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The preservation of total organic carbon of the Silurian Pridoli strata in the Milaičiai-103 well core of Western Lithuania

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The Pridoli series is one of the thickest and most complete stratigraphic intervals of the Silurian as well as other systems of the Lithuanian part of the Baltic sedimentary basin. In this study we present a sequence stratigraphic model of the sedimentary succession in the Milaičiai-103 core section. High resolution trend of concentrations of total organic carbon is presented in the developed stratigraphic context. The variability in the total organic matter amount in different sequence stratigraphic system tracts was statistically evaluated using the generalized linear mixed-effect modeling approach. The statistical analysis revealed that the highest concentrations of total organic carbon in the studied section are expected in a highstand and transgressive system tracts and significantly lower concentrations are expected in a lowstand and falling stage system tracts.

Key words: Silurian, Pridoli, total organic carbon, sequence stratigraphy, Silurian Baltic sedimentary basin

INTRODUCTION

Increasing demand and decreasing sources for oil and gas lead to other alternatives such as unconventional hydrocarbons. Preservational environments of such resources are still insufficiently studied. It is thought that layers with higher amounts of organic carbon form during anoxic conditions and are the result of rapid early burial of organic matter. It is believed that most layers with a high organic carbon content form during transgressions (Lüning et al., 2000) and are related to transgressive systems tracts. However, there are suggestions that these organic rich layers can form during early regression phases of a sea level cycle as well (Loydell et al., 2009). D. K. Loydell et al. (2009) analyzed lower Silurian "hot shales" in Jordan and they proposed that higher content of organic carbon can form during regression and associated anoxic conditions. They backed this theory by providing a range of palynological, carbon isotopic, graptolite preservational and sedimentological evidence, which showed that organic rich sediments formed during the episode of sea-level fall. Thus, different sea level and climatic settings could enhance preservation of organic material and apparently there is no simple general relation between the sequence architecture and the potential for preservation of organic carbon.

Moreover, the studied time interval – Pridoli epoch is at the center of attention in understanding large scale ecological and evolutionary turnovers of the Silurian period (Lehnert et al., 2013; Spiridonov et al., 2014; Spiridonov, Brazauskas, 2014). The determination of sedimentary processes and environments that lead to preservation of organic matter could have important consequences for understanding drivers of this deep time environmental change.

In the pioneering study of J. Lazauskiene et al. (2003) authors divided and described the Silurian succession into 10 depositional sequences. As a result, Pridoli was divided into two sequences of the third order: Early (S_9) and Late (S_{10}). Early Pridoli (Minija Formation) sequence shows a general shift of the litofacies zones to the southwest and eastward-directed retrogradation of the carbonate platform (Lazauskiene et al., 2003). Late Pridoli (Jūra Formation) indicates narrowing of the basin – the amount of the terrigeneous component in the sediments increased in the central part of the basin, and eventually suppressed carbonate accumulation on the open shelf (Lazauskiene et al., 2003).

In this study we related the variation of total organic carbon content in the Milaičiai-103 drill core to the sequence stratigraphic settings of the Pridoli strata part of the Silurian Baltic sedimentary basin of Western Lithuania (Figs. 1 and 2). The Milaičiai-103 core according to the detailed lithological and geophysical information of the Pridoli section was subdivided into six 4th-order depositional sequences. The determined content of total organic carbon (TOC) in rock samples was statistically tested for differences in the organic carbon content in different sequence stratigraphical system tract.

GEOLOGICAL SETTING

The Milaičiai-103 well is located on the eastern slope of the Silurian Baltic Basin (Paškevičius et al., 2012). The greater thickness of the succession (compared to the Ordovician succession) was caused by foreland bending and basin subsidence during the late Ordovician and Silurian. During this period, continental plates of Baltica, Laurentia and Eastern Avalonia collided. Collision led to rapid deepening of the basin (Lazauskiene et al., 2002).

