0.2
117	Ventspils	1084.5	0.4
118	Ventspils	1085.4	0.7
119	Ventspils	1087.9	0.0
120	Ventspils	1092.7	0.1
121	Ventspils	1098.4	0.9
122	Ventspils	1099.4	1.0
123	Ventspils	1100.4	0.8
124	Ventspils	1102.0	1.5
125	Ventspils	1104.1	0.4
126	Ventspils	1105.5	1.3
127	Ventspils	1106.4	1.6
128	Ventspils	1108.5	–0.5
129	Ventspils	1109.0	0.4
130	Ventspils	1110.7	–0.3
131	Ventspils	1115.0	–0.9

Šešuvis-11 section

Sample No.	Formation	Depth from the top, m	$\delta^{13}C$, ‰
1	Tilže	977.2	–4.3
2	Tilže	978.9	–3.2
3	Tilže	980.6	–3.3
4	Tilže	982.3	–2.8
5	Tilže	984.0	–2.9
6	Tilže	985.7	–2.6
7	Tilže	987.4	–2.6
8	Tilže	989.1	–2.7
9	Tilže	990.5	–1.1
10	Tilže	991.9	–1.0
11	Tilže	993.3	–0.1
12	Tilže	995.4	–0.2
13	Tilže	996.8	–0.5
14	Tilže	998.4	–1.5
15	Tilže	999.2	0.0
16	Tilže	1001.7	–0.2
17	Tilže	1003.5	0.6
18	Tilže	1005.0	–0.3
19	Jura	1005.4	–0.2
20	Jura	1008.4	1.2
21	Jura	1009.3	1.2
22	Jura	1010.6	0.8
23	Jura	1011.5	0.9
24	Jura	1012.3	0.8
25	Jura	1013.6	0.8
26	Jura	1015.4	0.8
27	Jura	1016.4	0.6
28	Jura	1017.6	0.4
29	Jura	1019.3	0.5
30	Jura	1020.4	0.5
31	Jura	1021.3	0.5
32	Jura	1022.4	1.2
33	Jura	1023.5	0.4
34	Jura	1024.4	0.8
35	Jura	1025.3	0.4
36	Jura	1027.2	0.0
37	Jura	1030.6	0.1
38	Jura	1032.9	0.5
39	Jura	1034.0	0.4
40	Jura	1035.1	0.5
41	Jura	1038.4	0.3
42	Jura	1040.0	0.0

Sample No.	Formation	Depth from the top, m	$\delta^{13}C$, ‰
43	Jura	1041.4	0.1
44	Jura	1042.9	0.1
45	Jura	1044.0	–0.4
46	Jura	1051.2	–0.9
47	Jura	1053.0	–0.9
48	Jura	1054.8	–1.0
49	Jura	1056.5	–0.2
50	Jura	1057.2	–0.8
51	Jura	1059.0	–0.8
52	Jura	1060.8	–0.6
53	Jura	1062.1	–0.2
54	Jura	1063.5	–1.0
55	Jura	1065.2	–1.0
56	Jura	1067.1	–0.1
57	Jura	1069.1	–0.2
58	Jura	1071.6	–0.7
59	Jura	1072.6	–1.0
60	Jura	1073.5	–0.3
61	Jura	1074.9	–0.1
62	Jura	1075.8	–0.9
63	Jura	1076.5	–0.7
64	Jura	1078.2	–0.6
65	Jura	1079.5	–0.6
66	Jura	1082.0	–0.8
67	Jura	1083.6	–0.3
68	Jura	1085.5	–2.2
69	Jura	1087.0	0.1
70	Jura	1088.4	0.1
71	Jura	1089.6	–0.1
72	Jura	1091.0	–0.6
73	Jura	1092.7	–0.7
74	Jura	1093.5	–0.7
75	Jura	1094.7	–0.8
76	Jura	1095.9	–1.1
77	Jura	1097.1	–0.8
78	Jura	1099.2	–0.6
79	Jura	1100.3	–0.9
80	Jura	1102.4	–0.6
81	Jura	1106.2	–0.5
82	Jura	1108.5	–0.6
83	Jura	1110.2	–0.3
84	Jura	1111.5	–0.2
85	Jura	1112.6	–0.3
86	Jura	1113.7	–0.5
87	Jura	1116.6	0.0
88	Jura	1117.5	–0.5
89	Jura	1118.7	–0.3
90	Minija	1119.3	–0.4
91	Minija	1121.0	–0.2
92	Minija	1122.6	0.0
93	Minija	1123.9	–0.6
94	Minija	1125.2	–0.3
95	Minija	1127.5	–0.9
96	Minija	1128.8	–0.8
97	Minija	1130.1	–0.5
98	Minija	1131.4	–0.4
99	Minija	1133.3	–0.3
100	Minija	1134.0	–0.3
101	Minija	1135.3	–0.2

