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Stable carbon isotope stratigraphy of the Silurian in the Jočionys-299 borehole (eastern Lithuania)

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Abstract. In recent years it has become commonplace to formalize chemostratigraphic units and identify isotopic zones (chemostratigraphic units) from excursions. Stable carbon isotopes have been used in solving stratigraphic problems in the Silurian for more than 30 years. $\delta^{13}C$ data supplement other stratigraphic proxies, allowing the subdivision of geological sections and more precise correlation. In this paper we give new $\delta^{13}C$ data from the Silurian section of the Jočionys-299 borehole, which is located in eastern Lithuania, crossing shallow marine and lagunal deposits. Based on $\delta^{13}C$ variability, the Ireviken carbon isotope excursion (CIE), the Šlilalė CIE, and probably the Valgu CIE have been identified in the investigated section. The Valgu CIE is linked to the lower part of the Švenčionys Formation. The Ireviken CIE is linked to the upper parts of the Švenčionys Formation and the Paprieniai Formation (rise in $\delta^{13}C$ values), the Jočionys Formation (moderately stable $\delta^{13}C_{carb}$ values) and the Verknė Formation (fall in $\delta^{13}C$ values). A small negative $\delta^{13}C$ shift is documented in the Pabradė Formation. Chemostratigraphy together with biostratigraphic data allow us to correlate eastern Lithuanian lithostratigraphic units (shallow marine environment) with the global Silurian Geochronological Scale more accurately.

Keywords: carbon isotopes, chemostratigraphy, Silurian, Lithuania.

INTRODUCTION

Stable carbon isotopes are often used in solving stratigraphic problems. In stratigraphy, carbon isotopes as a chemostratigraphic tool are mostly used alongside biostratigraphic data, and together the two are combined as event markers. The first high-resolution studies of carbon isotope variability in Silurian rocks and fossils started in the last decade of the last century. Some of the first studies on Silurian stable carbon isotopes were carried out by Corfield et al. (1992), Samtleben et al. (1996), Wenzel and Joachimski (1996), Kaljo et al. (1997), and others. With the development of analytical techniques, isotope research has become more active and Silurian carbon isotope data is rapidly increasing around the world. This has made it possible to carry out generalized studies on the variability of stable carbon isotopes in the Silurian (e.g. Cramer et al. 2011; Melchin et al. 2020).

There are several $\delta^{13}C$ excursions determined based on the data of $\delta^{13}C$ from carbonates and organic material in the Silurian. Some of the $\delta^{13}C$ changes are very well known and documented elsewhere around the world, others are still under discussion. The early and late Aeronian positive $\delta^{13}C$ excursion is documented in the Aeronian (e.g. Melchin and Holmden 2006; Štorch and Frýda 2009; Cichon-Pupienis et al. 2021). There are distinguished Kallholn, Valgu, and Sommerodde $\delta^{13}C$ excursions in the Telychian. The Kallholn stable carbon isotope excursion was identified based on $\delta^{13}C_{org}$ data and linked to the *Spirograptus turriculatus* Biozone in the Kallholn quarry, Sweden (Walasek et al. 2018). However, the Kallholn excursion is problematic, little known and under discussion. The Valgu $\delta^{13}C_{carb}$ excursion can be correlated with the *Pterospathodus eopennatus* ssp. n. 2 conodont Biozone (Munnecke and Männik 2009) or the *Monoclimacis griestoniensis* graptolite Biozone (Loydell et al. 2003). The Sommerodde excursion was determined based on stable carbon isotope data from organic material and can be correlated with the middle part of the *Oktavites spiralis* Biozone (Hammarlund et al. 2019). The well-known Ireviken positive $\delta^{13}C$ excursion is linked to early Sheinwoodian (e.g. Cramer et al. 2010) and the Mulde positive $\delta^{13}C$ excursion can be correlated with the *Pristiograptus parvus–Colonograptus ludensis* interval of the Homerian (e.g. Cramer et al. 2012; Fry et al. 2017; Rinkevičiūtė et al. 2022). There is a well-known major positive excursion of $\delta^{13}C$ named the Lau or the mid-Ludfordian carbon isotope excursion (e.g. Spiridonov et al. 2017; Kozłowski 2020; Frýda et al. 2021;). The Šilalė negative $\delta^{13}C$ excursion is documented in the lower Pridoli (e.g. Kaljo et al. 2012; Oborny et al. 2020; Spiridonov et al. 2020b) and the Klonk positive $\delta^{13}C$ at the Silurian–Devonian boundary (e.g. Małkowski 2009).

