A long-lasting steady period of isotopically heavy carbon in the late Silurian ocean: evolution of the δ^{13}C record and its significance for an integrated δ^{13}C, graptolite and conodont stratigraphy

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The mid-Ludfordian carbon isotope excursion (CIE) is probably the most intensively studied of all Palaeozoic geochemical events. This is mainly due to the fact that it represents the largest perturbation of the global carbon cycle during the entire Phanerozoic and the second largest in Earth's history. Herein an uninterrupted and complete δ^{13}C record is presented for the first time across the mid-Ludfordian carbon isotope excursion from the middle palaeolatitudes (Barrandian, Perunica, northern peri-Gondwana). Similar evolution of the δ^{13}C geochemical anomaly identified in middle palaeolatitudinal and palaeotropical regions enables three distinct chemostratigraphic zones (R-Zone, S-Zone and F-Zone) to be established, differentiated on the basis of their δ^{13}C dynamics. Application of the δ^{13}C chemostratigraphy has considerably improved correlation of earlier described Barrandian sections and allows re-evaluation of the duration of several gaps in sedimentary records. Detailed comparison of the δ^{13}C chemostratigraphic zonation with graptolite and conodont biostratigraphic zonations has resulted in a proposal for an integrated δ^{13}C, graptolite and conodont stratigraphy for the mid-Ludfordian interval. Analysis of the available δ^{13}C data on the global mid-Ludfordian CIE revealed that high δ^{13}C values attain a similar level during a long-lasting steady period. There is no statistically significant difference in the level of these high values among the δ^{13}C records obtained from different palaeocontinents. This fact suggests that the mid-Ludfordian δ^{13}C anomaly from different palaeocontinents originated from the same global oceanic isotopic reservoir rather than being independently evolved within small restricted epeiric basins. • Key words: Silurian, mid-Ludfordian carbon isotope excursion, global oceanic isotopic reservoir, integrated δ^{13}C, graptolite and conodont stratigraphy, LAU and Kozlowskii bioevents.

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The Silurian Period was considered for a long time to be a stable period in Earth history. However, this viewpoint has been dramatically altered over the last two decades as several distinct and rapid changes in the Silurian global carbon cycle have been described. These geochemical events were closely linked to major crises in the marine ecosystem as well as to palaeoclimatic changes (see Munnecke *et al.* 2003, Loydell 2007, and Calner 2008 for review). The most prominent perturbation in the Silurian global carbon cycle, named as the mid-Ludfordian carbon isotope excursion (Kaljo *et al.* 1997), has been considered to also represent the largest perturbation throughout the whole Phanerozoic and the second largest in Earth's history (Munnecke *et al.* 2003). On the other hand, the latter prominent geochemical event was preceded only by a moderate faunal crisis referred to as the LAU conodont bioevent (Jeppsson 1987), Kozlowskii graptolite bioevent (Urbanek 1993), and Pentamerid bioevent (Talent *et al.* 1993). The mid-Ludfordian carbon isotope excursion and the associated faunal turnover was hitherto documented from many palaeocontinents, in particular from different areas of Baltica (see Kaljo *et al.* 1997, Calner 2008, Eriksson *et al.* 2009, Jeppsson *et al.* 2012 and Kozłowski & Sobień 2012 for review), Australia (Talent *et al.* 1993, Andrew *et al.* 1994, Jeppsson *et al.* 2007, 2012), Laurentia (Barrick 2010), Perunica (Lehnert *et al.* 2003, 2007; Manda *et al.* 2012), Avalonia (Loydell & Frýda 2011), and the Carnic Alps (Histon & Schönlaub 1999, Brett *et al.* 2009, Histon 2012). The high magnitude of the $\delta^{13}C$ values makes the mid-Ludfordian carbon isotope excursion probably the most intensively studied of all Palaeozoic geochemical events.

In the present paper new data are presented on the evolution of the $\delta^{13}C$ anomaly based on study of the most complete and uninterrupted section in the Barrandian area (Perunica). Special attention is also placed on the significance of this data with regard to a global $\delta^{13}C$, graptolite and conodont stratigraphy. The main aims of the present study are as follows: (1) to describe the first complete $\delta^{13}C$ record across the mid-Ludfordian carbon isotope excursion from a middle palaeolatitude region, (2) to correlate the Barrandian sections using $\delta^{13}C$ chemostratigraphy, (3) to propose an integrated $\delta^{13}C$, graptolite and conodont stratigraphy for the middle Ludfordian, and (4) to compare the evolution of $\delta^{13}C$ records from different palaeocontinents.

Ludfordian of the Barrandian

Only a small part of the former Palaeozoic basin, known as the Prague Basin, is preserved and its relicts are sometimes referred to as the Prague Synform (Fig. 1). The latter basin is a younger component of the Proterozoic crustal block called the Barrandian (or Teplá-Barrandian terrane). Palaeomagnetic data from the Barrandian suggests a palaeoposition somewhere between 30 and 25 degrees S of the palaeoequator during the Ludfordian period (Torsvik 2009, Tasáryová *et al.* 2011). There is no evidence of a continental shoreline at any of the Silurian sections in the Barrandian. Facies distribution indicates that shallow water domains were surrounded by deeper and open marine settings dominated by hemipelagic deposition. Whether the Barrandian formed part of accreted peri-Gondwanan terrains (Stampfli *et al.* 2002) or it was a small isolated crustal block (microcontinent or terrane) often referred to as Perunica (Havlíček *et al.* 1994, Cocks & Torsvik 2002) is still a matter of discussion. Nevertheless, the latter seems to be the more likely scenario as the Silurian faunas of the Barrandian show a distinct affinity to the peri-Gondwanan as well as to the Baltic-Avalonian-Laurentian faunas, indicating that Perunica was located in the temperate zone (Kříž 1999a, 2008; Manda 2008; Budil *et al.* 2010; Tasáryová *et al.* 2011). Detailed descriptions of middle and late Ludfordian age strata in the Barrandian were published by Kříž (1992, 1998a) and Manda & Kříž (2006).

The Ludfordian strata of the Barrandian compose the upper part of the Kopanina Formation. Their facial development accounts for deposition in a rift-like basin with several bathymetric highs, like tectonic ridges along synsedimentary faults and former volcanic elevations (Kříž 1991). One of the latter emerged even above sea level during Ludfordian times and formed the so-called Svatý Jan Isle (Horný 1955). Shallow water limestone facies change rapidly laterally over short distances reflecting different rates of basin bottom subsidence or uplift (Kříž 1991, 1992, 1998a; Manda & Kříž 2006). The diverse movements of the tectonic blocks as well as global sea level fluctuations gave rise to a high number of varied biotopes which were inhabited by specific faunal communities (Havlíček & Štorch 1990, 1999; Kříž 1998b, 1999) and produced a rather complicated facial pattern.

Ludfordian of the Kosov area

The section described in the present paper (Kosov section No. JF195 by Frýda or No. 924 by Kříž & Manda) is located in the area of the Silurian Kosov Volcanic Center, which originated during the latest Wenlock interval. There is evidence that intense volcanic activity continued from the Wenlock up to the late Gorstian in this area (Fig. 1). As shown by Kříž (1992), synsedimentary movements and accumulations of volcanic products gave rise to a topographic high on the seafloor with preservation of relatively shallow water sedimentary deposits that persisted from the latest Wenlock up to the early Přídolí (Bouček 1934, Bouček & Přibyl 1955, Horný 1955, Kříž 1992). A latest Wenlock–early Ludlow volcano-sedimentary succession was overlain by limestone dominated successions of middle and late Ludlow (Ludfordian) age. Traces of volcanic activity manifested by the occurrence of thin beds of tuffites preserved within the Ludfordian strata probably represent volcanic material originating from an area outside the Kosov Volcanic Center.

Crinoidal grainstones were deposited during the *Neocucullograptus kozlowskii* Biozone (mid-Ludfordian) interval within the central part of the Kosov elevation and these are succeeded basin-ward by interbedded laminated shales and platy limestones (the so-called *Acanthalomina minuta* shales; Horný 1955). Shales with small nodules and thin beds of cephalopod wackestones are developed in the uppermost *N. kozlowskii* Biozone interval (Kříž 1992). A distinct sequence boundary was recognized at the top of the *N. kozlowskii* Biozone interval at all the studied sections within the Kosov area (Manda & Kříž 2006). The latter boundary represents the mass extinction level of the mid-Ludfordian graptolite faunas at the top of the *N. kozlowskii* Biozone (LAD of *Neocucullograptus kozlowskii*, and *Bohemograptus tenuis*) as well as the LAD of the pelagic ostracod *Entomis migrans* (see Štorch 1995a, b; Manda & Kříž 2006, Manda *et al.* 2012).

Three principal benthic communities [*Diacanthaspis* (*Acantholomina*) *minuta, Cardiola alata* and *Cheioptereia glabra* communities] occurred in the interval of the *N. kozlowskii* Biozone prior to the onset of the mid-Ludfordian carbon isotope excursion. The *Diacanthaspis* (*Acantholomina*) *minuta* Community, established by

