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Three global carbon isotope shifts in the Silurian of Podolia (Ukraine): stratigraphical implications

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Abstract. Podolia is a classical Silurian area in the southwestern part of the Ukraine. Shallow to open shelf rocks cropping out there are usually, except for a few dolomitic horizons, highly fossiliferous and therefore the biostratigraphy of the region has a long successful history. The Ukrainian meeting of the Subcommission on Silurian Stratigraphy of the International Union of Geological Sciences, held in 1983, became an important milestone. Tsegelnyuk et al. summarized different results and views in a field guide published for the meeting (*The Silurian of Podolia. The Guide to Excursion*. Naukova Dumka, Kiev, 1983) and introduced a practically new stratigraphical terminology, and in some parts of the section, also new age interpretation of the beds. For our paper carbon isotopes were studied in eight sections on the banks of the Dniester River and its tributaries, covering ca 80% of the Silurian succession (Pridoli excluded). Three positive δ^{13}C excursions were identified. The first excursion in the Kitaigorod 30 section reaches its peak value of 4.0‰ in the very bottom of the Demshin Subformation. The second shift reaches the peak value of 4.3‰ in the middle of the Muksha Subformation. The third shift is the most prominent one identified in the Silurian of Podolia – δ^{13}C values increase steadily through the Isakovtsy Subformation, reaching 6.9‰ in the top, and a slightly lower value of 6.6‰ occurs in the bottom of the Prigorodok Formation. In the “middle” Silurian of the World three major positive excursions have been identified: in the early and latest Wenlock and in the late Ludlow. The general character of the carbon isotope trend and stratigraphical positions of the excursions established in this paper demonstrate that in Podolia there occurs the same set of global shifts, which can be used for the improvement of regional and global correlation of Wenlock and Ludlow sections of that area. Some refinements are suggested, but some details need additional study.

Key words: carbon isotopes, correlation, Podolia, Silurian, stratigraphy, Ukraine.

INTRODUCTION

Podolia is a classical area of the Silurian in the southwestern part of the Ukraine, where various shallow to open shelf rocks crop out magnificently on the banks of the Dniester River and its tributaries. The outcrop area lies approximately from the Studenitsa River in the east up to the Nichlava in the west (some 30 km from Khotin, Fig. 1). Except for a few dolomitic horizons, these rocks are usually highly fossiliferous and therefore the biostratigraphy of the area has a long and successful history. English-language overviews of the study history, biostratigraphy, outcrop lithologies, fossil distribution charts, and palaeogeography are available in Tsegelnyuk et al. (1983), Koren et al. (1989), and Baarli et al. (2003), together with the most important references to the main primary data sources (mostly in Russian).

The above papers contain all of the basic data needed for a clear understanding of our study. Having in mind the main idea of our paper, we would like to underline only a few most important milestones from the 135-year-long history of stratigraphical research in the Silurian of Podolia. Kozlowsky (1929) summarized earlier results in a palaeontological monograph and established four subdivisions in the “etage de Scala” belonging to the upper Silurian. The stratigraphical classification by Nikiforova (1954) introduced a traditional terminology and interregional correlation which have partly been revised later (Nikiforova & Predtechensky 1972; Kaljo 1987). However, in the broad sense this classification is still in use in some publications. In the 1970s Petro D. Tsegelnyuk initiated a multidisciplinary revision of the sequence, including stratigraphy (especially lithostratigraphy), different groups of fossils, metabentonite beds for correlation purposes, etc. A large group of Ukrainian and some Russian colleagues worked together with him and a huge amount of new information was collected. The results and views, published by Tsegelnyuk et al. (1983) in a field guide of the Ukrainian meeting of the Subcommission on Silurian Stratigraphy of the International Union of Geological Sciences, created a practically new terminology and provided new age

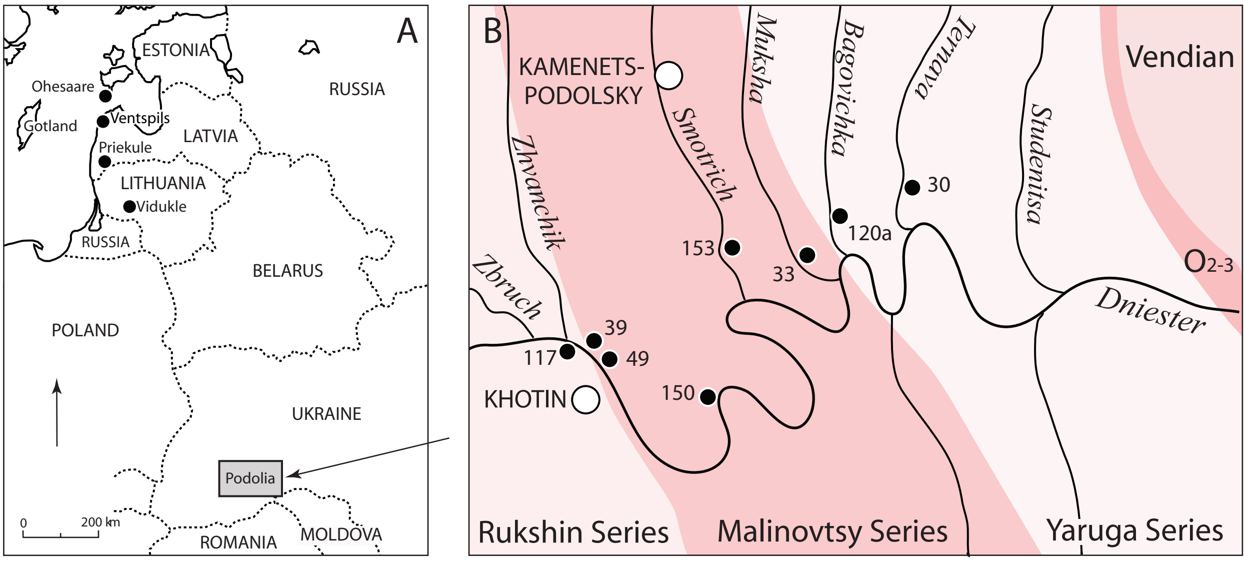

Fig. 1. Location of the study area (A) and sampled outcrops (B) on a simplified geological map (Meso- and Cenozoic rocks removed) of the Mid-Dniester part of Podolia. B is modified from a figure in Tsegelnyuk et al. (1983). The localities (filled circles) are marked by their numbers (from the left): Ataki 117, Zhvanets 39, Braga 49, Malinovtsy 150, Tsviklevtsy 153, Muksha 33, Bagovitsa 120a (close to the outcrop 120 of Tsegelnyuk et al. 1983), Kitaigorod 30.

interpretation of beds in some parts of the section. The situation of that time is illustrated in Fig. 2, based on a figure by Tsegelnyuk et al. (1983). Tsegelnyuk did not change his conception up to his emigration and end of studies in May 2002, except only a few refinements made in his doctoral thesis (1991). This stratigraphical framework (Fig. 2) has been practically unchanged or with small changes (Drygant 1994) in use in the Ukraine up to now (Gritsenko et al. 1999; Mõtus & Grytsenko 2007).

Since that time great progress has been made in the application of isotope methods in the study of palaeoenvironments, including facies and climatic conditions of the geological past, and especially in stratigraphical correlations. The last direction in isotope studies mainly makes use of relationships of carbon isotopes ($\delta^{13}C$) in rocks and the corresponding trends observed through sections (see methods below). The research performed in the Baltoscandian Silurian (Samtleben et al. 1996; Kaljo et al. 1997; Kaljo & Martma 2000, 2006; Munnecke et al. 2003; Martma et al. 2005) and elsewhere (Saltzman 2001; Cramer et al. 2006; Lehnert et al. 2003, 2007b) have shown that several well-defined $\delta^{13}C$ excursions can serve as independent markers for correlation purposes. At that the two most important criteria for the evaluation of results are (1) right density of sampling for isotope measurements and (2) exact biostratigraphic dating of excursions. The results from the Wenlock and Ludlow fulfil these requirements in the best way.

Carbon and oxygen isotopes in the Silurian of Podolia have been studied earlier by Azmy et al. (1998) within a wider project embracing also other areas, but due to the limited number of samples (21 brachiopod shells), no continuous and clear $\delta^{13}C$ trend was revealed. However, the early Wenlock excursion was traced on the basis of three samples in the Demshin Formation and dated as the *Monograptus riccartonensis* graptolite Biozone.