The purpose of this study is to document $\delta^{13}C_{carb}$ excursions in eastern Lithuania, spanning the entire Silurian strata, and to integrate new $\delta^{13}C_{carb}$ data with lithostratigraphic units, complemented by gamma-ray well logs and conodont biozonation. Integrated stratigraphy allows us to determine the age of the formations in eastern Lithuania and to better understand the completeness of the Silurian geological section of the shallow deposits in eastern Lithuania.

GEOLOGICAL SETTING

During the Silurian period Lithuania was located in the western part of Baltica, situated near the equator in the southern hemisphere (Cocks and Torsvik 2005), and was part of the Silurian Baltic Basin. The Jočionys-299 borehole is in eastern Lithuania (Fig. 1), where the Silurian succession is represented by shallow marine deposits. The borehole was drilled in the 1980s and is one of the few deep boreholes in good condition drilled in eastern Lithuania and contains several lithostratigraphic units which are stratotypes of the eastern Silurian Baltic Basin (see below). This is the primary reason why our chemostratigraphic research is based on the core material of the Jočionys-299 well. The second reason is that there are a series of studies on the lithostratigraphy and biostratigraphy of this borehole; the key information from these previous studies is provided below. In the Silurian of the Jočionys-299 borehole, seven formations were distinguished based on lithology and gamma-ray logs (Paškevičius and Brazauskas 1987): Švenčionys, Paprieniai, Jočionys, Verknė, Trakai, Sudervė and Pabradė (Fig. 2). The Švenčionys Formation is composed of grey limestone in the lower part and grey marlstone (234.2–204 m interval). The Paprieniai Formation consists of clayey dolostone. The stratotype of the Jočionys Formation lies in the Jočionys-299 borehole (173.6–189 m interval) and the formation is composed of grey wavy laminated dolostone with cavities and with low gamma-ray values (Fig. 2). The neostratotype of the Verknė Formation lies in the Jočionys-299 borehole. The Verknė Formation is subdivided into two parts, the lower part consists of grey microlaminated dolomitic marlstone and the upper part, reddish dolostone, contains interbeds or lenses of gypsum and celestine (Fig. 2). The Trakai Formation is composed of marlstone with interbeds of dolostone. The parastratotype of the Sudervė Formation lies in the Jočionys-299 well (Fig. 2) and consists of grey dolostone with marlstone interbeds. The stratotype of the Pabradė Formation is located in Jočionys-299 (90.3–105 m interval) and is composed of grey clayey dolostone.