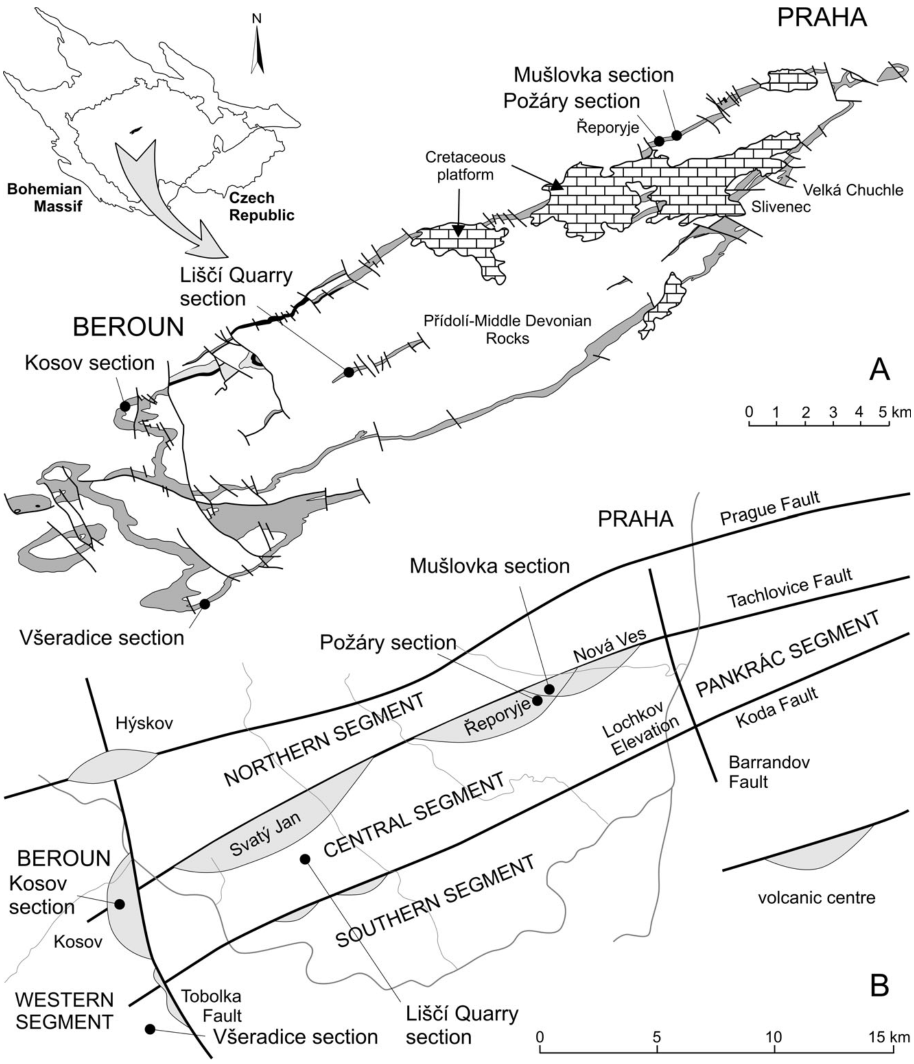


Figure 1. Distribution of Silurian rocks in the Barrandian (Perunica) including the position of the studied sections (A) and Silurian synsedimentary tectonics, volcanic and tectonic elevations, and segments (sub-basins) in the preserved parts of the Prague Basin (B; after Kříž 1991).

Havlíček & Štorch (1990), represents a moderately diversified faunal community restricted to shales and platy limestones deposited within a quite water environment below wave base. It is characterized by two common trilobite species [*Diacanthaspis* (*Acantholomina*) *minuta* and *Otarion diffractum*] and several species of brachiopods, cephalopods, dendroids, scolecodonts and crinoids (Havlíček & Štorch 1990, 1999; Štorch 1995a; Tonarová *et al.* 2011). The latter community is known from only a few localities of the Barrandian (*e.g*., Kosov quarries and Liščí Quarry; Horný 1955, Havlíček & Štorch 1990). The *Cardiola alata* Community established by Kříž (1998b) occurs in cephalopod limestones bearing relatively diverse bivalve and cephalopod faunas accompanied by rare trilobites, gastropods, brachiopods, graptolites and ostracods (Kříž 1998b, 2010, 2011; Manda & Kříž 2006). Both the *Diacanthaspis* (*Acantholomina*) *minuta* and *Cardiola alata* communities were replaced by the younger *Cheiopterenia glabra* Community in most of the studied Barrandian sections (Kříž 1999b, Manda & Kříž 2006). The *Cheiopterenia glabra* Community was interpreted by Kříž (1999b) as a community living within a deeper water and less oxygenated environment. This faunal community is restricted to the uppermost part of the *N. kozlowskii* Biozone interval and may be characterized by more than seven bivalve species. The bivalve *Cheiopterenia glabra* is the most common species, usually forming about 90 per cent of all bivalves present (Kříž 1999b, 2010). The bivalve dominated benthic fauna is associated with common pelagic and nektonic cephalopods. Brachiopods, ostracods, univalved molluscs and gastropods such as *Spirina* are also locally present (Manda & Kříž 2006).

The end of the *N. kozlowskii* Biozone correlates with a distinct change in sedimentation at each section. In the Kosov area the start of a new sedimentary cycle is documented by several beds of crinoidal grainstones in the interval just above the top of the *N. kozlowskii* Biozone. Higher up, platy nodular limestones intercalated with shales form a succession corresponding to the lower part of the newly established *Pristiograptus dubius postfrequens*

Partial-range Interval Zone [corresponding to the *Neocucullograptus kozlowskii-Pseudomonoclimacis latilobus* Interzone of Kozłowski & Sobień (2012), see *Graptolite zonation* below in Discussion] and bear faunas of the *Kosovopeltis-Scharyia-Metaplasia* Community by Havlíček & Štorch (1990, 1999). The latter faunal community is restricted to a post-extinction interval and is characterized by a low faunal diversity. Only eleven brachiopod species and two trilobite species have hitherto been described from these beds. This community was until now documented only from some sections in the Kosov area. In another part of the Barrandian this interval corresponds to a long gap in sedimentation (Lehnert *et al.* 2003, 2007a; Manda 2003; Manda & Kříž 2006). Facial development of this succession is very uniform at all sections in the Kosov area, in contrast to under- as well as over-lying successions.

The limestone beds containing the *Kosovopeltis-Scharyia-Metaplasia* Community are overlain by a succession of light grey thin-bedded skeletal limestones bearing the *Ananaspis fecunda-Cyrtia postera* Community of Havlíček & Štorch (1999). The thickness of this limestone succession is found to vary laterally quite rapidly across the studied Kosov sections (Kříž 1992). The *Ananaspis fecunda-Cyrtia postera* Community has been documented at several localities across the Barrandian. This faunal community is restricted to carbonate facies and is characterized by more than 40 species of brachiopods and more than 20 species of trilobites. Locally it is associated with common crinoids, gastropods, rare corals, cephalopods and other faunas. The uppermost beds of the *Ananaspis fecunda-Cyrtia postera* Community already fall within the *Pseudomonoclimacis latilobus-Slovinograptus balticus* Biozone as was shown by Manda *et al.* (2012).

Strata of latest Ludfordian age consist of crinoidal limestones bearing the *Prionopeltis archiaci-Atrypoidea modesta* Community in the central part of the Kosov elevation (Havlíček & Štorch 1990, Kříž 1992). Contemporaneous succession of platy limestone beds and shales deposited on the slope of the Kosov elevation. The first appearence of the index graptolite *Pristiograptus fragmentalis* is documented at all known sections above the appearance of the *Prionopeltis archiaci-Atrypoidea modesta* Community (see Přibyl 1983, Kříž *et al.* 1986, Manda *et al.* 2012). The *Prionopeltis archiaci-Atrypoidea modesta* Community, being the first post-carbon isotope excursion community, was highly diversified and it bears several new faunal groups (see Havlíček & Štorch 1990; Šnajdr 1980; Kříž 1998b, 1999b; Manda & Turek 2009). For example, during this period the origin of the long-lasting archaeogastropod clade Porcellioidea Koken *in* Zittel, 1895 is documented which forms part of marine communities for more than 350 Ma (late Silurian–Late Cretaceous; Bandel 1993, Frýda & Blodgett 1998, Frýda & Ferrová 2011). The oldest members of the latter archaeogastropod clade come from the *Prionopeltis archiaci-Atrypoidea modesta* Community of the Kosov area (Frýda 1997).

In the Kosov area the last Ludfordian (and thus also Ludlow) in age bed consists of a rusty-coloured cephalopod limestone bank overlying the crinoidal limestones bearing the *Prionopeltis archiaci-Atrypoidea modesta* Community. The rich cephalopod fauna of this bed had already been studied by Barrande (1865–1877) and elements of several cephalopod lineages are described from this level (Turek 1975, 1976; Kříž *et al.* 1986; Kříž 1998b; Manda & Turek 2009; Manda & Frýda 2010).

Previous studies of section No. JF195

The section being studied herein, referred to as section No. JF195, is located close to those described by Kříž (1992) as sections No. 418b and No. 783, however, the latter was unfortunately quarried out during the late 20^{th} to 21^{st} centuries. The lower part of section No. JF195 was firstly described by Lehnert *et al*. 2007a. The sedimentology of the Ludlow-Přídolí boundary interval in the uppermost part of the studied section was described by Čáp *et al.* (2003) and Čáp (2012). The cephalopod and trilobite faunas of the latter interval were described by Turek (1992) and Vokáč (1996, 1999). The facial development and micropalaeontological content of the lower part of the studied section was recently studied by Gocke *et al.* (2012). Tonarová *et al.* (2012) reported a low diversified scolecodont fauna from the same part of section No. JF195. A detailed study of the chitinozoan record of the entire section is in progress (Vodička in prep.).

The $\delta^{13}C$ record of the lower part of the section (approximately 10 m), including the upper part of the *Neocucullograptus kozlowskii* Biozone and lower part of the *Pr. dubius postfrequens* Partial-range Interval Zone, was studied previously by Lehnert *et al.* (2007a). The latter authors published the $\delta^{13}C_{carb}$ values for 20 samples and identified rather high fluctuations within layers prior to the mid-Ludfordian CIE, a rapid rise and then rather stable $\delta^{13}C$ values at the beginning of the mid-Ludfordian CIE. The study by Lehnert *et al.* (2007b) also gave a preliminary report of $\delta^{18}O$ values obtained from conodont apatite samples taken from three Barrandian sections (including section No. JF195), which clearly show a significant positive excursion in $\delta^{18}O$ values of at least 2‰.

Sampling and methods

Carbonates from the upper part of the late Silurian Kopanina Formation at the Kosov Quarry (section No. JF195; see also Lehnert *et al.* 2007a), were sampled along with basal layers of the overlying Požáry Formation (Přídolí in age) in order to investigate the complete carbon isotope record across the mid-Ludfordian CIE. This new sampling campaign included 98 samples for carbon isotope study and covered a stratigraphic interval ranging from the mid-Ludfordian (*N. kozlowskii* Biozone) to the lowermost Přídolí.

A few milligrams of rock powder (preferably micrite) were recovered with a dental drill from cut and polished slabs. Where possible, mudstones and wackestones were sampled, but analyses were also carried out on grainstones. The carbonate powder was reacted with 100% phosphoric acid at 70 °C using a Gasbench II connected to a ThermoFinnigan Five Plus masspectrometer. All values are reported in ‰ relative to V-PDB by assigning a $\delta^{13}C$ value of +1.95‰ and a $\delta^{18}O$ value of 2.20‰ to NSB 19. Accuracy and precision was controlled by replicate measurements of laboratory standards and was better than ±0.1‰ for both carbon and oxygen isotopes. The nonparametric Mann-Kendall test is used for testing the presence of the monotonic increasing or decreasing trend of $\delta^{13}C$ values.