Sample No.	Formation	Depth from the top, m	$\delta^{13}C$, ‰
102	Minija	1136.7	–0.7
103	Minija	1138.3	–0.7
104	Minija	1138.6	–0.7
105	Minija	1140.5	–0.6
106	Minija	1142.4	–0.6
107	Minija	1144.3	–0.7
108	Minija	1146.2	–1.5
109	Minija	1150.0	–0.7
	Kotuzhiny section		
1	Khudykivtsy	85.6	0.3
2	Khudykivtsy	86.6	0.7
3	Khudykivtsy	87.9	2.3
4	Khudykivtsy	88.8	1.6
5	Khudykivtsy	89.7	1.7
6	Khudykivtsy	90.6	2.4
7	Khudykivtsy	91.6	2.8
8	Khudykivtsy	92.5	2.2
9	Khudykivtsy	93.3	2.8
10	Khudykivtsy	94.5	2.6
11	Khudykivtsy	95.0	1.8
12	Dzvenygorod	96.0	0.9
13	Dzvenygorod	97.0	0.5
14	Dzvenygorod	98.0	1.9
15	Dzvenygorod	99.0	1.8
16	Dzvenygorod	100.0	1.2
17	Dzvenygorod	101.0	1.5
18	Dzvenygorod	102.0	1.1
19	Dzvenygorod	103.0	2.3
20	Dzvenygorod	104.0	0.8
21	Dzvenygorod	105.0	1.0
22	Dzvenygorod	106.0	–0.3
23	Dzvenygorod	107.0	1.1
24	Dzvenygorod	108.0	1.7
25	Dzvenygorod	109.0	1.5
26	Dzvenygorod	110.0	1.4
27	Dzvenygorod	111.0	–0.1
28	Dzvenygorod	112.0	–0.3
29	Dzvenygorod	113.0	0.2
30	Dzvenygorod	114.0	1.1
31	Dzvenygorod	115.0	0.0
32	Dzvenygorod	116.0	–0.4
33	Dzvenygorod	117.0	–0.2
34	Dzvenygorod	118.0	0.8
35	Dzvenygorod	119.0	1.7
36	Dzvenygorod	120.0	2.9
37	Dzvenygorod	121.0	4.5
38	Dzvenygorod	122.0	4.4
39	Dzvenygorod	123.0	3.6
40	Dzvenygorod	124.0	4.4
41	Dzvenygorod	125.0	3.8
42	Dzvenygorod	126.0	4.1
43	Dzvenygorod	127.0	3.6
44	Trubchyn	128.0	3.6
45	Trubchyn	129.0	3.5
46	Trubchyn	130.0	2.0
47	Trubchyn	131.0	1.8
48	Trubchyn	132.0	1.7
49	Trubchyn	133.0	0.3