The main idea of our study is to check the possibilities of carbon isotope stratigraphy in the classical Silurian of Podolia and to identify a general carbon isotope trend for the Wenlock and Ludlow series. We hope that the results of this study will allow us to design the next step of research with a specific sampling programme in order to solve the problems arising in the correlation of shallow- and deep-water rock sequences. The discussion of the current results will refer later to some possible solutions.

GEOLOGICAL SETTING AND MATERIAL

The main outline of the geological situation in the study area and location of the outcrops studied are shown in Fig. 1. Gently dipping Silurian and older rocks crop out only in deep river valleys under the horizontally lying Cretaceous rocks. The sampling and dating of samples in terms of local lithostratigraphy, fixing of unit boundaries, etc. were performed by V. P. Grytsenko and M.-A. Mõtus. The field guide by Tsegelnyuk et al. (1983) was used as a stratigraphical basis for sampling and for correlation of individual outcrop sections. However,

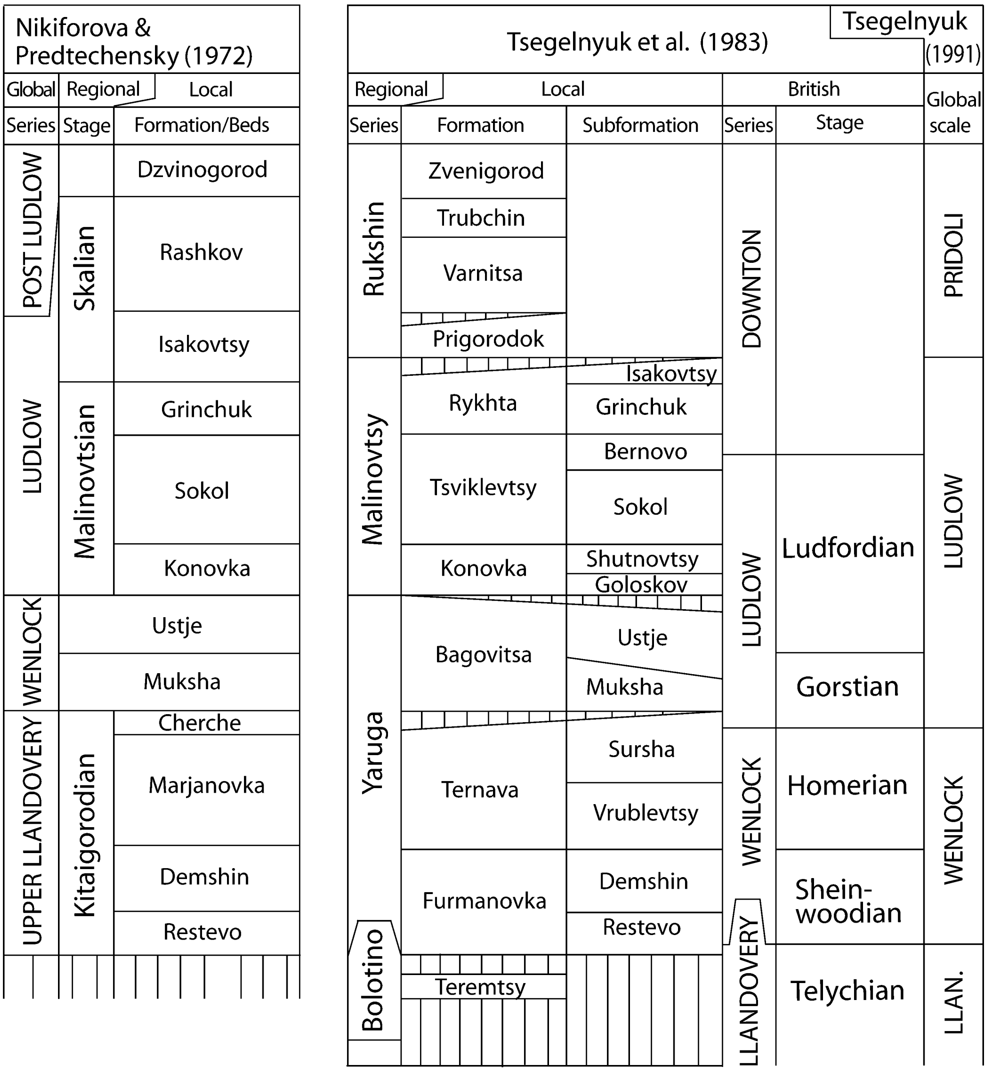

Fig. 2. Silurian stratigraphical terminology of Podolia and its correlation with global units. Modified from Tsegelnyuk et al. (1983).

the situation in the Dniester River Valley is much more complicated nowadays than it was during the Silurian Subcommission meeting in 1983. The construction of an electric power station dam (ca 120 m high) at Novodnistrovsk has raised the water level in the valley considerably, up to about 50 m ca 100 km upstream in the area of the upper Ludlow outcrops. Therefore many classical sections, or at least their lower parts, are under water now, but thanks to the dip of Silurian rocks towards the southeast, a continuous cross-section could be sampled.

All 8 outcrops (Fig. 1) were sampled at a regular 1 m interval. This gave us nearly 170 whole-rock samples, but there remained several unsampled intervals (marked as sampling gaps in the outcrop logs), including the lower Restevo and lower Sursha subformations, most of the Konovka Formation, and a few metres at the boundary between the Sokol and Bernovo subformations. These sampling gaps were intentional and will be filled during the succeeding project. Still, the most important parts (ca 80%) of the Silurian sequence of Podolia are well covered by samples and accomplishing the study tasks is sufficiently guaranteed by the collected data.

ANALYTICAL METHODS

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

Most of the analysed rocks are limestones with a rather low content of dolomite, however, real dolomites occur at some levels. For isotope analysis it is useful to know bands with a calcite–dolomite mixture and therefore a series of XRF analyses (from 48 samples) was performed by K. Orlova and T. Kallaste in the XRF Laboratory, Institute of Geology at Tallinn University of Technology (below abbreviated as IG TUT). The main components and some minor elements (Al_2O_3, SiO_2, Fe_2O_3, K_2O, CaO, MgO, etc., Table 1) were measured by

Table 1. Geochemical data based on XRF analyses of the Silurian rocks of Podolia

Locality, sample No.	Subformation, F. = Formation	CaO, %	MgO, %	Dolomite, %	Calcite, %	Terrigenous component, %
Kitaigorod 30-2	Restevo	39.0	2.4	8.3	65.2	24.8
Kitaigorod 30-6	Restevo	43.6	1.7	5.6	74.9	17.4
Kitaigorod 30-11	Demshin	46.9	1.5	5.4	80.9	12.7
Kitaigorod 30-15	Demshin	48.1	1.1	3.8	83.9	11.4
Kitaigorod 30-19	Demshin	45.5	1.8	6.4	77.8	14.3
Kitaigorod 30-22	Vrublevtsy	42.9	2.0	6.8	72.9	18.6
Kitaigorod 30-26	Vrublevtsy	43.5	2.2	8.0	73.2	18.7
Kitaigorod 30-32	Vrublevtsy	35.1	4.1	15.3	54.3	29.4
Kitaigorod 30-38	Vrublevtsy	48.9	1.3	4.8	84.8	9.7
Kitaigorod 30-41	Vrublevtsy	47.7	1.4	5.3	82.4	11.1
Bagovitsa 120a-3	Sursha	54.3	1.1	4.9	94.4	2.2
Bagovitsa 120a-7	Sursha	52.6	1.3	5.3	91.1	4.5
Bagovitsa 120a-12	Muksha	39.1	5.7	24.2	56.8	17.4
Bagovitsa 120a-15	Muksha	31.2	8.4	35.3	36.6	26.8
Bagovitsa 120a-18	Muksha	49.1	2.1	8.7	83.0	7.4
Bagovitsa 120a-22	Muksha	48.4	3.7	16.4	77.6	5.1
Bagovitsa 120a-27	Ustje	41.7	6.9	30.5	58.0	11.2
Muksha 33-2	Muksha	33.0	8.6	36.5	39.1	23.2
Muksha 33-5	Muksha	56.1	0.2	1.0	99.7	0.4
Muksha 33-9	Ustje	20.8	14.3	61.4	3.8	33.1
Muksha 33-10	Ustje	46.5	4.4	19.2	72.6	7.2
Muksha 33-11	Ustje	20.3	14.3	61.4	2.9	34.5
Muksha 33-17	Ustje	28.4	18.2	81.7	6.4	11.2
Muksha 33-24	Ustje	25.7	17.0	75.5	5.0	17.6
Muksha 33-31	Ustje	14.3	11.6	47.2	–0.1	50.7
Muksha 33-33	Goloskov	52.1	0.8	2.9	91.6	6.0
Tsviklevtsy153-2	Shutnovtsy	44.4	1.9	7.0	75.5	15.2
Tsviklevtsy 153-7	Sokol	42.9	2.3	8.5	72.1	18.1
Tsviklevtsy 153-14	Sokol	46.0	1.8	6.8	78.5	13.6
Tsviklevtsy 153-21	Sokol	48.1	1.4	5.1	83.2	11.0
Malinovtsy 150-3	Bernovo	33.5	3.8	13.7	52.4	31.7
Malinovtsy 150-6	Bernovo	50.0	1.0	3.5	87.3	7.4
Malinovtsy 150-14	Bernovo	46.1	1.5	5.5	79.3	12.9
Malinovtsy 150-21	Grinchuk	41.5	2.0	6.6	70.5	21.4
Malinovtsy 150-28	Grinchuk	47.0	1.6	5.8	80.7	12.8
Zhvanets 39-2	Grinchuk	36.2	3.3	11.8	58.2	28.4
Zhvanets 39-4	Grinchuk	29.5	5.1	18.9	42.4	37.2
Zhvanets 39-6	Grinchuk	39.5	4.2	16.8	61.5	19.7
Zhvanets 39-7	Grinchuk	55.7	0.6	2.7	98.1	0.4
Zhvanets 39-8	Isakovtsy	18.2	11.8	49.0	5.9	43.2
Zhvanets 39-10	Isakovtsy	38.2	12.5	56.7	37.4	4.6
Zhvanets 39-12	Isakovtsy	32.8	14.9	67.0	22.2	8.6
Zhvanets 39-15	Prigorodok F.	25.9	16.7	74.3	6.0	18.7
Zhvanets 39-17	Prigorodok F.	24.6	16.6	73.6	4.0	20.1
Ataki 117-2	Prigorodok F.	23.6	16.7	73.7	2.2	22.8
Ataki 117-4	Prigorodok F.	26.9	18.2	81.7	3.6	13.2