Results

Lithology and biostratigraphy

The middle and upper parts of the Kopanina Formation (approximately 25 m) and lowermost part of the overlying Požáry Formation (about 2 m) were studied from section No. JF195 at the Kosov locality. In the following paragraphs data regarding the lithology and biostratigraphy of the studied section are discussed as a framework for the description of the evolution of the $\delta^{13}C_{carb}$ record across the mid-Ludfordian CIE.

The lowest portion of the section (*ca* 3 m) consists of brown-grey calcareous shales containing nodules and lenses of micritic mud- and wackestones (Fig. 2A). The succession belongs to the upper part of the *Neocucullograptus kozlowskii* Biozone. A general trend towards increase of limestone content was observed in the highest portion of this interval with a limestone within the final beds of the sequence (Bed No. 13, see Lehnert *et al.* 2007a). Occurrence of dolomitic microsparite was documented within mudstone beds in the upper part of the succession (see also Gocke *et al.* 2012).

Two benthic communities [the *Diacanthaspis* (*Acantholomina*) *minuta* and *Cheioptereia glabra* communities] were found in the upper part of the *N. kozlowskii* Biozone at section No. JF195. The older *Diacanthaspis* (*Acantholomina) minuta* Community occurs within an interval of several metres in thickness. In contrast, species belonging to the younger faunal community, *Cheioptereia glabra* Community (Kříž 1999), were found only in the final bed (No. 13) of the sequence assigned to the *Neocucullograptus kozlowskii* Biozone. The boundary between beds 13 and 14 (level 0 m) is characterized by a distinct lithologic change from brown-grey calcareous shales with nodules and lenses of micritic mud- and wackestones to overlying compact thick-bedded packstones and grainstones (Fig. 2B, C). This change represents a distinct sequence boundary and probably also a short stratigraphic gap.

An interval of approximately 0.5 m in thickness of packstones to grainstones, bearing abundant unsorted crinoidal and brachiopod remains, forms the first sedimentary record above the latter sequence boundary. Fossils of stratigraphic significance have not been documented from this interval. Platy nodular limestones intercalated with shales occur higher up in the sequence forming rather thick (*ca* 11 m) and uniform unit that overlie the above-mentioned basal packstones to grainstones (Figs 2C–F, 3A). The interval occurring between level 0 m and 11.5 m corresponds to the main part of the *Pr. d. postfrequens* Partial-range Interval Zone (Fig. 4) and contains faunas of the *Kosovopeltis-Scharyia-Metaplasia* Community described by Havlíček & Štorch (1990). The overlying unit starts at level 11.5 m with two thick limestone beds separated by 10 cm of shale (Fig. 3B). Both beds bear rich coquinas formed of *Ananaspis fecunda* and represent the base of a 5.5 m thick succession of light grey thin-bedded skeletal limestones (Fig. 3C, D) bearing the *Ananaspis fecunda-Cyrtia postera* Community described by Havlíček & Štorch (1990). From the 17 m level the succession continues with mainly crinoidal limestones intercalated with calcareous shales and bears faunas of the highly diversified *Prionopeltis archiaci-Atrypoidea modesta* Community. The rusty-coloured cephalopod limestone bank (approximately 0.6 m in thickness) forms the last sedimentary record of Ludlow age (Fig. 3E). The succession overlying the cephalopod bank (at level 26 m approximately) already belongs to the *N. parultimus* graptolite Biozone of Přídolí age (Požáry Formation). Přídolí Series begins with thin limestone beds intercalated with thick intervals of calcareous shale (Fig. 3F). This rapid change in sedimentation reflects the basal Přídolian trangression.

$\delta^{13}C$ record

The globally observed mid-Ludfordian CIE is recorded at section No. JF195 with maximum $\delta^{13}C$ values of about +9‰ (Fig. 4). The samples from the pre-excursion interval show a gradual increase in $\delta^{13}C$ values from –0.33‰ to +2.96‰. As has already been shown by Lehnert *et al.* (2007a) high variability in $\delta^{13}C$ values is a typical feature of this interval, probably due to the rare occurrence of dolomitic microsparite. The sedimentological data revealed a sequence boundary between beds 13 and 14 and also suggests the presence of a short stratigraphic gap. The $\delta^{13}C$ value obtained from the last sample taken prior to the stratigraphic gap (*i.e.*, bed 13) is +2.63‰. The $\delta^{13}C$ values obtained from beds deposited just above the sequence boundary (Figs 2B, C, 4) rapidly increase from +2.28‰ (bed 14) to +7.09‰ (bed 18). It is noteworthy that the $\delta^{13}C$ reached such high values in an interval having a thickness of less than 0.8 m. In the following interval of about 1 m in thickness the $\delta^{13}C$ slowly increase to a value of approximately +8‰ at level 1.8 m.

The $\delta^{13}C$ values within subsequent rather thicker intervals (about 10 m thick) vary around a value of 8.3‰. The maximal $\delta^{13}C$ value was recorded close to the middle of this interval (9.02‰ at level 7.1 m above the top of bed 13; Fig. 3A). Forty-eight carbonate samples were analyzed for $\delta^{13}C$ from the interval between level 1.8 m and 11.5 m. Two groups of samples (first group of 20 samples preceding sample with the highest $\delta^{13}C$ value, and second group of 20 samples taken above the sample with the highest $\delta^{13}C$ value) were tested by the Shapiro-Wilk test, which revealed that a normal distribution of the $\delta^{13}C$ values in both groups cannot be rejected. The $\delta^{13}C$ values of samples from the first group (1.8 m to 7.1 m) seem to have a slightly increasing tendency and those from the second group (7.1 m to 11.5 m) a slightly decreasing tendency (Fig. 4). However, the nonparametric Mann-Kendall test showed a lack of statistically significant monotonic increasing or decreasing trend in $\delta^{13}C$ values for each of the groups. The results of the Mann-Kendall tests thus support an interpretation of the interval between level 1.8 m and 11.5 m as a long-lasting steady period of isotopically heavy carbon. The average as well as the median of all values from this interval are identical (8.28‰) with a standard deviation of about ±0.3‰.

Higher up in the section, at the level 11.5 m, two thick limestone beds intercalated with densely laminated calcareous shales are developed (Fig. 3C, D). These beds bear rich trilobite remnants of the phacopid species *Ananaspis fecunda*. The succession above these beds is characterized by much thinner and more densely packed limestone beds (Fig. 3D). The $\delta^{13}C$ values decrease evenly from the FAD of *Ananaspis fecunda* (+7.6‰) to the LAD of *Ananaspis fecunda* (+1.4‰). It is noteworthy that the decrease in the $\delta^{13}C$ values following the previous long-lasting steady period of high $\delta^{13}C$ values (Fig. 4) was much slower and smoother that the rapid rise in the $\delta^{13}C$ values at the beginning of the mid-Ludfordian CIE.

The succession of densely packed limestone beds occurring above the LAD of *Ananaspis fecunda* (about 17 m above bed 13) generally contains more fossil fragments than the beds in the overlying interval. In this succession the $\delta^{13}C$ values decrease to –1.3‰ and then vary between –1‰ to 0‰. The first beds of Přídolí age consist of thin limestone beds intercalated with thick intervals of calcareous shales. The $\delta^{13}C$ values from the basal limestone beds of the Požáry Formation seem to show an increasing trend (Figs 3F, 4).

Discussion

Graptolite biozonation

Low faunal diversity is generally a typical feature of extinction and post-extinction intervals and this quite often complicates establishment of biostratigraphic zones. This also holds true for both graptolite and conodont zonations at the level of the mid-Ludfordian CIE. The conodont zonation of the latter interval was recently discussed in detail (see Corradini & Barrick 2009, Corriga & Corradini 2009, Slavík *et al.* 2010, Slavík & Carls 2012, Jeppsson *et al.* 2012).

The graptolite zonation across the mid-Ludfordian CIE is not yet satisfactory, even though there are some distinct graptolite events that can be used for biostratigraphic purposes. Urbanek (1993, 1997) and Urbanek & Teller (1997) clearly showed a distinct exctintion level close to the LAD of *Neocucullograptus kozlowskii* (*i.e*, the Kozlowskii graptolite Bioevent). Urbanek & Teller (1997) described the graptolite faunas of this interval as follows: "Due to this event (*i.e*. Kozlowskii graptolite Bioevent) and the following faunal turnover, the graptolite sequence of the Ludfordian is distinctly bipartite, being composed of an early and late faunal assemblage, with only a few elements in common. The event resulted in the extinction of specialized early Ludfordian representatives of *Neocucullograptus* and *Polonograptus*, as well as of the last survivors of *Bohemograptus*, above which there appeared a low diversity assemblage composed only of relatively common *Linograptus posthumus* and *Pristiograptus dubius* s.l.". A recently published detailed study on the evolution of *Pristiograptus* (Urbanek *et al.* 2012) as well as new data regarding correlation of graptolite stratigraphic ranges and the mid-Ludfordian CIE (Manda *et al.* 2012, Kozłowski & Sobień 2012, and data herein) have proved useful for modifying the graptolite biostratigraphy of that interval (Fig. 5).

The mid-Ludfordian CIE started just after the Kozlowskii graptolite Bioevent and it ends at the level of the FAD of *Pseudomonoclimacis latilobus*. Urbanek *et al.* (2012) described a new subspecies within the *Pristiograptus dubius* lineage, *Pristiograptus dubius postfrequens* Urbanek, Radzevičius, Kozłowska & Teller, 2012, which occurs across the mid-Ludfordian CIE interval. The extremely low graptolite diversity during the mid-Ludfordian CIE strongly limits possibilities for a more detailed biostratigraphic graptolite zonation. It is considered by the authors that establishment of a *P. dubius postfrequens* Partial-range Interval Zone could therefore be a good compromise and it is defined herein as a new interval zone in accordance with the stratigraphic "rules" proposed by the second edition of the International Stratigraphic Guide (Salvador 1994).