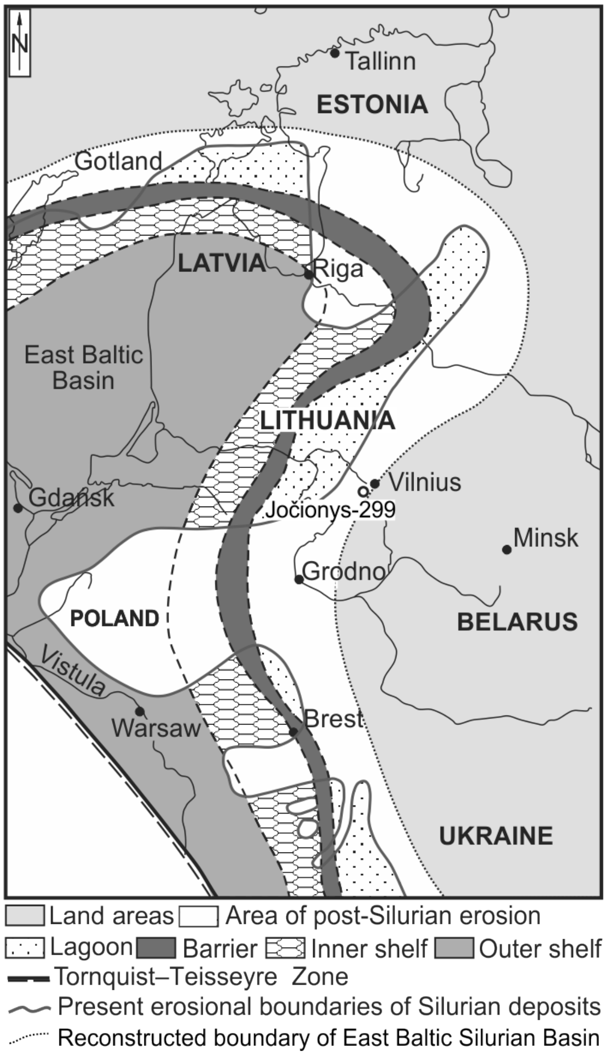

Fig. 1. Paleogeographic map of the East Baltic Silurian Basin Platform during the time of *Gothograptus nassa* (Homerian, Wenlock) (Einasto et al. 1986) and location of the Jočionys-299 borehole.