X-ray fluorescence spectrometry (XRF) using a VRA-30 device from Freiberger Präzisionmechanik. The contents of $CaCO_3$, $MgCa(CO_3)_2$ (Dol), and terrigenous component (Ter) were calculated according to the following formulas suggested by T. Kiipli (Kaljo et al. 1997): Ter = $(Al_2O_3 + SiO_2 + Fe_2O_3 + K_2O) \times 1.025$; dolomite = $4.57 \times (MgO - 0.025 \times Ter)$; calcite = $1.786 \times (CaO - 0.304 \times Dol)$. The corresponding results are presented in Table 1.

Carbon and oxygen isotope analyses were performed by T. Martma in the Laboratory of Mass Spectrometry, IG TUT, 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, the material was powdered and treated with 100% phosphoric acid at 100 °C for 15 min and analysed with a mass spectrometer. The first samples (widely spaced set) from the Kitaigorod 30, Bagovitsa 120a, Malinovtsy 150, Tsviklevtsy 153, Muksha 33, Zhvanets 39, and Ataki 117 sections were analysed by a Thermo Fisher Delta E mass spectrometer with an off-line preparation line. The second detailed set and those from Braga were analysed by the Delta V Advantage device with the GasBench II preparation line. Both sets of results were checked regularly against laboratory control samples and international standards. 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 brachiopod shells studied by Azmy et al. (1998) and the rocks used by us for carbon isotope analyses show very little or no diagenetic alteration. This was convincingly demonstrated by SEM, cathodoluminescence, and trace element studies (Azmy et al. 1998) and supported by data on the conodont colour alteration index (CAI) from different parts of the southwest Ukraine (Drygant 1994). According to the latter author, the CAI remains between 1 and 1.5 in the Silurian of eastern Podolia, showing that the rocks have been heated up to 60 °C (according to some other sources, up to 100 °C). Having in mind the above data and experience gained in the eastern Baltic and Gotland (Samtleben et al. 1996; Kaljo et al. 1997; Heath et al. 1998) where rocks are excellently preserved, we anticipate good results of carbon isotope analysis based on the bulk-rock samples from our study area in Podolia.

RESULTS

The results of the XRF analyses (Table 1) confirmed our earlier general knowledge (*op. cit.* in the introduction) that Wenlock and Ludlow rocks of Podolia are mainly different limestones with the MgO content remaining usually below 2% (in a few bands reaching up to 5%) and CaO ranging from 40 to 55%. Exceptions are dolomites of the Ustje and Isakovtsy subformations and Prigorodok Formation, where Mg and Ca oxides vary, respectively, within 15–18% and 20–33%. MgO-rich rocks have usually also more terrigenous components, but still rocks with values less than 25% (in Russian literature often classified as clayey or argillaceous limestones or dolomites) are predominating. Mean contents of calcite ($CaCO_3$), dolomite ($CaMg(CO_3)_2$), and terrigenous material by subformations (Table 2) are characteristic of shallow to mid-shelf settings (Nestor & Einasto 1997). Some trends were observed through the whole Podolian sequence studied. The contents of terrigenous components are in general rather small, being variable in the lower and more stable in the upper part of the sequence (Fig. 3). Dolomite content shows two cycles, the first

Table 2. Mean contents of calcite, dolomite, and terrigenous component in the Silurian rocks of Podolia by subformations (based on Table 1)

Subformation F. = Formation	Dolomite, %	Calcite, %	Terrigenous component, %	Number of samples
Prigorodok F.	75.8	4.0	18.7	4
Isakovtsy	57.6	21.8	18.8	3
Grinchuk	10.4	68.6	20.0	6
Bernovo	7.6	73.0	17.4	3
Sokol	6.8	77.9	14.2	3
Shutnovtsy	7.0	75.5	15.2	1
Goloskov	2.9	91.6	6.0	1
Ustje	53.8	21.2	23.6	7
Muksha	20.4	65.5	13.4	6
Sursha	5.1	92.8	3.4	2
Vrublevtsy	8.0	73.6	17.5	5
Demshin	5.2	80.9	12.8	3
Restevo	7.0	70.1	21.1	2

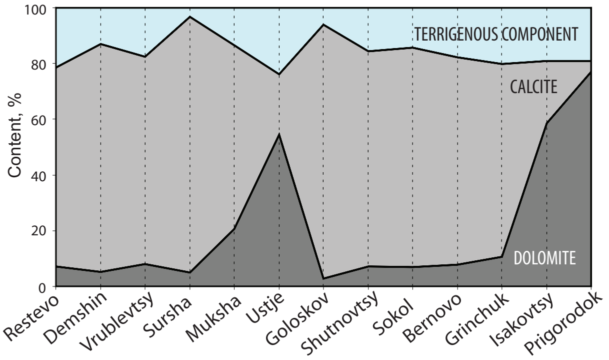

Fig. 3. Trends in the mean contents (%) of calcite, dolomite, and terrigenous component in the Silurian rocks of Podolia by subformations (based on Table 2).

ranging from the Restevo to Ustje subformations and the second from the Goloskov Subformation to the Prigorodok Formation. Both cycles are characterized in the lower 2/3 of the cycle by low, and in the upper 1/3 by increasing and high contents of dolomite, but by opposite contents and trend of calcite. No doubt the described cyclicity reflects changes in the facies-palaeogeographical situation in the basin and also environmental conditions in a wider context.

The results of carbon isotope analyses are presented in Table 3. Following a common tradition, we give besides $\delta^{13}C$ also $\delta^{18}O$ data, but we strongly underline that due to the specifics of the method whole-rock oxygen isotope data cannot be used for any palaeoclimatological or other environmental interpretations. More detailed explanation is available in our earlier papers (Kaljo et al. 1997; Martma et al. 2005). In the studied outcrop sections the $\delta^{18}O$ values (Table 3) vary from −3.2 to −6.9‰ (in a few samples up to −7.5‰), being close to the oxygen isotopic values in Silurian brachiopods and marine carbonates (Samtleben et al. 1996; Azmy et al. 1998). On the other hand, these values indicate that corresponding rocks were not seriously affected by later diagenesis. However, to some extent the $\delta^{18}O$ values are influenced by calcite and dolomite contents in the rock (Table 2) due to their different oxygen fractionation factors (Veizer 1983).