During the Pridoli the continent of Baltica along with the Laurentia and the Avalonia was moving to the north. Most of the present day Lithuania's territory was covered by shallow sea where carbonate sedimentation prevailed. According to G. Bičkauskas and N. Molenaar (2008a; 2008b), the main facies belts in the Pridoli ramp of the Baltic Basin could be considered as sabkha, inner-shallow ramp, mid ramp, outer ramp, lower ramp slope and deep basin (Fig. 1). Though, the presence of sabkha in the Pridoli is mostly inferential and still debatable.

The Milaičiai-103 well is located in the outer ramp facies belt. The outer ramp mainly consists of limestones, marls and shales. The dominant shelly fauna consists of crinoids, brachiopods, gastropods, ostracodes and bivalves. Low energy

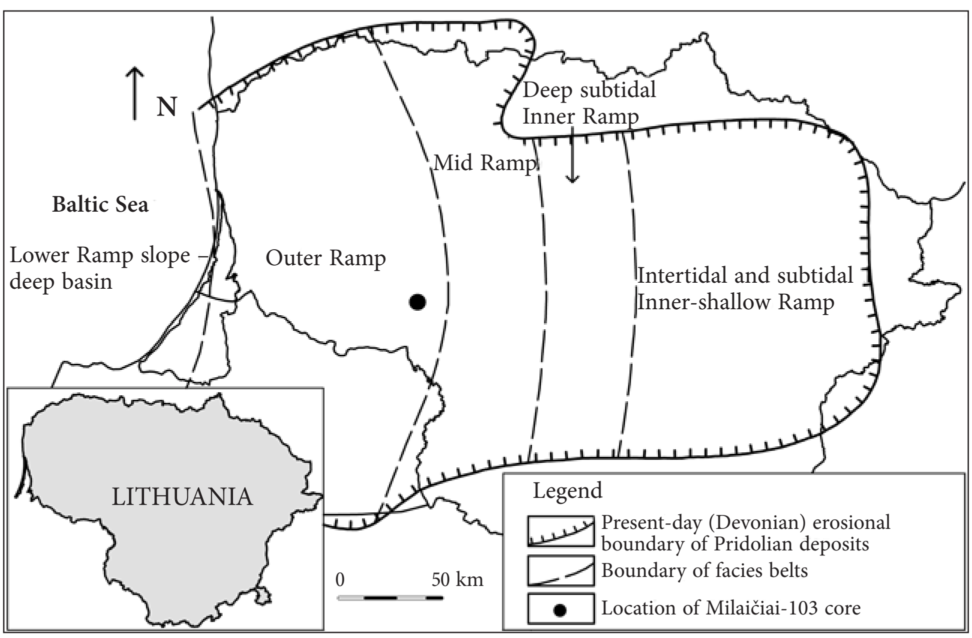

Fig. 1. Geographical location of the Milaičiai-103 core in relation to the facies belts of the Silurian Baltic Sedimentary basin (after Bičkauskas and Molenaar, 2008a)