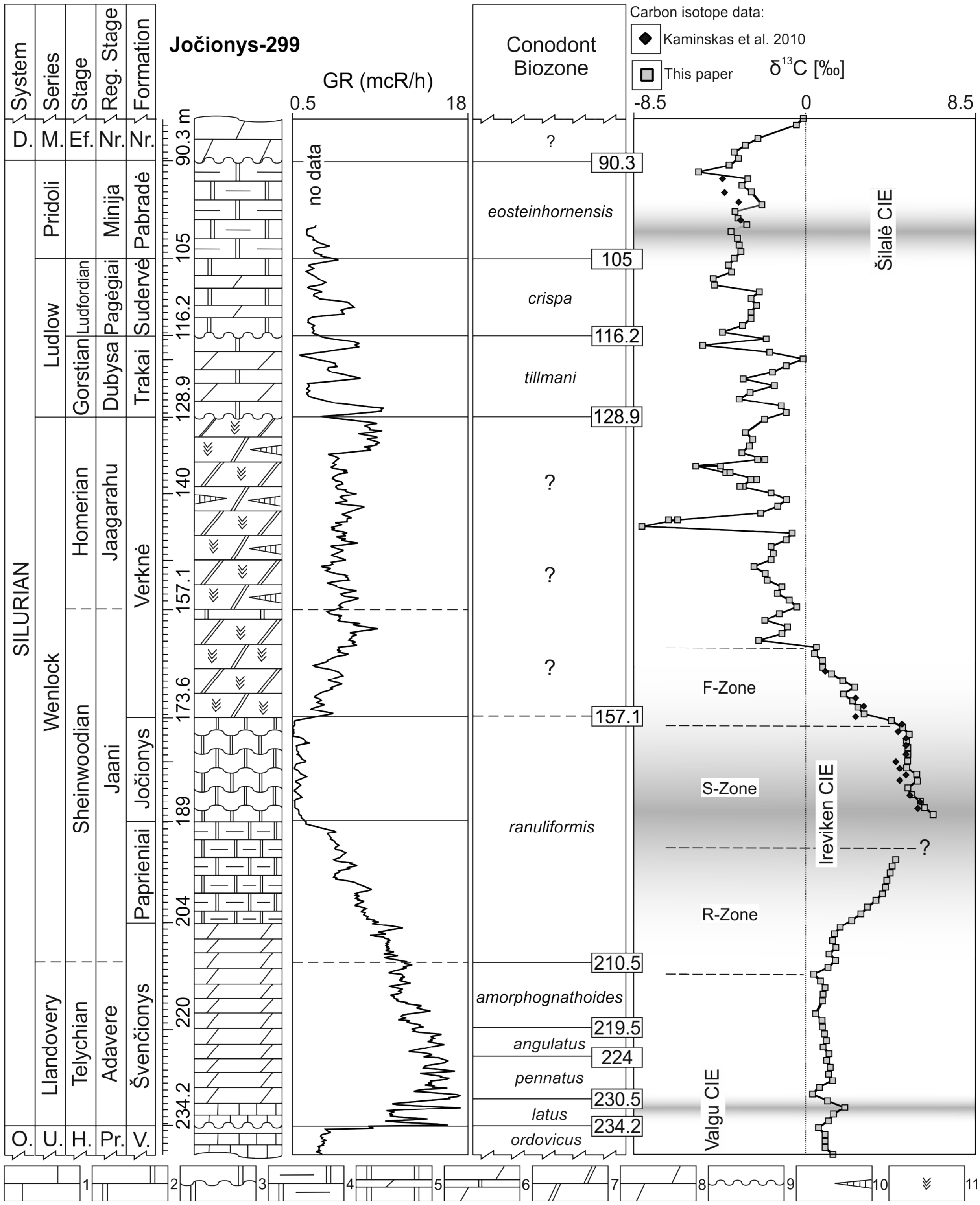

Fig. 2. Lithology, gamma-ray log, conodont biozones (after Paškevičius and Brazauskas 1987) and stable carbon isotopic curve of the Jočionys-299 borehole. *Abbreviations:* Reg. Stage – Regional Stage (after Paškevičius et al. 1994); GR – Gamma ray; D. – Devonian; M. – Middle; Ef. – Eifelian; Nr. – Narva; O. – Ordovician; U. – Upper; H. – Hirnantian; Pr. – Porkuni; V. – Vaineikiai. *Legend:* 1 – Limestone; 2 – Dolostone; 3 – Dolostone: wavy, laminated, cavernous; 4 – Argillaceous dolostone; 5 – Dolostone with marlstone interbeds; 6 – Marlstone with dolostone interbeds; 7 – Dolomitic marlstone; 8 – Marlstone; 9 – Hardground; 10 – Gypsum interbeds; 11 – Reddish in color.

Several Silurian biostratigraphic studies have been conducted on the Jočionys-299 borehole (Paškevičius and Brazauskas 1987; Spiridonov et al. 2015). Based on the conodont biostratigraphy, the *Aulacognathus latus, Pterospathodus pennatus, Pterospathodus amorphognathoides angulatus* and *Pterospathodus amorphognathoides amorphognathoides* biozones of the Telychian are distinguished in the Švenčionys Formation. There are *Kockelella ranuliformis* of the uppermost Telychian and the lower Sheinwoodian, *Ozarkodina tillmani* of the lower Gorstian, *Ozarkodina crispa* of the upper Ludfordian and *Ozarkodina eosteinhornensis* (= *"Ozarkodina" eosteinhornensis* s.l. after Jarochowska et al. 2021) of the lower Pridoli biozones, all distinguished in the investigated interval of Jočionys-299 (Fig. 2). No conodonts have been found in the 173.6–128.9 m interval or in the Verknė Formation of Jočionys-299.

In addition, several findings of thelodonts and acanthodians have been documented in this borehole (Karatajūtė-Talimaa et al. 1987). Thelodonts such as *Logania taiti* (Stetson) have been found in the lower part of the Verknė Formation and *Logania* sp., *Thelodus sculptilis* Gross, and *Thelodus parvidens* Agassiz in the Sudervė Formation. Two taxa of acantodian fauna *Cheiracanthoides* sp. n. 2 and *Poracanthodes punctatus* Brotzen have been identified in the Pabradė Formation of the Jočionys-299 borehole.