Table 3. Carbon and oxygen isotope data from the Silurian rocks of Podolia

Sample, No.	Subformation F. = Formation	Distance from the bottom, m	$\delta^{13}C$, ‰	$\delta^{18}O$, ‰
		Kitaigorod 30		
42	Vrublevtsy	41	−0.9	−5.1
40	Vrublevtsy	39	−0.9	−5.3
36	Vrublevtsy	35	−0.8	−5.4
34	Vrublevtsy	33	−0.9	−5.2
30	Vrublevtsy	29	−0.8	−5.9
28	Vrublevtsy	27	−0.6	−6.3
26	Vrublevtsy	25	−0.3	−5.8
25	Vrublevtsy	24	−0.3	−5.5
24	Vrublevtsy	23	−0.2	−5.7
23	Vrublevtsy	22	0.0	−5.5
22	Vrublevtsy	21	0.3	−5.5
21	Vrublevtsy	20	1.3	−4.8
20	Vrublevtsy	19	1.9	−5.6
19	Demshin	18	2.4	−4.0
18	Demshin	17	2.0	−4.9
17	Demshin	16	2.2	−4.6
16	Demshin	15	2.9	−5.0
15	Demshin	14	3.2	−5.4
14	Demshin	13	3.4	−4.7
13	Demshin	12	3.7	−3.8
12	Demshin	11	3.3	−5.1
11	Demshin	10	3.1	−4.7
10	Demshin	9	3.6	−4.6
9	Demshin	8	3.3	−5.0
8	Demshin	7	3.4	−5.1
7	Demshin	6	4.0	−4.2
6	Restevo	5	3.4	−5.3
5	Restevo	4	3.4	−4.5
4	Restevo	3	3.4	−5.0
3	Restevo	2	2.8	−5.3
2	Restevo	1	1.9	−6.1
1	Restevo	0	1.4	−6.3
		Bagovitsa 120		
31	Ustje	30	−0.1	−4.6
30	Ustje	29	0.8	−4.2
29	Ustje	28	0.9	−4.4
28	Ustje	27	0.5	−7.2
27	Ustje	26	0.5	−6.7
26	Muksha	25	1.1	−4.9
25	Muksha	24	1.2	−6.2
24	Muksha	23	2.5	−3.7
23	Muksha	22	2.7	−6.2
22	Muksha	21	4.3	−6.2
21	Muksha	20	4.0	−6.6
20	Muksha	19	3.7	−6.6
19	Muksha	18	4.3	−5.2
18	Muksha	17	4.3	−4.9
17	Muksha	16	4.1	−6.6
16	Muksha	15	4.1	−6.6
15	Muksha	14	3.5	−6.1
14	Muksha	13	3.7	−6.6
13	Muksha	12	4.3	−7.0
12	Muksha	11	2.0	−5.8
11	Muksha	10	1.6	−7.0
10	Sursha	9	0.2	−5.7
8	Sursha	7	−0.4	−6.1
7	Sursha	6	−0.8	−5.2
5	Sursha	4	−0.8	−6.5
4	Sursha	3	−0.7	−5.4
2	Sursha	1	−0.7	−6.0
1	Sursha	0	−0.9	−5.2
		Muksha 33		
34	Goloskov	34	0.1	−6.2
33	Goloskov	32	−1.5	−7.5
32	Ustje	31	−1.6	−4.0

Table 3. *Continued*

Sample, No.	Subformation F. = Formation	Distance from the bottom, m	$\delta^{13}C$, ‰	$\delta^{18}O$, ‰
31	Ustje	30	−1.6	−3.7
30	Ustje	29	−0.9	−4.0
29	Ustje	28	−1.3	−6.2
28	Ustje	27	−0.7	−6.6
27	Ustje	26	−1.0	−5.7
26	Ustje	25	−2.0	−4.9
25	Ustje	24	−3.4	−5.8
24	Ustje	23	−0.5	−6.0
23	Ustje	22	0.1	−6.6
22	Ustje	21	−1.5	−5.6
21	Ustje	20	−1.8	−6.3
20	Ustje	19	−1.4	−4.6
19	Ustje	18	−0.2	−4.7
18	Ustje	17	0.4	−5.0
17	Ustje	16	−0.7	−4.9
16	Ustje	15	−0.3	−6.5
15	Ustje	14	−0.5	−4.4
14	Ustje	13	0.2	−4.5
13	Ustje	12	−0.4	−4.6
12	Ustje	11	−1.6	−5.0
11	Ustje	10	−0.3	−4.7
10	Ustje	9	−4.3	−6.1
9	Ustje	8	0.5	−5.7
8	Ustje	7	−1.3	−5.5
7	Ustje	6	−1.6	−8.8
6	Muksha	5	0.5	−7.8
5	Muksha	4	0.8	−8.1
4	Muksha	3	1.4	−8.2
3	Muksha	2	2.5	−3.2
2	Muksha	1	2.3	−5.5
1	Muksha	0	3.2	−5.8
		Tsviklevtsy 153		
24	Sokol	23	−1.1	−6.5
23	Sokol	22	−1.0	−6.6
21	Sokol	20	−0.7	−6.6
20	Sokol	19	−0.6	−5.6
18	Sokol	17	−0.8	−7.0
16	Sokol	15	−0.8	−6.0
14	Sokol	13	−9.9	−7.0
12	Sokol	11	−0.9	−6.2
10	Sokol	9	−0.5	−6.3
8	Sokol	7	−0.9	−6.5
7	Sokol	6	−0.9	−6.8
5	Sokol	4	−0.7	−6.1
3	Sokol	2	−0.9	−6.5
2	Shutnovtsy	1	−0.9	−6.8
1	Shutnovtsy	0	−0.7	−6.5
		Malinovtsy 150		
29	Grinchuk	28	0.0	−6.1
28	Grinchuk	27	0.1	−6.3
26	Grinchuk	25	0.0	−7.0
25	Grinchuk	24	−0.2	−6.4
23	Grinchuk	22	0.5	−6.9
21	Grinchuk	20	−0.1	−6.7
20	Grinchuk	19	0.2	−5.9
19	Grinchuk	18	−0.1	−6.4
18	Grinchuk	17	0.1	−6.7
17	Bernovo	16	−0.4	−6.4
16	Bernovo	15	−0.2	−6.4
15	Bernovo	14	−0.6	−7.4
14	Bernovo	13	−0.8	−7.2
13	Bernovo	12	−0.3	−6.5
11	Bernovo	10	−0.1	−6.8
9	Bernovo	8	0.1	−6.4
7	Bernovo	6	−0.2	−7.4
6	Bernovo	5	0.3	−6.3
5	Bernovo	4	0.1	−5.9
3	Bernovo	2	0.2	−6.7
1	Bernovo	0	−0.1	−6.1
		Zhvanets 39		
17	Prigorodok F.	17	1.7	−5.0
16	Prigorodok F.	16	3.2	−4.4
15	Prigorodok F.	15	4.5	−4.9
14	Prigorodok F.	14	5.5	−5.1
13	Prigorodok F.	13	6.6	−4.5
12	Isakovtsy	12	5.9	−7.1
11	Isakovtsy	11	5.6	−6.7
10	Isakovtsy	9	4.5	−7.4
9	Isakovtsy	8	2.5	−4.7
8	Isakovtsy	7	1.3	−4.5
7	Grinchuk	6	−0.4	−6.4
6	Grinchuk	5	0.0	−6.6
5	Grinchuk	4	−0.1	−6.6
4	Grinchuk	3	−0.1	−6.8
3	Grinchuk	2	0.0	−7.2
2	Grinchuk	1	−0.2	−6.7
1	Grinchuk	0	−0.2	−6.6
		Ataki 117		
5	Prigorodok F.	4	2.4	−4.4
4	Prigorodok F.	3	3.5	−4.2
3	Prigorodok F.	2	5.0	−5.6
2	Prigorodok F.	1	6.2	−4.6
1	Prigorodok F.	0	5.9	−3.8
		Braga 49		
14	Prigorodok F.	11	−1.6	−4.2
13	Prigorodok F.	10	−1.4	−3.9
12	Prigorodok F.	9	−2.4	−5.5
11	Prigorodok F.	8	−2.7	−3.8
10	Prigorodok F.	7	−3.0	−4.1
9	Prigorodok F.	6	−0.9	−4.5
8	Prigorodok F.	5	0.8	−3.8
7	Prigorodok F.	4	3.9	−5.5
6	Prigorodok F.	3	4.8	−5.5
5	Prigorodok F.	2	4.8	−5.4
4	Prigorodok F.	1	6.2	−4.5
3	Prigorodok F.	0	5.9	−5.2
2	Isakovtsy	−1	6.9	−4.7
1	Isakovtsy	−2	6.3	−5.0

From the data presented in Table 3 and Figs 4 and 5 we can bring forth several carbon isotope excursions and specific intermediate intervals of the trend as follows:

1. **The first positive δ^{13}C excursion** identified in the Kitaigorod 30 section begins in the lowermost part of the Restevo Subformation. At 2 m above the bottom it reaches a value of 2.8‰ and a peak value of 4.0‰ in the very bottom of the Demshin Subformation. Upwards the δ^{13}C value decreases slightly, being still 3.7‰ in the middle of the Demshin Subformation (6 m higher) but decreasing gradually up to 2.4‰ in the upper part of the unit.
2. Samples from the Vrublevtsy Subformation of the Ternava Formation (Fig. 4, with a sampling gap in the lower part of the Sursha Subformation) show low or even negative δ^{13}C values.