Figure 2. Lower part of the Kosov section No. JF195. • A – brown-grey calcareous shales with nodules and lenses of micritic mud- and wackestones belonging to the upper part of the *Neocucullograptus kozlowskii* Biozone. • B – detailed view of the sequence boundary between limestone bed No. 13 bearing the *Cheiopterea glabra* Community (LAD of *B. bohemicus*) and the thickly-bedded packstones and grainstones of the overlying succession (*Pr. d. postfrequens* Partial-range Interval Zone). • C – about 0.5 m thick interval of the packstones to grainstones characterized by a rapid increase of the $\delta^{13}C$ values (chemostratigraphic R-Zone), bearing abundant unsorted crinoidal and brachiopod remains, forming the first sedimentary record above the sequence boundary. • D – lower part of a succession of platy nodular limestones intercalated with shales (lower part of chemostratigraphic S-Zone) bearing the *Kosovopeltis-Scharyia-Metaplasia* Community (lower part of the *Pr. d. postfrequens* Partial-range Interval Zone). • E – general view of the succession of platy nodular limestones intercalated with shales showing position of tuffitic layer (dark horizon) belonging to the lower part of the *Pr. d. postfrequens* Partial-range Interval Zone. • F – detailed view of figure D showing a high thickness of limestone beds. Scale: A, F – 0.25 m; B – 0.1 m; C – 0.2 m; D, E – 0.5 m.

Pristiograptus dubius postfrequens Partial-range Interval Zone

This interval biozone is named after *Pristiograptus dubius postfrequens,* a species having mass occurrences in the mid-Ludfordian CIE interval (Kozłowski & Sobień 2012, Urbanek *et al.* 2012) and one of the few graptolites occurring within it. The base of the biozone is placed at the last appearance of *Neocucullograptus kozlowskii*, and the top is placed at the first appearance of *Pseudomonoclimacis latilobus*. Except for *Pr. d. postfrequens*, *Linograptus posthumus* is the only common taxon within the *P. dubius postfrequens* Partial-range Interval Zone (Urbanek & Teller 1997). The type locality of the *P. dubius postfrequens* Partial-range Interval Zone is the Mielnik-1 borehole.

General shape of the $\delta^{13}C$ excursion

Newly gathered data have revealed the first complete $\delta^{13}C$ record from middle palaeolatitudes across the mid-Ludfordian carbon isotope excursion at localities where no prominent stratigraphic gap is present. The course of the mid-Ludfordian CIE can be divided into several distinct geochemical phases that show differing $\delta^{13}C$ dynamics and that can be used for defining chemostratigraphic zones. The extensive period of the *Neocucullograptus kozlowskii* Biozone is characterized by slowly increasing $\delta^{13}C$ values that are rather variable, ranging between 0‰ and +3‰. In contrast to the latter, the rising phase (R-Zone) of the mid-Ludfordian CIE is rather short and it is seen to start just after a distinctive sequence boundary. The R-Zone is defined herein by a very rapid increase in $\delta^{13}C$ values and is equivalent to the rising limb of the mid-Ludfordian CIE. In the case of section No. JF195 at Kosov the $\delta^{13}C$ values rapidly increase from +2‰ to more than +8‰ over an interval about 1.8 m. The subsequent steady phase (S-Zone) is defined as a long-lasting steady period of high $\delta^{13}C$ values (Fig. 4). The $\delta^{13}C$ values at the Kosov section vary during the S-Zone within a narrow interval around +8.3‰. The final falling phase (F-Zone) is defined by a slow and even decrease of $\delta^{13}C$ values. At the end of the F-Zone the $\delta^{13}C$ values attained are lower than those for the interval prior to the isotope excursion (Fig. 4). The $\delta^{13}C$ values drop down to values below 0‰ in the final stages (F-Zone) in section No. JF195 at Kosov. The type locality of the $\delta^{13}C$ chemozones of the mid-Ludfordian CIE is the section No. JF195 at Kosov.

The lower and upper boundaries of chemostratigraphic zones (R-, S- and F- zones) established herein are defined on the basis of a statistically significant change in the evolution of the $\delta^{13}C$ record. In contrast to biostratigraphy, the different definition of the chemostratigraphic boundaries is due to the fact that the evolution of any geochemical signal in sea-water represents a continuous process and at any precise time and location the geochemical signal is represented by just one real number (*e.g.*, the value of the isotopic ratio). However, the biostratigraphic signal could just be represented by only two values, 1 and 0, describing the presence or absence of a particular taxon.

Comparison of the general shapes of the $\delta^{13}C$ records with other sections world-wide revealed their strong similarity (*i.e.*, three distinct phases of $\delta^{13}C$ record: rapid rise of the $\delta^{13}C$ values, steady period of high $\delta^{13}C$ values, slow decline of $\delta^{13}C$ values that reach lower values than those observed prior to the excursion). Besides the Barrandian area, this general shape of the mid-Ludfordian carbon isotope excursion has also been recorded in different areas of Baltica (Gotland, Poland; Jeppsson *et al.* 2007, 2012; Kozłowski & Munnecke 2010; Kozłowski & Sobień 2012), Australia (Broken River Province; Jeppsson *et al.* 2007, 2012) and Laurentia (Nevada – Saltzman 2001, Frýda *et al.*, unpublished data). For the reasons mentioned above, the chemostratigraphic zonation of the mid-Ludfordian carbon isotope excursion established herein could also be used for the latter areas and thus also for intercontinental correlations.

Application of high resolution $\delta^{13}C$ chemostratigraphy in the Barrandian

The chemostratigraphic zones outlined above may be used to estimate the duration of the stratigraphic gaps recorded at some sections within the Barrandian (Manda 2003; Lehnert *et al.* 2003, 2007; Manda & Kříž 2006, fig. 3; Manda *et al.* 2012). The presence of a distinct stratigraphic gap at the Mušlovka Quarry was suggested by Manda (2003) and confirmed by Lehnert *et al.* (2003, 2007) based on $\delta^{13}C$ records from the Mušlovka Quarry and Požáry sections. In 2012 Manda *et al.* recognized an extended stratigraphic gap also from a deeper, offshore environment based on $\delta^{13}C$, sedimentologic and biostratigraphic data recorded at a section near the village of Všeradice.

The $\delta^{13}C$ record at the Mušlovka Quarry section reached maximum values of about +4.6‰ (Lehnert *et al.* 2007a). This maximum value highlights the presence of a long stratigraphic gap at this section that includes the upper part of the R-Zone, the entire S-Zone and the lower part of the F-Zone (thus covering almost the entire *Pr. d. postfrequens* Partial-range Interval Zone). Similarly the maximum $\delta^{13}C$ value at the Požáry section reaches a level of +3.5‰ (Lehnert *et al.* 2007a). The latter value suggests an even slightly longer stratigraphic gap in comparison with the Mušlovka Quarry section. Lehnert *et al.* (2007a) and Gocke *et al.* (2012) described occurrences of palaeokarst features (sediment-filled dissolution cavities in beds) at the Požáry section which provide independent evidence for

Figure 3. Upper part of the Kosov section No. JF195. • A – succession of platy nodular limestones with the highest $\delta^{13}C$ values (the middle of chemostratigraphic S-Zone) intercalated with shales (*Pr. d. postfrequens* Partial-range Interval Zone). • B – basal beds (beginning of the chemostratigraphic F-Zone) of a succession with light grey thin-bedded skeletal limestones bearing the *Ananaspis fecunda-Cyrtia postera* Community (upper part of the *Pr. d. postfrequens* Partial-range Interval Zone). • C – general view of the limestone succession bearing the *Ananaspis fecunda-Cyrtia postera* Community (upper part of the *Pr. d. postfrequens* Partial-range Interval Zone; F-Zone). • D – detailed view of figure C showing a low thickness of limestone beds in the middle of the F-Zone. • E – rusty coloured cephalopod limestone bank (about 0.6 m thick) forming the last sedimentary record of Ludlow age. • F – basal Přídolian succession (Požáry Formation) of thin limestone beds intercalated with thick intervals of calcareous shale (*N. parultimus* Biozone). Scale: A, B, D – 0.25 m; C – 0.5 m; E, F – 0.1 m.

stratigraphic gaps at this level. However, the diagenetic overprint caused by dissolution and dolomitisation processes may also decrease the maximum $\delta^{13}C$ values (Lehnert *et al.* 2007a). On the other hand, occurrences of dolomite at the Požáry section as well as at the Kosov section (Lehnert *et al.* 2007a, Gocke *et al.* 2012, present study) could also indicate the same sedimentary process as described in detail by Kozłowski & Sobień (2012). Slavík *et al.* (2010) recently presented independent evidence based on their conodont data for the distinct stratigraphic gap at the Požáry section.

The $\delta^{13}C$ record from the deeper water environment (Všeradice section) published recently by Manda *et al.* (2012) showed the absence of higher $\delta^{13}C$ values across the mid-Ludfordian CIE. Manda *et al.* (2012) reported a thick, inversely graded intra-formational conglomerate overlying a shale-dominated sequence ending with a thin bed of fine-grained mud-wackestone and bioturbated tuffitic shale (Manda *et al.* 2012, fig. 8). The intra-formational conglomerate probably represents a canalized debris flow and its fauna (preserved in the matrix of the conglomerate) suggests transport from a nearby shallow water environment. As shown by Manda *et al.* (2012), rounded pebbles in the conglomerate include four lithological types that differ also in their fossil content: (1) small rounded pebbles of dark grey wackestone with cephalopods and the bivalve *Cheiopteria glabra* indicating the latest *Neocucullograptus kozlowskii* Biozone age; (2) rounded pebbles of brachiopod-trilobite wackestone with the trilobite *Ananaspis fecunda*; (3) small angular intraclasts of rusty fine-grained packstone with ostracods, the brachiopod *Atrypa* sp. and the trilobite *A. fecunda*; and (4) intraclasts that represent probably exhumed limestone nodules with *Entomis migrans* (*i.e. Saetograptus linearis-Neocucullograptus kozlowskii* biozones in age).

The recently collected data from the Kosov section allows the duration of the stratigraphical gap at the Všeradice section to be re-evaluated. In contrast to the interpretation given by Manda & Kříž (2006, fig. 4) and Manda *et al.* (2012), new comparison of the $\delta^{13}C$ records suggests a much longer stratigraphic gap, which includes the entire R-Zone, S-Zone, and almost completely the F-Zone (thus the entire *Pr. d. postfrequens* Partial-range Interval Zone). It is most likely that the age of the intra-formational conglomerate corresponds to the end of the *Pr. d. postfrequens* Partial-range Interval Zone or beginning of the *Ps. latilobus* Biozone, but it may certainly be dated as being prior to the end of the interval of the *Ananaspis fecunda-Cyrtia postera* Community. This interpretation is supported by finds of intraclasts containing the trilobite *A. fecunda* within the intra-formational conglomerate and by finds of *Ps. latilobus* and *Sl. balticus* in the bed just above the intra-formational conglomerate (Manda *et al.* 2012). The rather low maximum $\delta^{13}C$ value obtained from the matrix of the intra-formational conglomerate (+1.09‰) provides evidence for an age corresponding to the uppermost part of the F-Zone (Fig. 4).