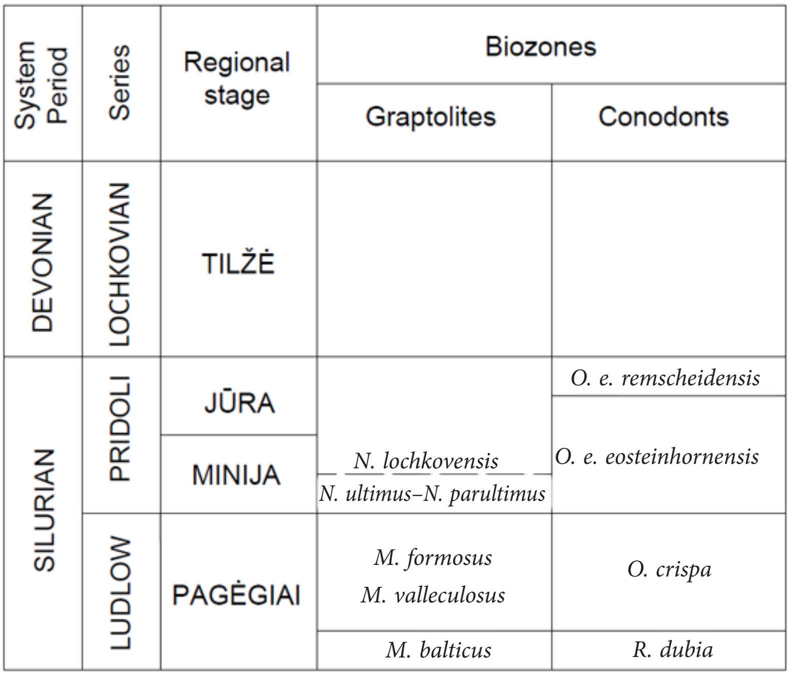

Fig. 2. Stratigraphical scheme of the Upper Silurian and the Lowest Devonian of Lithuania (after Brazauskas et al., 2004)

sedimentary environment is typical of the outer ramp facies belt. Layers form below the wave base mainly dominated by pelagic and storm deposition (Bičkauskas, Molenaar, 2008a; 2008b).

At the present time the biostratigraphic and chemostratigraphic data in the Milaičiai-103 core are still lacking. The stratigraphic subdivision of the Pridoli strata and placement of boundaries is based on the gross lithological features of the core material. Subsequently the boundary placement is rather approximate bearing in mind relative monotonicity of the section. The base of the Minija formation was distinguished in the base of clayey dolomitic marlstones at a depth of 1 160 m. The base of the Jūra formation was distinguished at the base of the argillite layer at a depth of 1 015 m which marks a highly contrasting lithofacies contact. The top of the Jūra formation (940 m) is marked by transition to the red dolostones of the Lower Devonian Tilžė formation.

MATERIALS AND METHODS

Determination of concentration of total organic carbon

In order to determine the variability of the amount of organic matter in the Pridoli of Milaičiai-103 drill core the loss-on-ignition (LOI) method has been used according to O. Heiri et al. (2001). The interval for this study spanned from 929 up to 1 159 metres depth. Total 401 samples were taken for the analysis. The samples were powdered in a ceramic dish. Loss-on-ignition percentage was determined using the SNOL 30/1300 furnace at the Department of Geology and Minerology of Vilnius University, Lithuania. Each powdered sample was put into a heat resistant crucible and weighted. Weighted samples were oven-dried at 105 °C temperature for 24 hours. Having the oven-dried samples weighted (DW_{105}) they were ashed at 550 °C temperature for 4 hours. The combusted samples were weighted once again (DW_{550}). These measurements were used to calculate LOI:

$$LOI_{550} = ((DW_{105} - DW_{550}) / DW_{105}) \times 100, \quad (1)$$

where LOI_{550} represents LOI at 550 °C, DW_{105} represents the dry weight of the sample before combustion, and DW_{105} is the dry weight of the sample after heating to 550 °C. The weighted loss of mass was considered to be proportional to the concentration of organic carbon in the sample.

Results obtained by the LOI method sometimes could be positively biased because of loss of volatile compounds, structural water of clay minerals or metal oxides, or of inorganic carbon (Heiri et al., 2001). For this purpose the LOI results were recalculated to TOC using the transfer function calibrated to the data from another well (Kurtuvėnai-161) samples of the Silurian period which were analyzed using infrared (IR) spectroscopy (data of Donatas Kaminskas). Additionally, 36 random samples from the Kurtuvėnai-161 well core were combusted and TOC was measured using the LOI method. Using these two datasets, the resulting measurements were regressed using the PAST program applying the linear model approach (Hammer et al., 2001). The linear regression showed that there was a significant correlation ($r = 0.53$, $p = 0.0008$) between the total organic matter determined by the LOI method (x) and IR spectroscopy (y). The determined linear transfer function is as follows:

$$y = 0.4660 \times x - 0.88287. \quad (2)$$

Function (2) was used to calculate the organic matter content calibrating the LOI data to the obtained regression (Fig. 3). Data points which show zero or negative concentrations using the regression equation were set to an arbitrary small positive number which is close to zero (in this case 0.001%). The recalculated values were further used for statistical analyses.