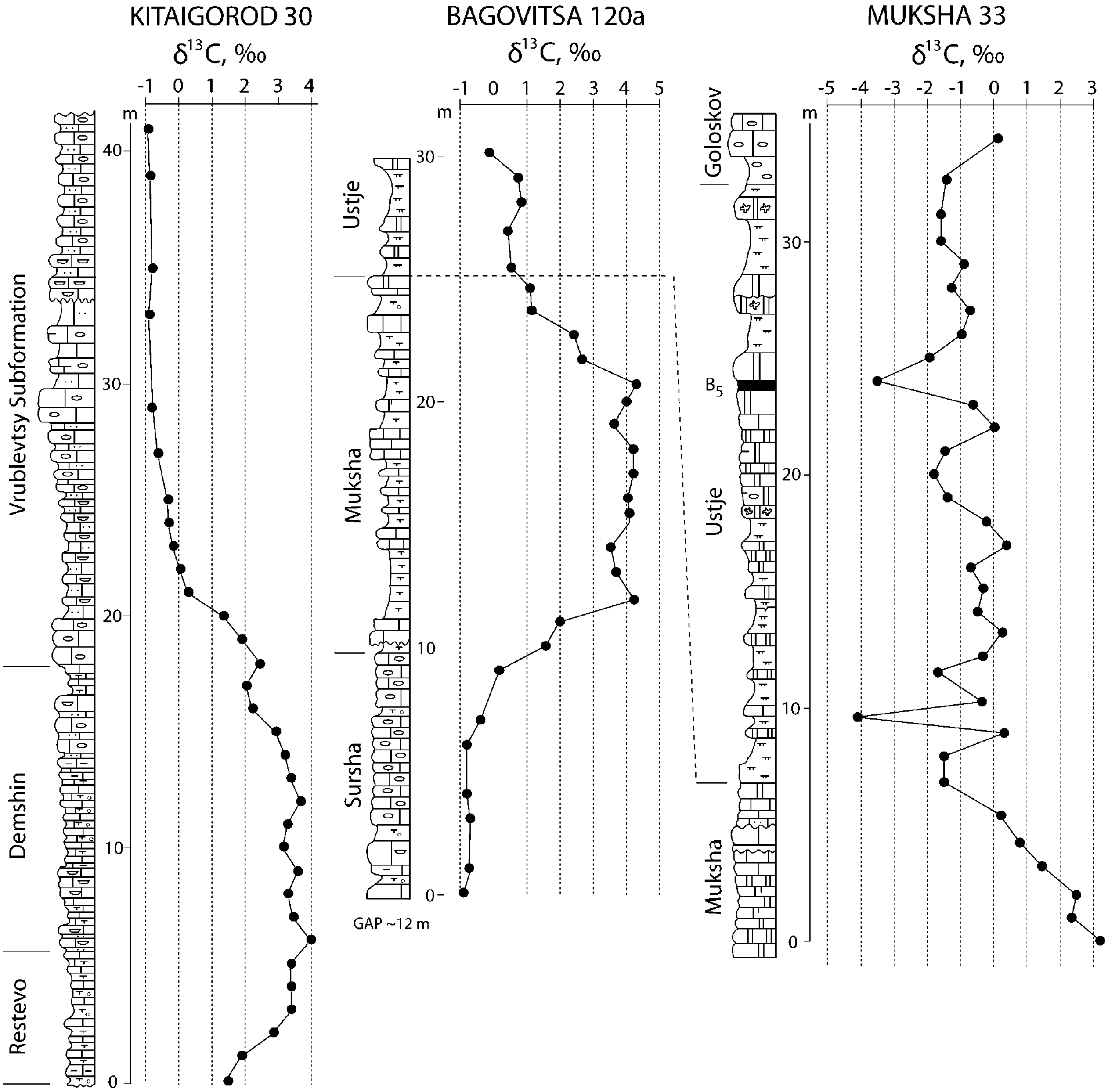

Fig. 4. Carbon isotope (δ^{13}C) trends in the lower Silurian sections of Podolia. Lithologic logs modified from Tsegelnyuk et al. (1983). For legend see Fig. 5.

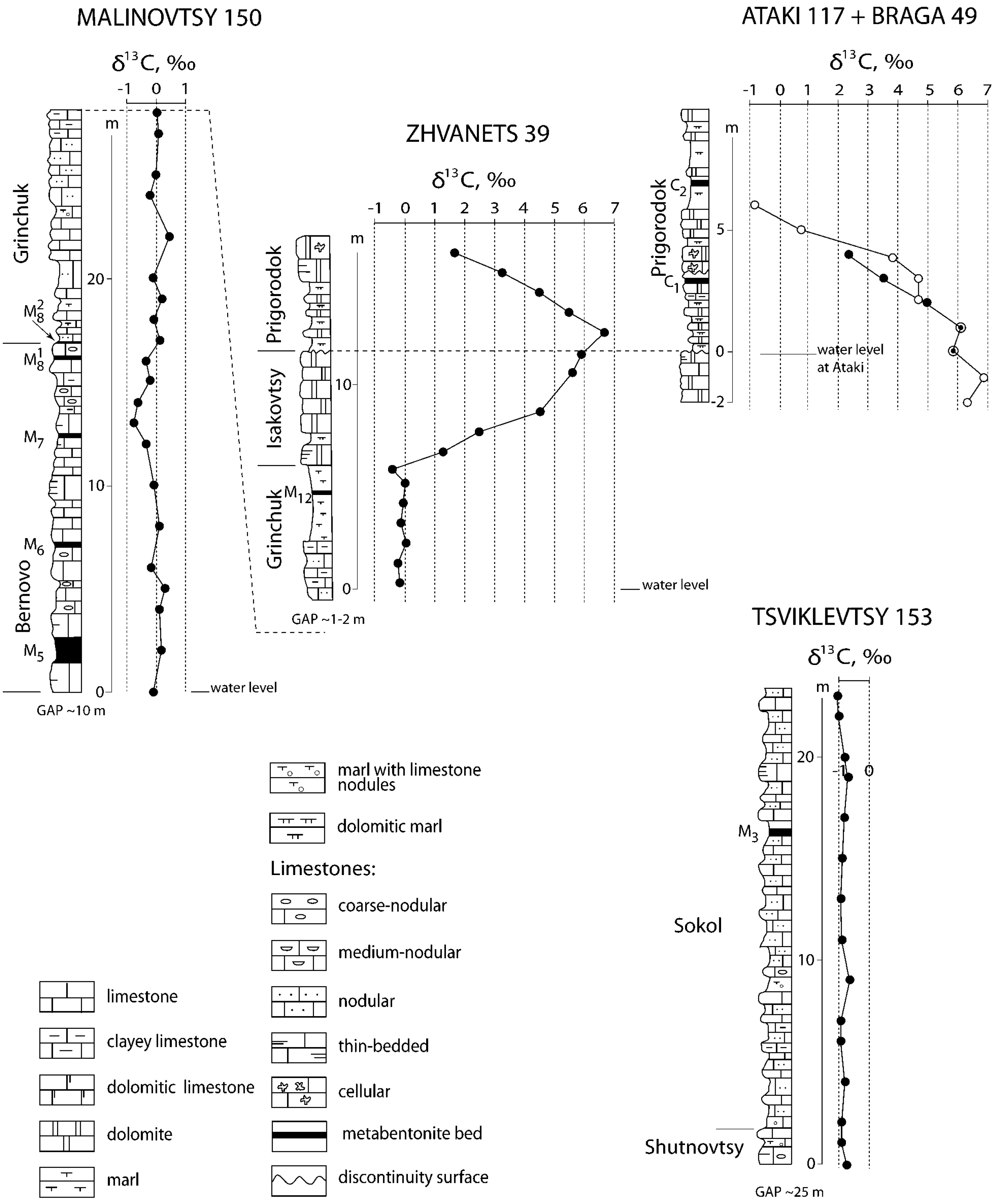

Fig. 5. Carbon isotope ($\delta^{13}C$) trends in the upper Silurian sections of Podolia. Lithologic logs modified from Tsegelnyuk et al. (1983). $\delta^{13}C$ values at Braga 49 shown by open circles.