Major elements (oxides), trace elements, and mineralogy of Wenlock rocks from the Jočionys-299 borehole were investigated by Kaminskas (2001) with a later study on $\delta^{13}C$ and $\delta^{18}O$ composition of dolostones from the Jočionys, Verknė (lower part) and Pabradė formations (Kaminskas et al. 2010), and he suggested seepage-reflux/burial (for the Jočionys Formation) and evaporative/mixing zone (for the Verknė and Pabradė formations) dolomitization models.

MATERIALS AND METHODS

Samples for the $\delta^{13}C_{carb}$ analysis were taken from a depth interval of 238.7–84.1 m from the Jočionys-299 well core at approximately 1 m interval. The interval of 194–188 m went missing in 1985 after reorganization of the Lithuanian well core storage (borehole information). About 2 g of rock was ground into powder for isotope measurement.

The stable carbon isotope composition was analyzed using traditional techniques (e.g. Rinkevičiūtė et al. 2021) by the Thermo Gasbench II in tandem with the Thermo Delta V isotope ratio mass spectrometer at the Nuclear Research Department of the State Research Institute Center for Physical Sciences and Technology, Vilnius, Lithuania. All samples were loaded into 10 mL Labco Exetainer vials, flushed with He, and later treated with 99.99% H_3PO_4 at 50 °C for 10 h.

The isotope data were normalized against the reference materials IAEA-CO-8 ($\delta^{13}C_{carb}$ = –5.764 ± 0.032%) and NBS 18 ($\delta^{13}C_{carb}$ = –5.014 ± 0.035%). The standard deviation (1 sigma) for the sample analyses was 0.06%. $\delta^{13}C_{carb}$ values are given as parts per mille (‰) relative to VPDB.

$\delta^{13}C_{carb}$ STRATIGRAPHY

The lowermost Silurian $\delta^{13}C_{carb}$ excursion starts from 1.4‰ at 238.7 m depth and rises rapidly to 2‰ at 231.7 m (Fig. 2). Above, the values gradually fall to 0.4‰ at 229.7 m depth. In the 229–211.8 m interval, the $\delta^{13}C_{carb}$ values remain relatively stable and vary around 1‰. In the upper part of the Širvinta Formation, the $\delta^{13}C_{carb}$ values gradually rise from 0.44‰ at 211.8 m to 6.4‰ at 188 m (Paprieniai Formation). In the 188–175 m interval (Jočionys Formation), the $\delta^{13}C_{carb}$ values vary slightly around 5–6‰ (Fig. 2). The $\delta^{13}C_{carb}$ values gradually fall in the lower part of the Verknė Formation from 4.32‰ at 174 m to –2.29‰ at 151 m and are then moderately stable for the 150–146 m depth interval (vary from –0.39‰ to –2.53‰). Thereafter, the $\delta^{13}C_{carb}$ values rapidly fall to –8.1‰ at 145 m, gradually rise to –0.9‰ at 141 m and are moderately stable for the 141–129 m interval (upper part of the Verknė Formation). In the Trakai Formation, the $\delta^{13}C_{carb}$ values fluctuate from –5.07‰ to –0.08‰ (129–116 m interval). The $\delta^{13}C_{carb}$ values rise from –4.08‰ (116 m depth) to –2.25‰ (110 m depth) in the lower part of the Sudervė Formation. The upper part of the Sudervė Formation and the lower part of the Pabradė Formation are characterized by low $\delta^{13}C_{carb}$ values. The values vary from –4.55‰ to –3.16‰ (109–98 m interval). The $\delta^{13}C_{carb}$ values rise to –2.13‰ at 97 m depth and fall to –5.28‰ at 92.1 m in the topmost part of the Silurian in the Jočionys-299 borehole.