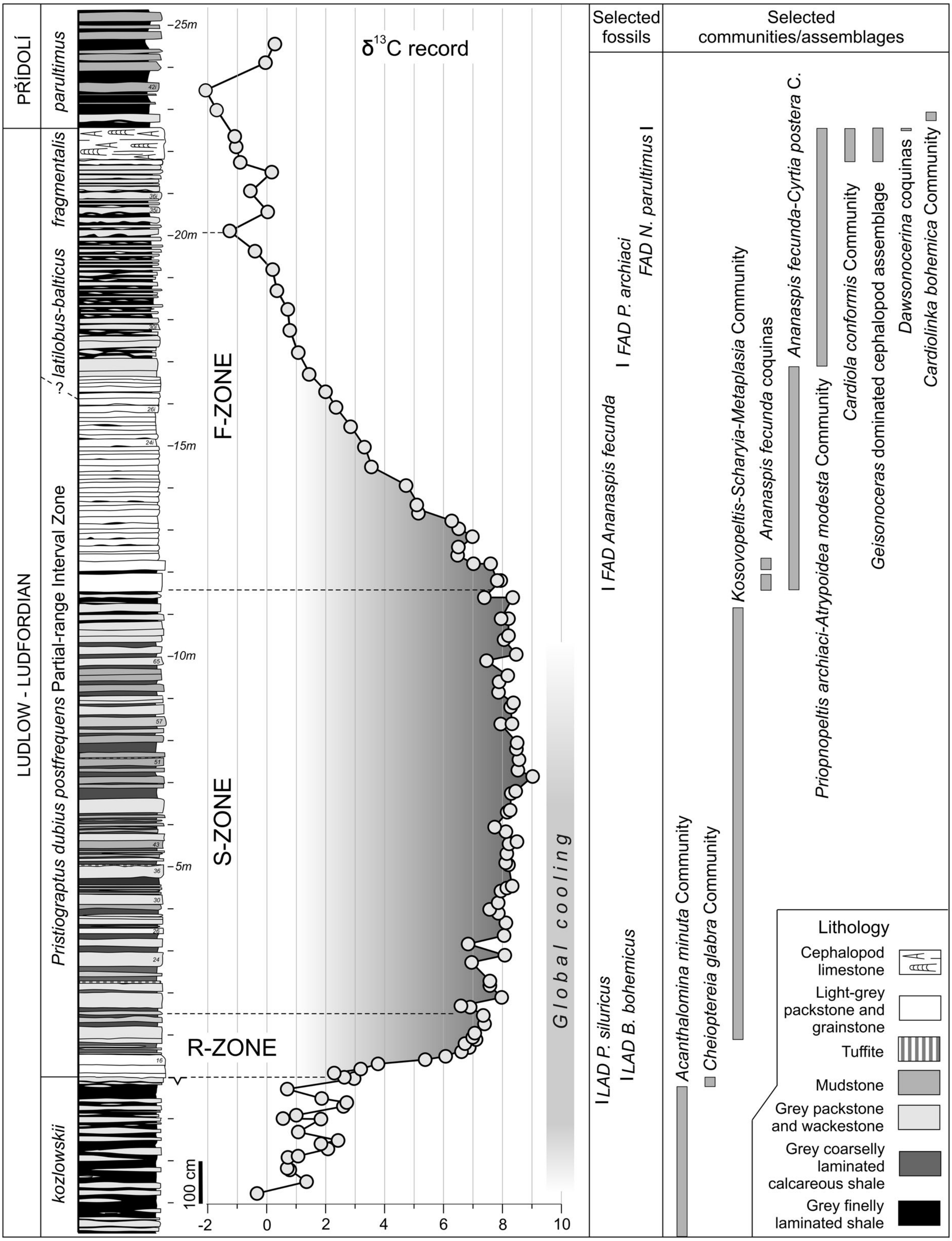
Relationship between the $\delta^{13}C$ record and water depth

The relationship between the $\delta^{13}C$ record and sea water depth during the mid-Ludfordian CIE has already been studied and discussed with regard to several basins. The published data concerning mainly shallow water environments clearly shows that the beginning of the mid-Ludfordian CIE is connected with rapid shallowing (Lehnert *et al.* 2003, 2007; Eriksson & Calner 2006; Jeppsson *et al.* 2012). Kozłowski & Munnecke (2010) compared sequence stratigraphy analyses of Gotland and the Holy Cross Mountains and concluded that "the positive Ludlow $\delta^{13}C$ excursion is connected with prolonged low-stand conditions with small, internal transgressive pulses". Recently, records of a rapid shallowing were found even in the deep water environment of Baltica (Kozłowski & Sobień 2012). Lowstand conditions have been suggested for a period of high $\delta^{13}C$ values by various authors (Kozłowski & Sobień 2012, but see also Eriksson & Calner 2006, Lehnert *et al.* 2007b). The end of the mid-Ludfordian CIE, characterized by a slow and even decrease in the $\delta^{13}C$ values (F-Zone), has been interpreted as a period of transgressive trend (Calner & Eriksson 2006, Kozłowski & Sobień 2012).

Silurian sedimentation in the Prague Basin was influenced by several active synsedimentary faults (see detailed model in Kříž 1991, 1992). This complex development renders analysis of transgresive-regressive trends difficult as sedimentation was influenced by two independent processes – global transgresive-regressive oscillations on one side, and local changes in subsidence rate on the other side. As shown by Kříž (1991, 1992) each of the several blocks recognized in the Prague Basin underwent a different and very complex evolution. For these reasons our interpretation of changes in the relative water depth based on data from the studied section No. JF195 at Kosov has to be considered as being preliminary.

The pre-excursion interval belonging to the *Neocucullograptus kozlowskii* Biozone is characterized by sedimentation of brown-grey calcareous shales containing nodules and lenses of micritic mudstones and wackestones. The

Figure 4. The $\delta^{13}C$ record across the mid-Ludfordian carbon isotope excursion at the Kosov section No. JF195 with basic data on lithology and biostratigraphy.


PŘÍDOLÍ
LUDLOW - LUDFORDIAN
parultimus
fragmentalis
latilobus-balticus
Pristiograptus dubius postfrequens Partial-range Interval Zone
kozlowskii
δ13C record
F-ZONE
S-ZONE
R-ZONE
Global cooling
–25m
–20m
–15m
–10m
–5m
100 cm
-2
0
2
4
6
8
10
Selected fossils
LAD P. siluricus
LAD B. bohemicus
FAD Ananaspis fecunda
FAD P. archiaci
FAD N. parultimus
Selected communities/assemblages
Acanthalomina minuta Community
Cheiopterea glabra Community
Kosovopeltis-Scharyia-Metaplasia Community
Ananaspis fecunda coquinas
Ananaspis fecunda-Cyrtia postera C.
Priopnopeltis archiaci-Atrypoidea modesta Community
Cardiola conformis Community
Geisonoceras dominated cephalopod assemblage
Dawsonocerina coquinas
Cardiolinka bohemica Community
Lithology
Cephalopod limestone
Light-grey packstone and grainstone
Tuffite
Mudstone
Grey packstone and wackestone
Grey coarselly laminated calcareous shale
Grey finelly laminated shale

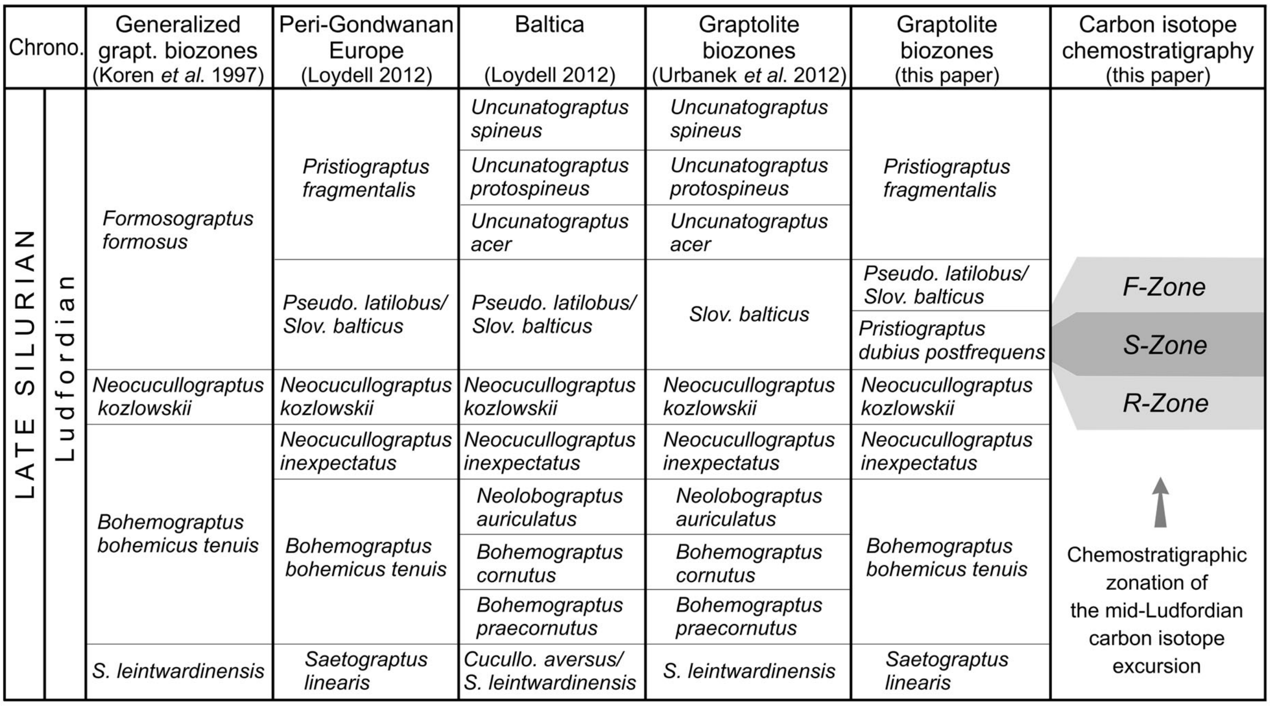


Figure 5. Generalized graptolite biozones of the Ludfordian (Koren' *et al.* 1996), graptolite biozonation for Baltica and Peri-Gondwanan Europe (Loydell 2012), graptolite biozonation for Poland and Lithuania (Urbanek *et al.* 2012), and herein proposed modification of the latter graptolite zonation by addition of the *Pristiograptus dubius postfrequens* Partial-range Interval Zone. Note relationship of the herein established chemostratigraphic zonation of the mid-Ludfordian CIE and graptolite biozonation (compare with Cramer *et al.* 2010).

latter succession ends with a distinctive sequence boundary which probably also represents a short stratigraphic gap. Increase in carbonate content in the upper part of this succession is suggestive of a shallowing trend. The stratigraphic gap between beds 13 and 14 probably originated during a rapid shallowing event. This interpretation fits well with the increase of $\delta^{18}O$ values recorded from conodont apatite, which is recognized as starting at the Kosov section about two metres below the LAD of *Neocucullograptus kozlowskii*, and thus with evidence for a global cooling trend connected with ice build-up in high latitudes and sea-level drop (Lehnert *et al.* 2007b).