3. **The second positive δ^{13}C excursion** begins in the Bagovitsa 120a section at the boundary of the Sursha and Muksha subformations (just above the boundary with the value of 1.6‰). The peak value (4.3‰) is reached thrice in the middle of the latter unit within an interval of 8–9 m (Fig. 4). The curve in this interval is more like a plateau (most of values over 4‰), not a double-peaked excursion as in Vidukle and elsewhere (Martma et al. 2005; Cramer et al. 2006). The δ^{13}C values decrease to ca 1‰ at the top of the Muksha Subformation and become even lower in the Ustje Subformation. In the Muksha 33 outcrop the falling limb of the excursion was observed at the base of the section (Fig. 4).
4. The next long interval, including the Ustje Subformation of the Bagovitsa Formation, parts of the Konovka (mainly not sampled), Tsviklevtsy, and the lower Rykhta (Grinchuk) formations are characterized by δ^{13}C values close to 0 or lower. The negative values of the trend are connected mostly with the Ustje dolomitic rocks (often between −1.5 and −2.0‰). Higher in the section, in the lower part of the Tsviklevtsy Formation (Sokol Subformation) negative values (−0.5 to −1.0‰) are less variable but rise close to zero (−0.3 to +0.1‰) in its upper part (Bernovo Subformation). A couple of anomalous more negative analyses (−0.8 and −0.6‰) were registered in the very top of the Bernovo Subformation. The values continue to increase also in the Rykhta Formation, still rather modestly in the lower part (Grinchuk Subformation), where δ^{13}C values remain between –0.4 and +0.5‰ (Fig. 5).
5. **The third positive δ^{13}C excursion** begins in the Zhvanets 39 section at the very bottom of the Isakovtsy dolomites (belonging to the upper part of the Rykhta Formation) with an initial value of 1.3‰ and continues into the Prigorodok Formation. This is the most prominent shift identified in the Silurian of Podolia so far: δ^{13}C increasing steadily through the Isakovtsy Subformation reaches 5.9‰ in the top and the peak value of 6.6‰ in the bottom of the Prigorodok Formation (Fig. 5). Upwards in the sequence the falling limb of the excursion follows at a rate of ca 1‰ per 1 m (see Table 3, e.g. sample Zhvanets 39-17 shows 1.7‰ 4 m higher). In addition to Zhvanets 39, the main section studied, this excursion was identified also in two nearby outcrops (at Ataki and Braga villages, Fig. 5). In the latter section a maximum value of 6.9‰ was reached already in the topmost Isakovtsy Subformation and after a short plateau-like trend (5.9–6.2‰) in the lowermost Prigorodok Formation the values decrease rather quickly. Small differences between the characters of the trends observed in Zhvanets and Braga need some additional checking, but a curve compiled using mean values for the above three sections (Fig. 6) demonstrates rather smooth and regularly rising and falling limbs of the excursion. Our sampling programme did not allow tracing a continuation of the δ^{13}C curve into the Pridoli. This gap in studies will be improved during the next stage of the project.

DISCUSSION AND STRATIGRAPHICAL IMPLICATIONS

The locations of the above excursions were identified in terms of local lithostratigraphy, which clearly fixes the position of an excursion in the sections. Our next task is to date these excursions based on the international stratigraphical standard classification. Figure 2 demonstrates different views on the time correlation of the Podolian Silurian with sequences elsewhere. One reason for the appearance of discrepancies was the correlation of shallow-water Podolian sections containing shelly faunas with deep-water graptolitic sections in the northwestern Ukraine (Volynia) and southwestern Belarus. Because of the lack of graptolites in Podolia this correlation was based mainly on the distribution of 29 metabentonite beds (Tsegelnyuk 1980; Tsegelnyuk et al. 1983). Volcanic ash beds are potentially a good correlation tool but, as shown by Kiipli & Kallaste (2002), a special integrated study of the geochemical properties of bentonites and detailed biostratigraphical control of samples is needed. In the 1970s–1980s these aspects were not sufficiently studied and later results (Kiipli et al. 2000) gave rise to certain doubts, which are reflected in Figs 2 and 6.

The aim of this project was not to discuss in detail reasons for former contradictory results but to produce new data that can generate independent evidence for geological correlation. Carbon isotope correlation has offered a series of successful examples (e.g. Saltzman 2001; Brenchley et al. 2003; Munnecke et al. 2003), and this encourages us to present here our results as follows. In order to make reading of the discussion easier, we add here a composite δ^{13}C trend of Podolia correlated with an East Baltic curve (Fig. 6).

The early Sheinwoodian excursion

The first positive δ^{13}C excursion identified by us in the Restevo and Demshin subformations (Figs 4 and 6) and earlier by Azmy et al. (1998) is clearly the same global carbon isotopic shift that is most widely known from many parts of the world. We prefer to name it the early Sheinwoodian excursion in order to be as exact as possible and to avoid mixing different kinds of terminology (e.g. Ireviken). This excursion was first described in the lower Wenlock localities of Gotland