Statistical procedures

In order to test the differences in total organic carbon (TOC) variation in the samples which were assigned to the four kinds of system tracts, which were also assigned to the 4th-order cycles, we applied the methodology of the so-called generalized linear mixed models (GLMMs). Generalized linear models (GLMs) are the extension of ordinary linear regression models for differing (non-Gaussian) error structures of variables and GLMMs are extension of the later models for situations where there is non-independence in data structures (i. e. when there is hierarchical clustering of observations) by including random (between groups) effects in addition to the fixed effects (Hedeker, 2005).

In this application we used cycles as experimental replicates for the effects of different system tracts on concentrations of organic carbon in rock samples. The estimated categorical variable mixed effect linear model has a form of: *TOC ~ System tract + (System tract | Cycle)*. The statistical testing and analysis was performed in the **R** program environment using the restricted maximum likelihood (REML) approach which is available in the package '*lme4*' (Bates et al., 2013; R Development Core Team, 2015).

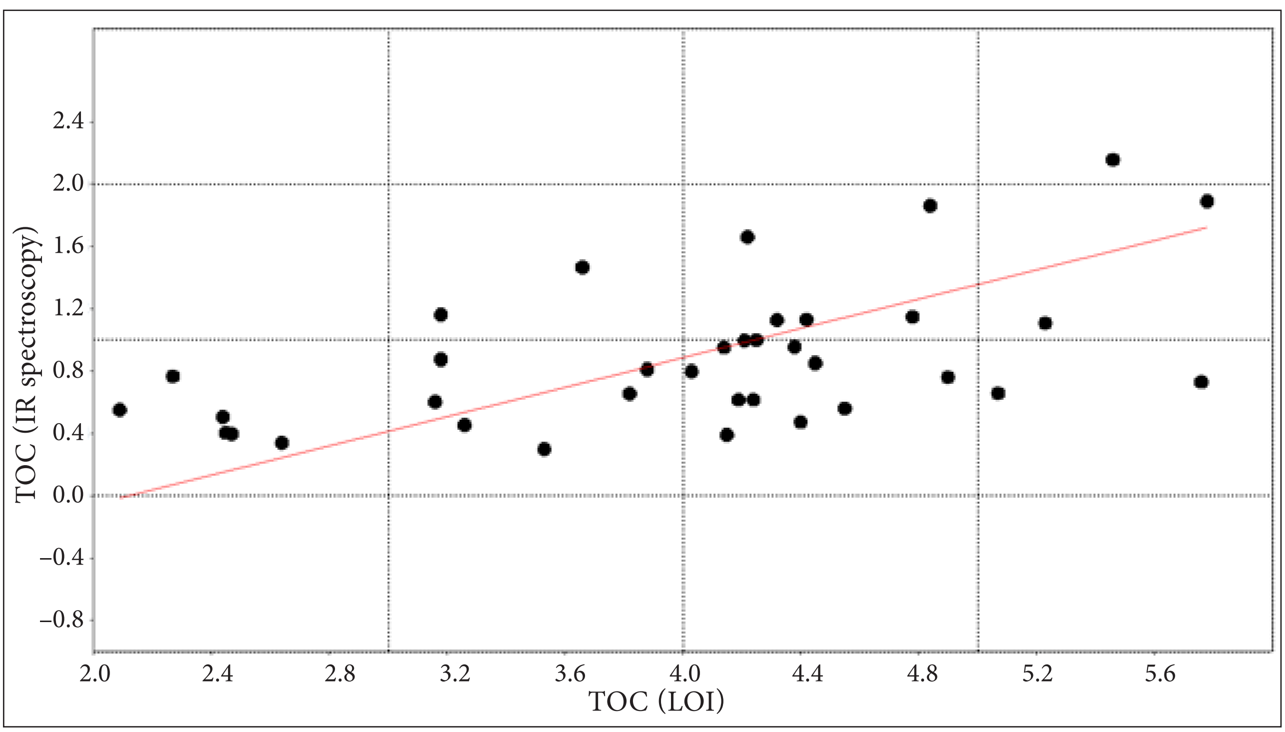

Fig. 3. Regression model which was used as a transfer function in estimating TOC from the LOI data. $y = 0.4660 \times x - 0.88287$, $r = 0.53$; $p = 0.0008$, $n = 36$

RESULTS

Description of sedimentary cycles

The Pridoli succession of the Milaičiai-103 well core was divided into the six transgression-regression (T-R) cycles which were estimated to be the 4th-order cycles (Fig. 4) (*sensu* Miall, 2010). Subsequently these 4th-order sedimentary cycles of the Pridoli succession were also divided into a number of system tracts. System tracts were established according to the lithology. As a result, these tracts are considered to be independent from total organic carbon measurements which enabled rigorous statistical testing.