DISCUSSION

The excursion of $\delta^{13}C_{carb}$ and biozonation of conodonts in the Jočionys-299 well core allowed precise correlation with the other parts of the Silurian Baltic sedimentary basin as well as with the Silurian time scale (Fig. 3; Melchin et al. 2020). All stratigraphic data confirmed that the Švenčionys Formation of the Jočionys-299 borehole belongs to the Telychian strata. There are three established carbon isotope excursions in the Telychian: 1) the Kallholn CIE, distinguished in the *Spirograptus turriculatus* graptolite Biozone (Walasek et al. 2018); 2) the Valgu CIE, documented at the boundary of the *Pterospathodus*

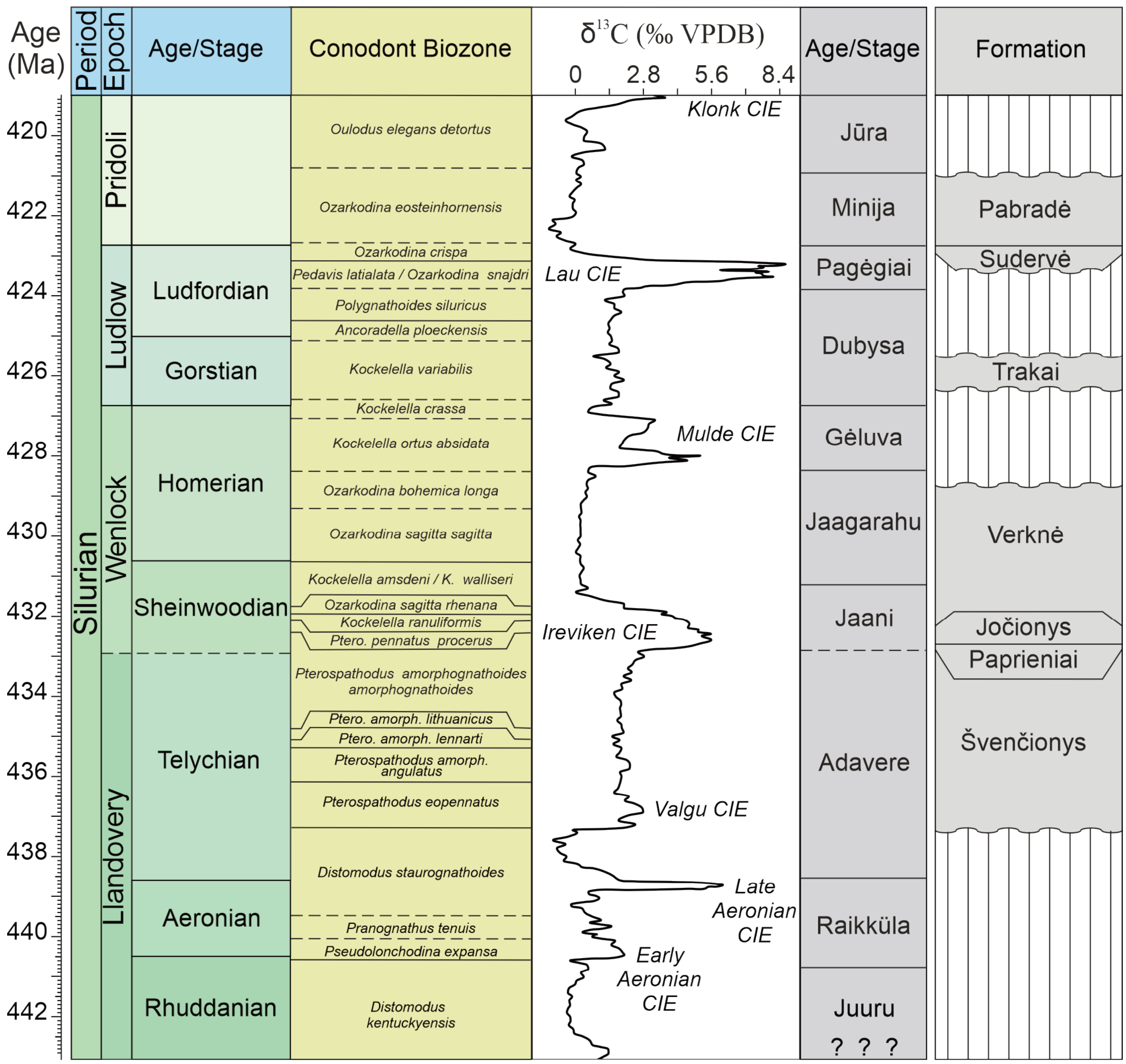

Fig. 3. Silurian time scale and conodont zonation (Melchin et al. 2020), Lithuanian regional stages and correlation of lithostratigraphic units of the Jočionys-299 borehole with the generalized $\delta^{13}C$ curve.

eopennatus–Pterosphatodus amorphognathoides angulatus conodont biozones (Munnecke and Männik 2009) or likely in the *Monoclimacis griestonensis* graptolite Biozone (Loydell et al. 2003); 3) the Sommerodde CIE, established in the middle part of the *Oktavites spiralis* graptolite Biozone (Hammarlund et al. 2019). However, the Kallholn and Sommerodde stable carbon isotope excursions were determined based on stable carbon isotope material from organic material and are not discernible in deposits of shallow marine environments. There is a positive $\delta^{13}C_{carb}$ shift in the lower part of the Švenčionys Formation in the Jočionys-299 borehole (Fig. 2). The $\delta^{13}C_{carb}$ values demonstrate a positive excursion of ~1.6‰ that commences between 233.7 m (1.18‰) and 229.9 m (0.39‰), and lies within the upper part of the *Aulacognathus latus* Biozone (Brazauskas 1987), which can be correlated with the *Pterospathodus eopennatus* Biozone (Männik 2007). This could be interpreted as the Valgu CIE.