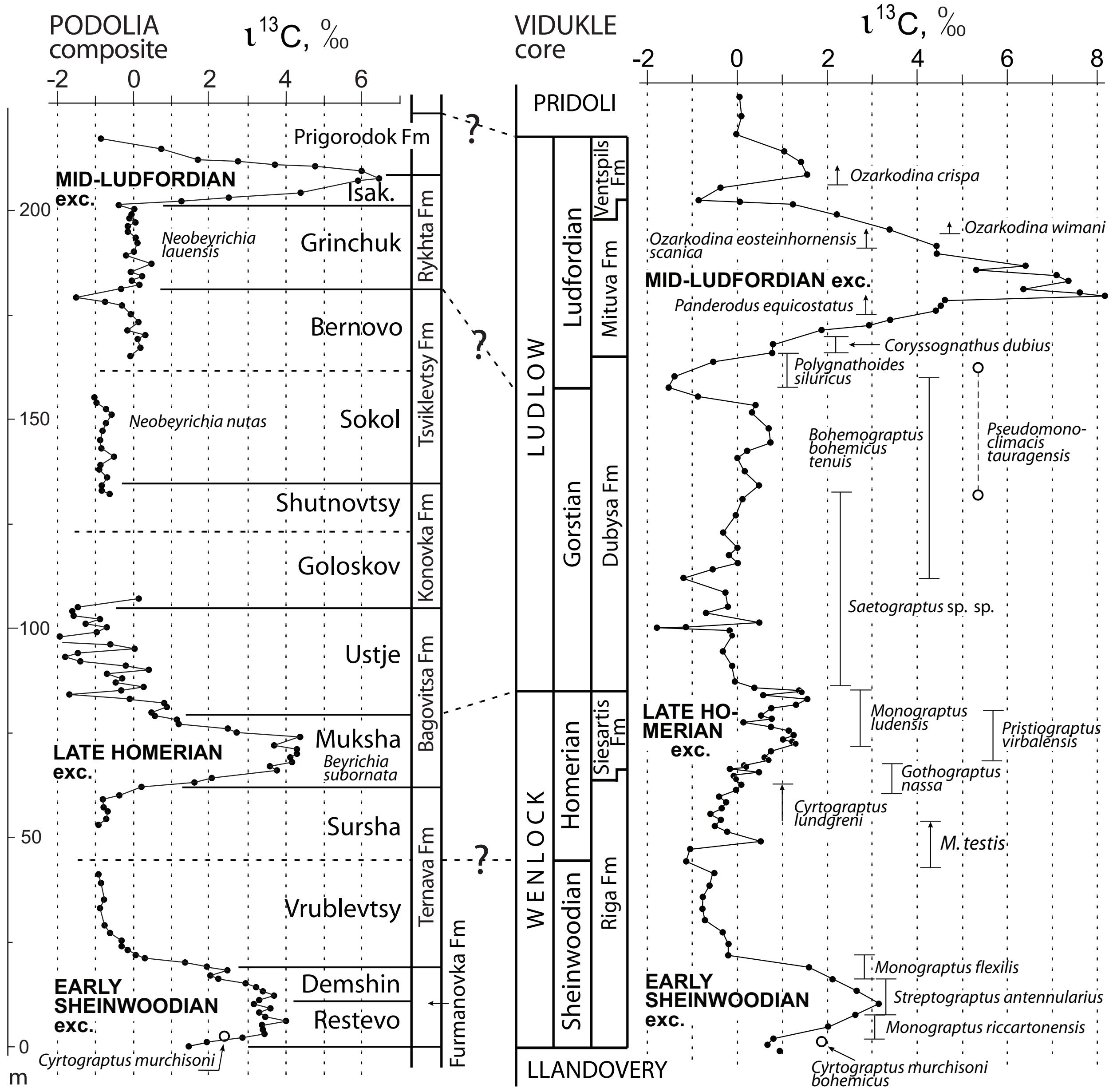

Fig. 6. Composite carbon isotope (δ^{13}C) trend of the Wenlock and Ludlow of Podolia correlated with that of the Vidukle core, Lithuania. The latter is modified from Martma et al. (2005). The ostracode species noted (according to Abushik 1983) in Podolia show the occurrence of the species in the corresponding unit. Unit names to the right of the curve are subformations except the Prigorodok Formation (Fm) in the top. Isak. = Isakovtsy. At the Vidukle curve are shown ranges or single occurrences of the named fossils.

(from the Upper Visby to lowermost Slite Beds, nowadays termed formations; for summary see Munnecke et al. 2003) and has often been tied to the Ireviken Event by Jeppsson (1990). This excursion is well known also in the East Baltic (lower part of the Jaani Regional Stage or Riga Formation; Kaljo et al. 1997, 1998; Martma et al. 2005) and Wales (Loydell & Frýda 2007), in several localities in North America (Saltzman 2001; Cramer & Saltzman 2005; Noble et al. 2005) and Australia (Talent et al. 1993). Depending on local geological history, the shape of the excursion may be somewhat different, but mostly the curve is rather wide and moderately high (4–6‰). The parameters of the shift in the Furmanovka Formation of Podolia are very much the same and also the stratigraphical position of the respective beds fits well with a general understanding of timing of this early Sheinwoodian excursion.

Kaljo & Martma (2006) discussed the correlation of the shift with graptolite biozones and showed that increase in the $\delta^{13}C$ values begins within the *Cyrtograptus murchisoni* Biozone*,* the peak occurs in the *Monograptus riccartonensis* or *Streptograptus antennularius* Biozone, and the falling limb ends in the *M. flexilis* Biozone. This definition, however, contains no information about the isotope trend through the *Cyrtograptus centrifugus* Biozone, missing in many sections. These refinements may help to specify the position of the Restevo and Demshin subformations in the correlation chart, but an uncertainty, caused by distribution problems of *Cyrtograptus centrifugus*, remains.

Tsegelnyuk (1976) reported two important graptolites, *Cyrtograptus murchisoni* and *C. murchisoni bohemicus*, from the Restevo Subformation (2–2.2 m from the bottom) at Kitaigorod Village, which places the beginning of the excursion in the Kitaigorod section unambiguously into the *C. murchisoni* Biozone. Another question is how close it is to the lower boundary of the Wenlock, defined by the appearance of *C. centrifugus*. Both species are known also in the Baltic, and recently Loydell & Jeppsson (2006) identified *C. bohemicus* on Gotland from the unit c of the Upper Visby Formation at Ireviken. Still, this level is clearly higher than occurrences in the East Baltic, and especially in Podolia. We suppose that the missing *C. centrifugus* interval of the $\delta^{13}C$ excursion in the Restevo Subformation is a short one and therefore the shift begins very shortly above the lower boundary of the Wenlock.

Loydell & Frýda (2007) have recently shown that in the Banwy River section, Wales, the early Sheinwoodian excursion commences in the upper *C. murchisoni* Biozone; the *C. centrifugus* Biozone is characterized by generally lower $\delta^{13}C$ values. These new data fix rather clearly relationships of graptolite biozones and beginning of the early Sheinwoodian $\delta^{13}C$ excursion. Still, debates about the position of the Llandovery–Wenlock boundary is not concluded yet and the suggested (Aldridge et al. 1993) Datum 2 of the Ireviken Event as a correlative level for the boundary GSSP needs to be checked for a possible gap (Loydell et al. 2003) and perhaps some additional criteria should also be added (Männik 2007). Meantime we use the official IUGS terminology.

The late Homerian excursion with or without an extension into the early Ludlow

The second positive $\delta^{13}C$ excursion identified in the Muksha Subformation (Figs 4 and 6) is more complicated for firm correlation due to global and local stratigraphic uncertainties. In global sense, this shift is not so widely known as the previous one and different views have been expressed about the shape of the curve and its dating. Recent papers by Cramer et al. (2006) and Kaljo & Martma (2006) demonstrate practically identical double-peaked excursions, the former in Nevada and Tennessee in North America and the latter in Estonia, Latvia, and Lithuania in the East Baltic. Both groups of authors conclude that the excursion begins within the *Gothograptus nassa–Pristiograptus dubius–P. parvus* interval above the last occurrence datum of *Monograptus flemingii* and ends in the *Colonograptus deubeli* (Tennessee) or *C. ludensis* Biozone (Baltic). Besides this conclusion, Cramer et al. (2006) noted that Berry & Murphy (1975) found several Ludlow graptolites (*Neodiversograptus nilssoni*, *Saetograptus colonus*, *Bohemograptus bohemicus*) in the Simpson Park I section, Nevada, in the lower part of the lime mudstone-wackestone bed of the Roberts Mountain Formation. If the graptolite sampling data are correctly interpreted, then the above graptolites date the beds with the second peak of the Mulde excursion (terminology of Cramer et al. 2006) as the very beginning of the Ludlow. They discussed different possibilities, but did not find any satisfactory explanation. This finding is in strong contradiction also with Baltic data, especially with those from graptolitic sequences (Priekule and Ventspils in Latvia, Kaljo et al. 1997, 1998; Vidukle in Lithuania, Martma et al. 2005), where the *N. nilssoni* Biozone lies above the double-peaked late Homerian excursion bed. The $\delta^{13}C$ trend in the early Ludlow of the Baltic shows dominantly negative values, and the same was documented by Corfield et al. (1992) for Britain.

The above discussion about dating the second peak in the Simpson Park, Nevada, is essential in the context of our study in Podolia because, as outlined in the introduction and shown in Fig. 2, Tsegelnyuk et al. (1983) correlated the Bagovitsa Formation with the lowermost Ludlow. Considering the carbon isotope data from the East Baltic (Kaljo et al. 1997, 1998; Martma et al. 2005), Gotland (Samtleben et al. 2000), and Poland (Porębska et al. 2004), this correlation is clearly unlikely for the relevant part of the Muksha Subformation. At the same time, negative values revealed in the Ustje Subformation fit well with those from the lower Ludlow of the Baltic area *sensu lato* and elsewhere (*op. cit.* above). On the basis of those and also some biostratigraphical data (not discussed here in detail, but see Koren et al. 1989; Gritsenko et al. 1999 and references therein), we prefer to correlate the Muksha Subformation with the uppermost Wenlock. Besides isotope data, most trustworthy information is provided by ostracodes (Abushik 1983; a few noted in Fig. 6) and also some other shelly fauna groups (Gritsenko et al. 1999), but their interpretation is a much more complicated task. We leave the

Ustje Subformation at the bottom of the Ludlow, and this means that the series boundary lies within the Bagovitsa Formation. The situation is very similar to that with the Rootsiküla Regional Stage of Estonia, whose upper part was recently transferred, based on the conodont argumentation, to the Ludlow Paadla Regional Stage (Viira & Einasto 2003). It might be added that the dolomitic rocks of the upper part of the Rootsiküla Stage have often been correlated with the Ustje Subformation (Abushik 1983; Kaljo 1987).