Sample No.	Formation	Depth from the top, m	$\delta^{13}C$, ‰
50	Trubchyn	134.0	0.6
51	Trubchyn	135.0	0.1
52	Trubchyn	136.0	0.0
53	Trubchyn	137.0	–0.3
54	Trubchyn	138.0	–0.2
55	Trubchyn	139.0	–0.6
56	Trubchyn	140.0	–0.1
57	Trubchyn	141.0	0.3
58	Trubchyn	142.0	–0.2
59	Trubchyn	143.0	–0.1
60	Trubchyn	144.0	0.1
61	Trubchyn	145.0	0.0
62	Trubchyn	146.0	–0.3
63	Trubchyn	147.0	–0.7
64	Trubchyn	148.0	0.1
65	Trubchyn	149.0	0.2
66	Trubchyn	150.0	–0.2
67	Trubchyn	151.0	–0.5
68	Trubchyn	152.0	–0.5
69	Trubchyn	153.0	–0.4
70	Trubchyn	154.0	0.4
71	Varnytsya	155.0	0.0
72	Varnytsya	156.0	–0.3
73	Varnytsya	157.0	0.2
74	Varnytsya	158.0	–0.7
75	Varnytsya	159.0	–1.3
76	Varnytsya	160.0	–1.9
77	Varnytsya	161.0	–1.9
78	Varnytsya	162.0	–1.1
79	Varnytsya	163.0	–3.2
80	Varnytsya	164.0	–1.9
81	Varnytsya	165.0	–1.6
82	Varnytsya	166.0	–0.8
83	Varnytsya	167.0	–1.7
84	Varnytsya	168.0	–2.4
85	Varnytsya	169.0	–1.6
86	Varnytsya	170.0	–1.6
87	Varnytsya	171.0	–2.5
88	Varnytsya	172.0	–2.5
89	Varnytsya	173.0	–2.5
90	Varnytsya	174.0	–1.7
91	Varnytsya	175.0	–0.9
92	Varnytsya	176.0	–2.2
93	Varnytsya	177.0	–1.9
94	Varnytsya	178.0	–2.1
95	Varnytsya	179.0	–2.9
96	Varnytsya	180.0	–2.7
97	Varnytsya	181.0	–0.7
98	Varnytsya	182.0	–2.6
99	Varnytsya	183.0	–1.8
100	Varnytsya	184.0	–1.9
101	Varnytsya	185.0	–2.2
102	Varnytsya	186.0	–2.6
103	Varnytsya	187.0	–1.5
104	Varnytsya	188.0	–2.9
105	Varnytsya	189.0	–1.3
106	Varnytsya	190.0	–0.8
107	Varnytsya	191.0	–0.7
108	Varnytsya	192.0	–2.0
109	Varnytsya	193.0	–3.9
110	Varnytsya	194.0	–2.6

Sample No.	Formation	Depth from the top, m	$\delta^{13}C$, ‰
111	Varnytsya	195.0	–2.1
112	Varnytsya	196.0	–0.2
113	Varnytsya	197.0	–0.4
114	Varnytsya	198.0	–0.8
115	Varnytsya	199.0	–0.1
116	Varnytsya	200.0	0.4
117	Varnytsya	201.0	1.1
118	Varnytsya	202.0	–0.9
119	Varnytsya	203.0	–0.9
120	Varnytsya	204.0	0.0
121	Varnytsya	205.0	–1.4
122	Varnytsya	206.0	–2.2
123	Varnytsya	207.0	–2.6
124	Varnytsya	208.0	–1.8
125	Varnytsya	209.0	–1.8
126	Varnytsya	210.0	–2.8
127	Varnytsya	211.0	–5.0
128	Varnytsya	212.0	–3.5
129	Varnytsya	213.0	–3.0
130	Varnytsya	214.0	–3.9
132	Prygorodok	215.0	–2.5
133	Prygorodok	216.0	–2.1
134	Prygorodok	217.0	–2.5
135	Prygorodok	218.0	–2.7
136	Prygorodok	219.0	–2.8
137	Prygorodok	220.0	–2.8
138	Prygorodok	221.0	–2.0
139	Prygorodok	222.0	–0.6
140	Prygorodok	223.0	–0.9
141	Prygorodok	224.0	–1.4
142	Prygorodok	225.0	0.3
143	Prygorodok	226.0	–0.8
144	Prygorodok	227.0	–1.6
145	Prygorodok	228.0	–1.7
146	Prygorodok	229.0	–0.8
147	Prygorodok	230.0	0.0
148	Prygorodok	231.0	0.1
149	Isakivtsy	232.0	0.3
150	Isakivtsy	233.0	0.3
151	Isakivtsy	234.0	0.4
152	Isakivtsy	235.0	0.3
153	Isakivtsy	236.0	–0.3
154	Isakivtsy	237.0	–0.1
155	Isakivtsy	238.0	–0.2
157	Isakivtsy	239.0	–0.3
158	Isakivtsy	240.0	–0.3
159	Grinchuk	241.0	0.1
160	Grinchuk	242.0	–0.3
161	Grinchuk	243.0	0.1
162	Grinchuk	244.0	0.3
163	Grinchuk	245.0	0.5
164	Grinchuk	246.0	0.4
165	Grinchuk	247.0	–0.1
166	Grinchuk	248.0	0.3
167	Grinchuk	249.0	0.1
168	Grinchuk	250.0	–0.1
169	Grinchuk	251.0	0.0
170	Grinchuk	252.0	0.1
171	Grinchuk	253.0	0.2
172	Grinchuk	254.0	0.1