Sedimentation of packstones and grainstones containing abundant unsorted crinoidal and brachiopod remains occurring just above the stratigraphic gap is interpreted as being a product of gravity flows that probably took place at the beginning of a moderate transgression and/or at time of increasing subsidence rate of some blocks at the Kosov area causing increase of accommodation space. The limestone beds belonging to the *Pr. d. postfrequens* Partial-range Interval Zone and deposited during periods of significant subsidence in the Kosov area, which was volcanically and structurally active (Kříž 1991), are remarkedly extensive and thick-bedded in appearance. Considerable thickness of the limestone beds (up to 25 cm) as well as much higher carbonate content in comparison with the previous interval (*i.e.*, the *Neocucullograptus kozlowskii* Biozone) may suggest a rather shallow environment during lowstand (stillstand) conditions. This monotonous succession probably reflects the destruction of a shallow carbonate platform during lowstand (stillstand) conditions. Deposition of a large volume of coarsely laminated calcareous shales (Fig. 2B, C) may reflect a limited function of the carbonate factory during lowstand (stillstand) conditions and was probably caused by a rapid increase of accommodation space during a period of significant subsidence at the Kosov area. The main volume of the thickly-bedded limestone strata consists of fine, intensively re-worked bioclasts (Figs 2D–F, 3A). Lowstand (stillstand) conditions during the S-Zone (lower part of the *Pr. d. postfrequens* Partial-range Interval Zone) seem to be also indirectly supported by the fact that this interval corresponds to long stratigraphic gaps and karstification in the shallower part of the basin preserved in the NE area of the Barrandian (Lehnert *et al.* 2003, 2007a; Manda 2003; Manda & Kříž 2006; Gocke *et al.* 2012).

The preliminary data regarding $\delta^{18}O$ values from conodont apatite suggests that a positive anomaly in $\delta^{18}O$ values of at least +2‰ occurred from the beginning of the mid-Lufordian CIA to the second half of the interval (at least to the beginning of the *O. snajdri* Zone – Lehnert *et al.* 2007b), and thus during the R-Zone and at least during the

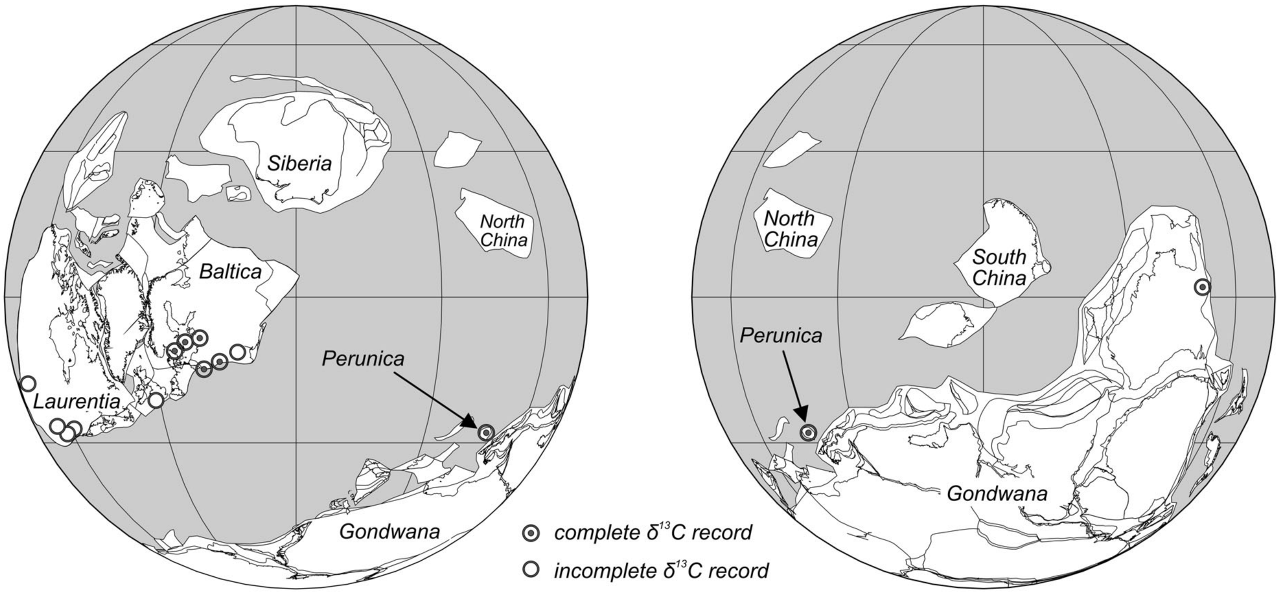


Figure 6. Palaeogeographical distribution for published δ^{13}C records of the mid-Ludfordian carbon isotope excursion (palaeogeographic reconstruction modified after Torsvik 2009).

first half of the S-Zone. The δ^{18}O anomaly was connected with distinct global cooling and this fits well with the observed stratigraphic gaps and karstification recognized in the shallower parts of the Barrandian area as well as with suggested lowstand (stillstand) conditions in deeper parts of the Barrandian (section No. JF195 at Kosov, Všeradice).

The succession equivalent to the upper part of the *Pr. d. postfrequens* Partial-range Interval Zone (F-Zone) and that bearing the *Ananaspis fecunda-Cyrtia postera* Community is characterized by thinner and more densely packed limestone beds (Fig. 3C, D). These limestones were probably deposited during a slow transgression when the δ^{13}C values slowly and evenly decreased from a value of +7.6‰ to +1.4‰. Judging from the palaeontological data available the subsequent carbonate succession bearing the *Prionopeltis archiaci-Atrypoidea modesta* Community was probably deposited in a shallower environment. The Požáry Formation of Přídolian age starts with a distinct transgression (Fig. 3F).

Relationship between the δ^{13}C record and palaeolatitude

During the last two decades the mid-Ludfordian carbon isotope excursion has been recorded from a variety of areas and several different environments. These datasets enable analysis of the relationship between the δ^{13}C record and palaeolatitudinal position. However, such an analysis has to be restricted only to similar environments in order to limit the bathymetric dependence of the δ^{13}C values. In addition, such an analysis is complicated by the nature of the δ^{13}C records. The published δ^{13}C records are often based on sparse sampling or on analyses of different lithological types within one section (limestones, dolostones, calcareous shales), and sometimes sections contain long gaps in the sedimentary record. For these reasons the δ^{13}C records have been distinguished for the analysis herein according to presence or absence of the steady period of high δ^{13}C values. Even though the mid-Ludfordian CIE has been recorded from different areas of Baltica, Laurentia, NE Gondwana (Australia), Avalonia, and Perunica, the δ^{13}C records with the steady period of high δ^{13}C values have only been described from three palaeocontinents (Baltica, NE Gondwana, and Perunica).

During the Ludfordian Baltica (Gotland, Scania, and the Holy Cross Mountains) had a palaeolatitudinal position of about 15 degrees south of the palaeoequator (*e.g.*, Cocks & Torsvik 2002). The Broken River Province (NE Australia) from where the mid-Ludfordian CIE has been documented was located close to the palaeoequator (Fig. 6). According to different models the Barrandian (= Perunica) was situated between 25 and 30 degrees south of the palaeoequator. Thus, a complete δ^{13}C record including the S-Zone has only been described from areas located within a band from the equator to about 30 degrees south. Comparison of these δ^{13}C records clearly reveals that the δ^{13}C values during the steady period (S-Zone) reached similar maximal values (Fig. 7). This fact suggests that the δ^{13}C excursion from different palaeocontinents was linked with the same global oceanic reservoir rather than being evolved independently within restricted small epeiric basins.

Recently published data from Eastern Poland (Kozłowski & Sobień 2012) presents the only δ^{13}C record from a deep-water environment with a steady period preserved

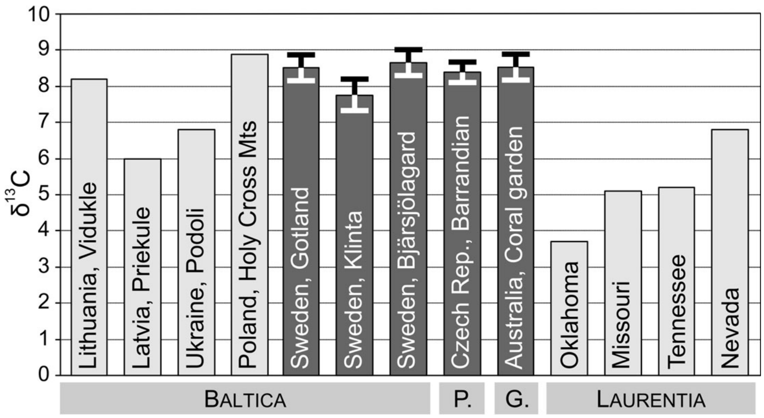


Figure 7. Diagram showing amplitude of the $\delta^{13}C$ records at different palaeogeographical positions. The $\delta^{13}C$ records with a flat top formed during the steady period of high $\delta^{13}C$ values (S-Zone) are marked by dark grey colour, the $\delta^{13}C$ records lacking the S-Zone are denoted by light grey colour.

during which the $\delta^{13}C$ reaches values of about +6.5‰. Kozłowski & Sobień (2012) discussed the relationship between the $\delta^{13}C$ record and water depth. Their analysis clearly showed a strong dependence between the $\delta^{13}C$ record and water depth.