However, some doubts remain in Podolia and we very much hope that the real stratigraphical value of graptolite occurrences in the Simpson Park outcrop, discussed in Cramer et al. (2006), will be checked carefully soon. Noble et al. (2005) demonstrate several interesting Wenlock carbon isotope curves from the Canadian Arctic, which show a double-peaked $\delta^{13}C_{org}$ excursion in the upper Homerian fitting well with Baltic ones. Yet, the $\delta^{13}C_{carb}$ curve they present is very variable, partly deeply negative (–2‰), and it is hard to see any similarities with the Baltic late Homerian trend. Having in mind the above discussion about the Simpson Park section, we note that Noble et al. (2005) report a low $\delta^{13}C_{org}$ positive shift (to ca –30‰) within the *Lobograptus progenitor* Biozone in the Twilight Creek section, Bathurst Island. The shift occurs ca 12 m above the lower boundary of the Ludlow and is not visible in the $\delta^{13}C_{carb}$ curve. We think that the above C_{org} shift may suggest one more possible explanation of the Simpson Park case.

The middle Ludfordian excursion

The excursion is well recognizable thanks to very high values reported from different localities in beds close to the top of the Ludlow. The highest $\delta^{13}C$ values are known from Australia (12–13‰, Andrew et al. 1994), Scania of Sweden (11‰, Wigforss-Lange 1999), Gotland, Lithuania, and the Prague Basin (8‰, Samtleben et al. 1996, 2000; Martma et al. 2005; Lehnert et al. 2007b); in several localities the values remain below 6‰ (Saltzman 2001; Lehnert et al. 2007b). There has been some discussion about the dating of this excursion (see for an overview Martma et al. 2005; Kaljo & Martma 2006), but researchers more or less agree that the excursion begins within or above the *Polygnathoides siluricus* conodont and *Neocucullograptus kozlowskii* graptolite biozones. The end of the excursion is less clear, being somewhere below the first appearance datum of the conodont *Ozarkodina crispa* (Kaljo & Martma 2006; Lehnert et al. 2007b) or within this zone (Samtleben et al. 2000) depending on how to interpret the position of the Sundre Beds. The peak shift is usually correlated with the *N. kozlowskii* Biozone (e.g. Azmy et al. 1998; Saltzman 2001) or higher, embracing also the topmost Ludfordian (Jeppsson et al. 2005). The latter correlation was opposed by Kaljo & Martma (2006). On the basis of the Kosov section, Lehnert et al. (2007b) showed that peak values occur above the last occurrences of *N. kozlowskii*, but this could be more an artefact caused by a facies change. In the Prague Basin the main peak was recorded in the beds with the *Ananaspis fecunda–Cyrtia postera* community. *Monograptus latilobus* has been found above these beds, but well below the upper boundary of the Ludlow. The *M. latilobus* graptolite Biozone occurs in the drill core sections of eastern Poland at the very beginning of the upper Ludfordian (Urbanek 1997).

The Isakovtsy Subformation and Prigorodok Formation, accommodating the third $\delta^{13}C$ excursion in Podolia (Figs 5 and 6), have been classified and placed in the stratigraphical scheme rather differently. According to Nikiforova & Predtechensky (1972), these form one unit, the "Isakovtsy Beds", at the bottom of the Skalian Stage (Fig. 2). Tsegelnyuk et al. (1983) introduced two separate units – the Isakovtsy Subformation in the Malinovtsy Series and the Prigorodok Formation in the Rukshin Series and a gap between them (Fig. 2). The age of the Prigorodok Formation is not clearly stated but according to the correlation charts in their paper, it seems to be at the very beginning of the Pridoli or just below it. Kaljo (1987) placed the Prigorodok Formation again into the Skalian Stage, but correlated the Isakovtsy and Prigorodok formations with the upper Ludlow. Koren et al. (1989) dropped both into the topmost Malinovtsy Series (or Stage?) and upper Ludfordian. Drygant (1994) summarized his scheme in sense of time in the same way – he considered Isakovtsy and Prigorodok as separate formations within the Skalian, but belonging in the topmost Ludlow at the level of the *Ozarkodina crispa* conodont Biozone.

This mess of different views can be clarified using carbon isotope stratigraphy. We refer here to our recent papers (Martma et al. 2005; Kaljo & Martma 2006), where our understanding about the dating of the mid-Ludfordian excursion is demonstrated. We have analysed mainly East Baltic and Gotland $\delta^{13}C$ data (Samtleben et al. 1996, 2000), but also biostratigraphy. On the basis of these views we conclude that in Podolia analogically the excursion in the Isakovtsy and Prigorodok formations should be of mid- to early late Ludfordian age, but the upper part of the latter unit reaches the top of the Ludlow. This conclusion is consistent with views by Drygant (1994) but we do not know limits of his *O. crispa* Biozone.

The gap between the Isakovtsy and Prigorodok formations is not clearly seen in the shape of the carbon isotope trend (Figs 5 and 6), but it may exist like in Kosov quarry in the Prague Basin (Lehnert et al. 2007b). The gaps connected with sea level lowering during a carbon isotope event are widely known phenomena and have been used as an indicator of a short-lived glacial event in the late Ludlow (Lehnert et al. 2007a), but the idea that these support a glaciation seems to be premature.

CONCLUSIONS

1. Three positive $\delta^{13}C$ excursions were identified, based on the analyses of 149 whole-rock samples. The first excursion in the Kitaigorod 30 section, beginning in the Restevo Subformation, reaches its peak value of 4.0‰ in the very bottom of the Demshin Subformation. The second one reaches the peak value of 4.3‰ in the middle of the Muksha Subformation. The third shift is the most prominent one identified in the Silurian of Podolia: steady increase in $\delta^{13}C$ values through the Isakovtsy Subformation, reaching 5.9–6.9‰ in the top of the unit. In Zhvanets the peak value of 6.6‰ is reached in the bottom of the Prigorodok Formation.
2. In the “middle” Silurian three major positive global excursions have been identified as follows: in the early Sheinwoodian (early Wenlock), late Homerian (late Wenlock), and middle Ludfordian (late Ludlow). The general character of the carbon isotope trend and stratigraphical positions of excursions show that the same set of global shifts was established by the present study in Podolia.
3. Different aspects of these $\delta^{13}C$ excursions confirm their utility for the improvement of regional and global correlation of Wenlock and Ludlow sections of Podolia. However, full application of results in regional stratigraphy depends on several details that need additional study.

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Kolm globaalset süsinikisotoopide suhte anomaaliat Podoolia (Ukraina) Siluris: stratigraafilised järeldused

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Podoolia on klassikaline suhteliselt madalaveeliste Siluri kivimite levikuala. Dnestri jõe keskjooksu orgudes paljanduvad kivimid (enamasti lubjakivid) on kivistisrikkad ja fossiilid on olnud aluseks traditsioonilise stratigraafilise liigestuse loomiseks ning vastavate üksuste rööbistamiseks Balti ja muude alade skeemidega. 1983. aastal Podoolias toimunud Rahvusvahelise Siluri Stratigraafia Alamkomisjoni väljasõiduistungi toimumiseks koguti arvuka kollektiivi poolt P. D. Tsegelnjuki juhtimisel väga suur hulk uudset paleontoloogilist jm materjali, loodi uus litostratigraafiline liigestus ja revideeriti ka rea stratoonide geoloogilist vanust. Peamised raskused tekkisid korrelatsioonil teiste alade ja graptoliidifaatsiesega, kuivõrd kasutatud bentoniidikihtide uuring ei olnud sel ajal piisaval tasemel. Käesolev uurimus on katse rakendada süsinikisotoopide koostise (suhte) muutustel tuginevat stratigraafiat. On uuritud ligi 200 kivimipala, mis iseloomustavad *ca* 80% kogu Podoolia Siluri läbilõikest (ilma Pridoli ladestikuta), määrates kivimite kemismi ja δ^{13}C väärtusi. On kindlaks tehtud kolme globaalse levikuga positiivse anomaalia esinemine ka Podoolia Siluris: esimene algab Restevo alamkihistus ja selle tipmised väärtused (4,0‰) on määratud Demshini alamkihistu alguses; teise ekskursiooni tipp (4,3‰) leidub Muksha alamkihistu keskel ning kolmanda, kõige prominentsema anomaalia δ^{13}C kõrgeimad väärtused ulatuvad Isakovtsy alamkihistu ja Prigorodoki kihistu piirikihtides 6,9‰. Isotoop- ja biostratigraafiline korrelatsioon lubab väita, et esimene anomaalia paikneb Wenlocki (Sheinwoodi) alguses, teine Wenlocki lõpus (Kesk- kuni Ülem-Homer) ja kolmas Ludlow' teises pooles (Kesk-Ludford). Need dateeringud lubavad täpsustada Podoolia vastavate ümbriskivimite vanust ja korrelatsiooni nii naaberalade kui ka rahvusvahelise standardstratigraafia suhtes.