The lower boundary of the *Kockelella ranuliformis* Biozone (or the upper boundary of *Pterospathodus amorphognathoides amorphognathoides*) marks the Llandovery–Wenlock boundary (Brazauskas 1987), and the base of the Wenlock correlates with the base of the Paprieniai Formation in Lithuania (Paškevičius et al. 1994). According to the Silurian time scale (Melchin et al. 2020), the upper boundary of the Llandovery disagrees with the upper boundary of the *amorphognathoides* Biozone (Fig. 3), and the Wenlock base can be correlated with the base of the Ireveken CIE. The $\delta^{13}C_{carb}$ values rise in the upper part of the Paprieniai Formation or at the upper boundary of the *amorphognathoides* Biozone (Fig. 2) and reach the maximum in the Jočionys Formation (*ranuliformis* Biozone) in the Jočionys-299 borehole. This is a distinct positive $\delta^{13}C_{carb}$ excursion interpreted as the Ireviken CIE and confirms the lower Sheinwoodian. However, the $\delta^{13}C_{carb}$ values in the upper part of the Švenčionys Formation and the Paprieniai Formation gradually rise (R-Zone) and the values of $\delta^{13}C_{carb}$ are relatively steady in the Jočionys Formation (S-Zone). Based on those observations, this interval can be correlated with the $\delta^{13}C_{carb}$ rising phase, and the Jočionys Formation with the relatively steady phase of $\delta^{13}C_{carb}$ values of the Ireviken CIE (Fig. 3).

Conodont fauna is absent in the Verknė Formation. The positive $\delta^{13}C_{carb}$ excursion gradually falls in the lower part of the Verknė Formation and this interval could be correlated with the falling phase (F-Zone) of the Ireviken CIE and belong to the upper Sheinwoodian Stage (Fig. 3). As no distinct positive $\delta^{13}C_{carb}$ excursion (e.g. duplex of the Mulde CIE) has been detected above the Ireviken CIE, the later Verknė deposits are early Homerian in age.