Few records (see Jeppsson *et al.* 2012 for review) of extremely high $\delta^{13}C$ values reaching up to +11‰ have been recorded and these only from very particular and very shallow-water environments that often include stromatolites. These extremely high $\delta^{13}C$ values were probably influenced by special conditions in partly restricted, lagoonal environments (Wigforss-Lange 1999, 2007).

Duration of the $\delta^{13}C$ excursion

Estimation of the duration of the individual phases of the $\delta^{13}C$ excursion is important for understanding and modeling this event. Biostratigraphic zonations based on graptolites or conodonts provide rather high degree of stratigraphic resolution within Silurian strata, however, this relative age zonation has not yet been calibrated to absolute ages. The main reason for such a situation is a lack of geochronological methods with the required precision. The average duration of the Silurian graptolite biozones is about 1 Ma or less (see Loydell 2012), but this is a value which roughly corresponds to one standard deviation of absolute age determination for the most precise geochronological methods available today. For these reasons the duration of individual phases of the mid-Ludfordian $\delta^{13}C$ excursion has to be estimated indirectly using sedimentologic methods.

There are hitherto only two published time estimations of the duration of the mid-Ludfordian CIE (Kozłowski & Sobień 2012; Jeppsson *et al.* 2007, 2012), both of which are based on simple comparison of the total thickness of strata deposited during the $\delta^{13}C$ excursion and those deposited during the entire Ludfordian interval. However, utilization of the latter method is prone to a variety of serious problems. Firstly, this estimation presumes that the rate of sedimentation remained roughly the same throughout the Ludfordian interval and this is a very problematic simplification. Secondly, the absolute age data used for the calculations on both the lower and upper boundaries of the Ludfordian are still very uncertain.

Estimation of the timespan of the mid-Ludfordian CIE was performed with regard to two different environments occurring on the palaeocontinent of Baltica – a shallow-water carbonate platform on Gotland (Jeppsson *et al.* 2007, 2012), and a periplatform setting on a neritic carbonate platform in Eastern Poland (Kozłowski & Sobień 2012). The calculation using data from the latter environment seems to be more reliable because of the more complete sedimentary record and rather uniform sedimentation rate.

The mid-Ludfordian CIE starts with a very rapid shift in $\delta^{13}C$ values during the R-Zone. The duration of this period was estimated as being less than 4000 years in the periplatform setting (Kozłowski & Sobień 2012) and about 600 years in the shallow-water carbonate platform (Jeppsson *et al.* 2007). The latter estimation is unlikely due to the occurrence of a stratigraphic gap at the beginning of the mid-Ludfordian CIE on the shallow-water carbonate platform and distinct facial changes recognized on Gotland (Calner & Eriksson 2006; Eriksson & Calner 2007; Jeppsson *et al.* 2007, 2012).

The duration of the steady period characterized by high $\delta^{13}C$ values (S-Zone) was estimated maximally as 120 000 years within the periplatform setting (Kozłowski & Sobień 2012) and to less than 180 000 years on the shallow-water carbonate platform (Jeppsson *et al.* 2012). However, the latter estimation includes a slightly longer period (time units 2–6 of Jeppsson *et al.* 2012) than that being equivalent to the S-Zone.

The new data from the Kosov section presented herein also makes a comparison of duration in individual phases (zones) of the mid-Ludfordian CIE possible. If we assume a similar rate of deposition across the isotopic excursion at the Kosov section and use the duration of the S-Zone from the periplatform setting (about 120 000 years), then time intervals of about 18000 years for the R-Zone and about 100 000 years for the F-Zone are obtained. It is noteworthy

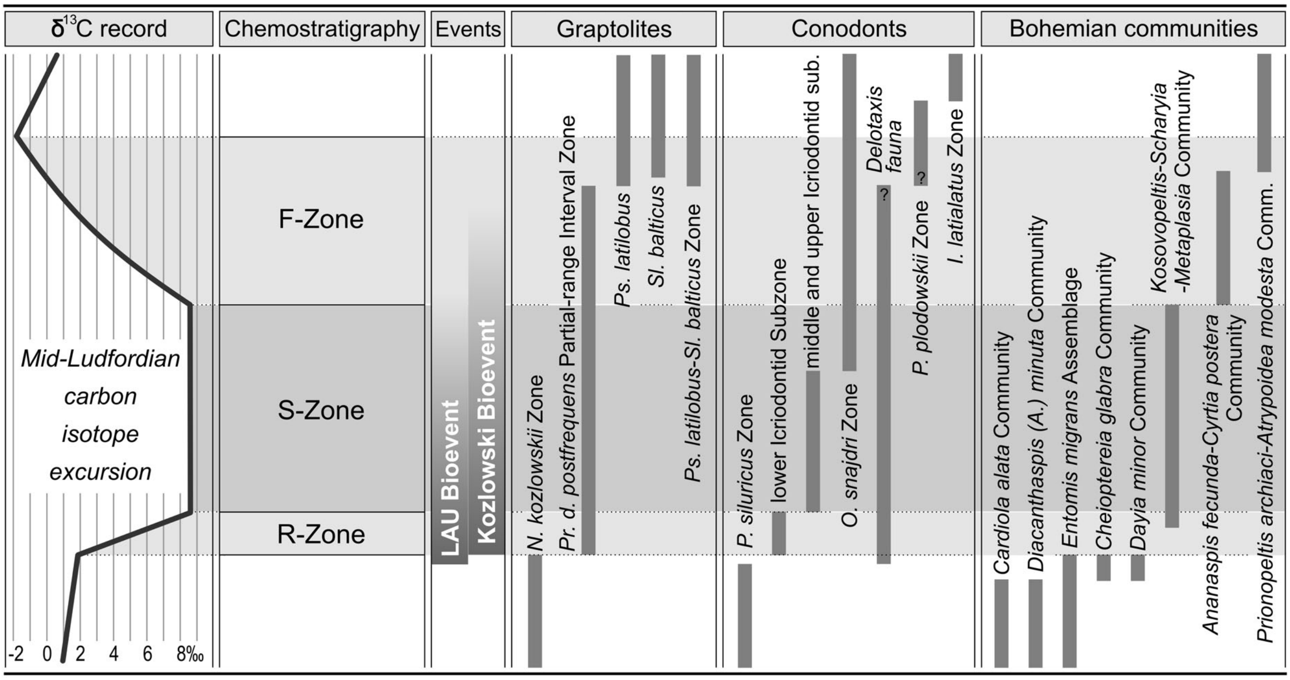


Figure 8. Diagram showing a proposal for an integrated δ13C, graptolite and conodont stratigraphic zonation for the mid-Ludfordian interval. Global graptolite biozonation (Loydell 2012) modified by the addition of the *Pr. d. postfrequens* Partial-range Interval Zone. The conodont zonation from Jeppsson *et al.* (2012) based on data from Baltica and NE Gondwana is used herein. Alternative conodont zonation for the LAU and post-LAU Event intervals (*e.g.*, Slavík *et al*. 2010, Slavík & Carls 2012) is also shown even though its relationship to the δ13C record as well as to the conodont zonation by Jeppsson *et al.* (2012) is poorly known. Note that the δ13C chemostratigraphy provides the same or even better stratigraphic resolution for the mid-Ludfordian period than earlier established biostratigraphic zones and, in contrast to the latter, it may be used for correlations of areas belonging to different faunal provinces.

that the latter estimation is similar to the residence time of carbon in modern oceans. The shape of the δ13C curve during the F-Zone is also typical for exponential decay (Fig. 4) that will allow future modeling of this geochemical event. Nevertheless tectonic movements and changes of accommodation space in the Kosov block make these detailed estimations rather premature.

Integrated δ13C, graptolite and conodont stratigraphy

The chemostratigraphic zones (R-, S- and F- zones) of the mid-Ludfordian CIE differentiated on the basis of their δ13C dynamics had a duration of about 100 000 years or less. These zones could be used for global correlation of areas belonging to different faunal provinces in contrast to biostratigraphic zones. A combination of the chemostratigraphic and biostratigraphic zonations enables a new integrated stratigraphic scale for the middle of the Ludfordian to be proposed.

Integrated δ13C and graptolite stratigraphy

The pre-excursion period characterized by slowly increasing δ13C values ends at the upper boundary of the *Neocucullograptus kozlowskii* Biozone as was shown by Lehnert *et al.* (2007a) at the Kosov section (No. JF195) as well as at the deeper water Všeradice section by Manda *et al.* (2012). This boundary is characterized by mass extinction of the middle Ludfordian graptolite fauna (LAD of *Neocucullograptus kozlowskii* and *Bohemograptus tenuis*; see Štorch 1995a, b; Manda *et al.* 2012). The LAD of *Neocucullograptus kozlowskii* occurs just before the mid-Ludfordian CIE also on Baltica (Kozłowski & Sobień 2012). On the other hand, the beginning of the *Ps. latilobus-S. balticus* Biozone occurs just after the mid-Ludfordian CIE on Baltica and in the Barrandian (Kozłowski & Sobień 2012, Manda *et al.* 2012).

The beginning of the chemostratigraphic R-Zone fits well with the end of the *Neocucullograptus kozlowskii* Biozone (Fig. 8). The *Ps. latilobus-S. balticus* Biozone starts just before the end of the chemostratigraphic F-Zone. It is not possible to subdivide the interval between the end of the *N. kozlowskii* Biozone and beginning of the *Ps. latilobus-S. balticus* Biozone (*i.e*., the *Pr. d. postfrequens* Partial-range Interval Zone) into additional shorter graptolite biozones because of the lack of available graptolite taxa in contrast to what may be achieved using δ13C chemostratigraphy. The boundary of the chemostratigraphic S- and F-zones occurs roughly in the middle of the *Pr. d. postfrequens* Partial-range Interval Zone.