The *Ozarkodina tillmani* conodont Biozone, which can correspond to the *Kockelella variabilis* Biozone (by Cramer et al. 2011), is distinguished in the Trakai Formation, identifying the lower part of the Dubysa Regional Stage of the Gorstian, and the *Ozarkodina crispa* Biozone is distinguished in the Sudervė Formation, in the upper part of the Pagėgiai Regional Stage of the upper Ludfordian (Fig. 3). No positive $\delta^{13}C_{carb}$ excursion (e.g. Lau CIE) has been detected in the Trakai and Sudervė intervals. Therefore, the Sudervė Formation can be correlated with the post-Lau CIE and with the uppermost part of the Ludlow. Similar successions of conodont biozones and $\delta^{13}C_{carb}$ excursions of the Ludlow have been established in central and eastern Lithuania (Radzevičius et al. 2016; Spiridonov et al. 2020a).

The *Ozarkodina eosteinhornensis* Biozone of the lower Pridoli is distinguished in the Pabradė Formation (Fig. 2). The conodont succession is continuous (Melchin et al. 2020) and probably without gaps. The $\delta^{13}C_{carb}$ values are low in the Pabradė Formation as well as in the Sudervė Formation. The interval with low $\delta^{13}C_{carb}$ values is interpreted in the lower part of the Pabradė Formation as the Šilalė Low excursion and is under discussion (Kaljo et al. 2012; Spiridonov et al. 2020b).

CONCLUSIONS

The stable carbon isotope analysis from carbonates ($\delta^{13}C_{carb}$) of the Jočionys-299 borehole revealed the presence of the Ireviken CIE and probably the positive Valgu and negative Šilale carbon isotope excursions.

The Valgu CIE is distinguishable in the lower part of the Švenčionys Formation. The rising zone of the Ireviken CIE is linked to the upper parts of the Švenčionys Formation and the Paprieniai Formation. An interval with moderately stable $\delta^{13}C_{carb}$ values falls within the Jočionys Formation, and the fall zone is established in the lower part of the Verknė Formation. A possible Šilalė negative excursion has been detected in the Pabradė Formation.

The base of the Wenlock in the Jočionys-299 borehole cannot be correlated with the base of the Paprieniai Formation, and it lies in the upper part of the Švenčionys Formation.

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Stabiilsetel süsiniku isotoopidel põhinev Siluri stratigraafia Jočionys–299 puurläbilõikes (ida-Leedu)

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Viimase 30 aasta jooksul on stabiilsete süsiniku isotoopide (δ^{13}Ccarb) uuringud leidnud üha laiemat kasutamist Siluri ajastu stratigraafias. Stratigraafilisi skeeme on täiendatud kemostratigraafiliste ühikutega – isotooptsoonidega. δ^{13}Ccarb andmestiku kasutamine koos teiste stratigraafiliste meetoditega võimaldab läbilõigete detailsemat liigestamist ja usaldusväärsemat korrelatsiooni.

Artiklis on esitatud Jočionys-299 puurläbilõike δ^{13}Ccarb uuringute tulemused, mis võimaldavad läbilõikes fikseerida Irevikeni (vastab Paprieniai ja Jočionyse kihistutele ning Verknė kihistu basaalsele osale) ja tõenäoliselt ka Valgu (Švenčionyse kihistu alumises osas) ning Šlilalė (Pabredė kihistu alumine osa) isotoopsündmuste (CIE) intervallid. Kemostratigraafilise andmestiku integreerimine biostratigraafilisega võimaldab ida-Leedu siluriaegsete madalveeliste setete usaldusväärset korrelatsiooni globaalse Siluri geokronoloogilise skaalaga.