Integrated $\delta^{13}C$ and conodont stratigraphy

Data from Baltica and NE Gondwana (Australia) highlights the coincidence of the FAD of the *P. siluricus* conodont Biozone with the last "normal" $\delta^{13}C$ values occurring just before the onset of the mid-Ludfordian carbon isotope excursion (see review in Jeppsson *et al.* 2012). The upper boundary of the *P. siluricus* conodont Biozone is somewhat problematic with regard to its utility because, as was noted by Jeppsson, the latter conodont species is extremely rare in its last occurrences (about one element of this species to about 10 000 elements of another conodont species). On the other hand, no occurrence of *P. siluricus* has been recorded within younger strata showing high $\delta^{13}C$ values on any paleocontinent (Fig. 8). In the Barrandian, the last *P. siluricus* was also found in the uppermost *N. kozlowskii* Biozone just below the appearance of the *C. glabra* Community and below the Kozlowskii graptolite extinctions (for summary see Lehnert *et al.* 2007a and Manda *et al.* 2012). Thus, the beginning of the chemostratigraphic R-Zone fits well not only with end of the *P. siluricus* conodont Biozone, but also with the end of the *Neocucullograptus kozlowskii* Biozone.

The chemostratigraphic R-Zone of the mid-Ludfordian CIE begins at the Kosov section just above a sequence boundary which probably also corresponds to a short stratigraphic gap. This sequence boundary is most probably identical with the ¾ discontinuity at the base of the Eke Formation on eastern Gotland, which was described as a submarine discontinuity-level with phosphorite and glauconite coatings overlain by rounded pebbles of the Hemse Marl (Jeppsson *et al.* 2012). The equivalent of the ¾ discontinuity was found also at further regions outside of Gotland – Lithuania (see review in Jeppsson *et al.* 2012), Austria (Histon & Schönlaub 1999, Brett *et al.* 2009), and Nevada (Frýda *et al.*, unpublished data).

The chemostratigraphic R-Zone of the mid-Ludfordian CIE corresponds to the basal part of the *Pr. d. postfrequens* Partial-range Interval Zone as shown by data from Perunica and Baltica (Lehnert *et al.* 2007a, Kozłowski & Sobień 2012, Manda *et al.* 2012). The beginning and the end of the chemostratigraphic R-Zone fits also with the beginning of the Lower Icriodontid Subzone of Jeppsson *et al.* (2012) in Baltica and Australia (see review in Jeppsson *et al.* 2012).

The chemostratigraphic S-Zone being equivalent to the steady phase of the mid-Ludfordian CIE with high $\delta^{13}C$ values corresponds to the middle part of the *Pr. d. postfrequens* Partial-range Interval Zone as shown by data from Perunica and Baltica (Kozłowski & Sobień 2012, Manda *et al.* 2012). The chemostratigraphic S-Zone is equivalent to the Middle and Upper Icriodontid subzones of Jeppsson *et al.* (2012) as well as to the lower part of the "*Ozarkodina*" *snajdri* Zone in Baltica and NE Gondwana. The beginning of the "*Ozarkodina*" *snajdri* Zone occurs long before the end of the S-Zone and this has been well documented at several sections in Baltica and Australia (see data in Jeppsson *et al.* 2012).

Knowledge regarding conodont biostratigraphy of the Ludfordian strata in the Barrandian is rather limited. Only three sections (Mušlovka, Požáry, and Všeradice) within this stratigraphic interval were hitherto studied in detail (Schönlaub *in* Kříž *et al.* 1980; Kříž *et al.* 1986; Lehnert *et al.* 2007a; Slavík *et al.* 2010, 2012). Unfortunately, there are well documented stratigraphic gaps starting at the end of the *N. kozlowskii* Zone that have different stratigraphic ranges in all the sections mentioned above. The latter gaps were clearly evidenced by $\delta^{13}C$ chemostratigraphy, carbonate petrology and later also by conodont biostratigraphy (Manda 2003; Manda *et al.* 2012; Lehnert *et al.* 2003, 2007; Slavík *et al.* 2010, Slavík & Carls 2012; Gocke *et al.* 2012). The available conodont data shows that the stratigraphic interval just before the mid-Ludfordian CIE belongs to the *P. siluricus* conodont Biozone. The last *P. siluricus* was found within the uppermost *N. kozlowskii* Zone just below the appearance of the *C. glabra* Community and below the Kozlowskii graptolite bioevent (for summary see Manda *et al.* 2012). The "*Ozarkodina*" *snajdri* Zone starts close to the end of the mid-Ludfordian CIE in the Mušlovka Quarry (Lehnert *et al.* 2007a). It has to be noted that the documented later occurrence of "*Ozarkodina*" *snajdri* in the Barrandian is probably due to sampling bias.

The chemostratigraphic F-Zone of the mid-Ludfordian CIE characterized by a slow and even decrease in $\delta^{13}C$ values corresponds to the upper part of the *Pr. d. postfrequens* Partial-range Interval Zone. The end of the F-Zone falls already within the *Ps. latilobus-S. balticus* Biozone (Kozłowski & Sobień 2012, Manda *et al.* 2012, and discussion above). The *Ps. latilobus-S. balticus* Biozone as well as the subsequent *Pristiograptus fragmentalis* Biozone are younger than the mid-Ludfordian CIE. The first occurrence of "*Ozarkodina*" *crispa* was documented close to the middle of the *Pristiograptus fragmentalis* Biozone (Kříž *et al.* 1986, Manda *et al.* 2012).

Slavík *et al.* (2010) and Slavík & Carls (2012) recently studied the effect of the mid-Ludfordian LAU Event on the conodont faunas of the Barrandian. These two studies focused on the Požáry section are the only modern conodont studies across the mid-Ludfordian CIE within the Barrandian area. Slavík & Carls (2012, p. 816) stated that "the Požáry section has been found to be the most suitable one for detailed conodont research of the Ludfordian strata". The present authors have some doubts regarding this statement for several reasons. Firstly, there is undoubted evidence in support of the presence of several stratigraphic gaps at the Požáry section ($\delta^{13}C$ chemostratigraphy, Lehnert *et al.* 2007a). These gaps were also indirectly suggested by Manda & Kříž (2006) and later by Slavík *et al.*

(2010) on the basis of benthic faunas and conodont distributions. Thus, the Požáry section is rather unsuitable as a section for detailed biozonation research, at least with regard to the interval of the mid-Ludfordian LAU Event, in contrast to other sections in the Barrandian (*e.g.*, Kosov area). The presence of these stratigraphic gaps as well as dolomitization together with karstification effects (see Lehnert *et al.* 2007a) render the Požáry section an inappropriate location for the required correlation of conodont biozonation and $\delta^{13}C$ chemozonation. On the other hand, Slavík & Carls (2012) clearly showed the great potential of conodont biostratigraphy for future more detailed subdivision of the late Ludfordian interval, the time period succeeding the mid-Ludfordian CIE.

$\delta^{13}C$ chemostratigraphy and benthic communities

It is noteworthy that the stratigraphic ranges of benthic communities at all the studied Bohemian sections regardless of their facies correspond well with both graptolite biozonation as well as chemostratigraphic zonation across the mid-Ludfordian CIE. The end of the *Cheioptereia glabra* Community fits well with the end of the *N. kozlowskii* Biozone as well as with the beginning of the R-Zone (Fig. 8). The subsequent *Kosovopeltis-Scharyia-Metaplasia* Community disappears at the end of S-Zone of the mid-Ludfordian CIE. The onset of the *Ananaspis fecunda-Cyrtia postera* Community fits with the beginning of the F-Zone and this community disappeared just before the end of the F-Zone. The *Prionopeltis archiaci-Atrypoidea modesta* Community occurs after the mid-Ludfordian CIE.

Conclusions

New $\delta^{13}C$ data across the mid-Ludfordian CIE interval from the Barrandian has highlighted several new aspects that are of importance for both regional and global stratigraphic correlations as well as for the increased understanding of this most prominent Phanerozoic carbon isotope excursion. The main conclusions are summarized below:

1. The newly collected data has provided for the first time a complete $\delta^{13}C$ record across the mid-Ludfordian carbon isotope excursion from middle palaeo-latitudes (northern peri-Gondwana). Evolution of this $\delta^{13}C$ isotopic anomaly was observed to be the same at tropical and middle latitudinal regions (Baltica and NE Gondwana). The course of the anomaly may be divided into several distinct geochemical phases differentiated on the basis of $\delta^{13}C$ dynamics (Fig. 4). The mid-Ludfordian carbon isotope excursion started with a rapid increase in $\delta^{13}C$ values, continued with a long-lasting steady period of high $\delta^{13}C$ values, and ended with a period during which the $\delta^{13}C$ values slowly and evenly decrease to values observed as being lower than those prior to the isotope excursion. These periods of differing $\delta^{13}C$ dynamics are used herein to define a new $\delta^{13}C$ chemostratigraphic zonation (R-, S-, and F-zones) of the mid-Ludfordian CIE.

2. Application of this $\delta^{13}C$ chemostratigraphy enables a high resolution correlation of earlier described Barrandian sections. New data reveals that a stratigraphic gap in shallower environments recorded at the Mušlovka Quarry and Požáry sections is equivalent to the upper part of the R-Zone, entire S-Zone and lower part of the F-Zone (thus almost the entire *Pr. d. postfrequens* Partial-range Interval Zone). On the other hand, the stratigraphic gap described from a deeper water environment at the Všeradice section corresponds to the entire R-Zone, S-Zone, and almost the complete F-Zone (thus to the entire *Pr. d. postfrequens* Partial-range Interval Zone). The application of the new chemostratigraphic zones proposed herein enables a much better stratigraphic resolution than that available using solely the graptolite and conodont biostratigraphic scale. The applicability of the latter biostratigraphic zonation is strongly limited by the very low diversity and abundance of graptolites and conodonts during the post-extinction period at the beginning of the mid-Ludfordian CIE.

3. The newly established $\delta^{13}C$ chemostratigraphic zonation is used for intercontinental correlations of the mid-Ludfordian CIE and for unification of the graptolite and conodont biostratigraphic zonation with the $\delta^{13}C$ chemostratigraphy. This analysis resulted in a proposal for an integrated $\delta^{13}C$, graptolite and conodont stratigraphy for the mid-Ludfordian (Fig. 8).

4. Comparison of the $\delta^{13}C$ records revealed that $\delta^{13}C$ values during a long-lasting steady period of high $\delta^{13}C$ values (forming the flat top of the $\delta^{13}C$ curves) reached very similar absolute values regardless of the palaeogeographic position of the locality. This fact suggests that isotopic anomalies from different palaeocontinents originated from the same global oceanic isotopic reservoir rather than being evolved independently within small restricted epeiric basins.

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