The first T-R cycle was distinguished in the interval at 1 160 and 1 113 metres depth. All four system tracts were distinguished in this cycle. The first system tract (interval 1 135–1 146.9 m) was attributed to a highstand system tract (HST). HST mainly consists of dolomitic marlstones. Lithologically similar is the succeeding falling stage system tract (FSST). Upwards dolomitic marlstone is replaced with more carbonate material and here the lowstand system tract (LST) is established (interval 1 138.6–1 130 m). It mostly consists of argillaceous limestone. The fourth interval is attributed to the transgressive system tract (TST) (1 130–1 326 m), which is dominated by dolomitic and clayey marlstone. Above, dolomitic marlstone is replaced with argillaceous limestone and this overlaying layer is replaced with more clayey rocks. It indicates the beginning of the second T-R cycle which was distinguished in the interval at 1 113 and 1 083 meters depth. It begins from the previous HST (interval 1 126–1 111 m) and later is succeeded by short FSST (interval 1 111–1106.5 m). The latter interval is mainly composed of argillaceous limestones. Above there is LST established (interval 1 106.5–1 098 m) which is composed of intercalation of dolomitic and argillaceous limestones and dolomitic marlstones. Succeeding TST (interval 1 098–1 091 m) is composed of argillaceous limestones. This layer has elevated the carbonate content at the bottom and it is more argillaceous at the top. On the top of it HST (interval 1 091–1 081 m) was distinguished. The uppermost interval is composed of argillaceous limestones which are replaced by dolomitic marlstone at the top.

The third T-R cycle is established in the interval from 1 083.5 and up to 1 060 m. It continues from the previous HST and further proceeds to FSST (1 081–1 077 m). Dolomitic marlstone is replaced by argillaceous limestone, thus suggesting that depositional environment changed from the deeper to the shallower one. LST (1 077–1 072) is lithologically similar to FSST – marlstone and argillite overlie argillaceous limestone. The interval (at 1 072–1 068 metres depth) is interpreted here as representing TST: a shallower depositional environment is replaced by a deeper one. Next HST is distinguished in the interval between 1 068 and 1 055 m. It is dominated by argillites (or shales) and dolomitic marls.

In the middle part of the previously described HST the fourth T-R cycle was established at the 1 060.3 and 1 016 metres depth. This cycle is most probably incomplete because a transgressive part of the cycle is missing (limestones are directly overlain by argillites of the Jūra formation). Overall three system tracts were established. The lower part of the cycle begins from dolomitic marlstones which formed during HST. The falling-stage system tract (1 055–1 027 m) is represented by similar lithology as HST and certainly shows a strong aggradational character. At the top of the 4th T-R cycle a regressive part or FST (interval 1 027–1 016.5 m) is distinguished. Dolomitic marlstone in the interval is replaced with dolomitic marlstone interbedded with argillaceous limestone. This system tract delineates unconformity which formed due to 3rd-order (*sensu* Miall, 2010) sea level changes.

The fifth T-R cycle was distinguished in the interval from 958.4 to 1 016 metres depth. Overall four system tracts were established. The first tract is interpreted as HST (interval 1 016–1 005 m) and it is mostly composed of argillite. The following dolomitic marlstone interval from 1 005 to 978.7 m could be interpreted as representing the falling stage system tract. This succession is followed by increasingly carbonatic rocks (dolomitic marlstones) which were interpreted as representing LST (interval 978.7–968 m). Above this layer situated limestones and dolomitic marlstones reflect the deepening trend of the sedimentary environment and are interpreted here as representing TST (interval 968–961 m). The last established system tract is HST (interval 961–954 m) which is mostly represented by dolomitic clayey marlstones.

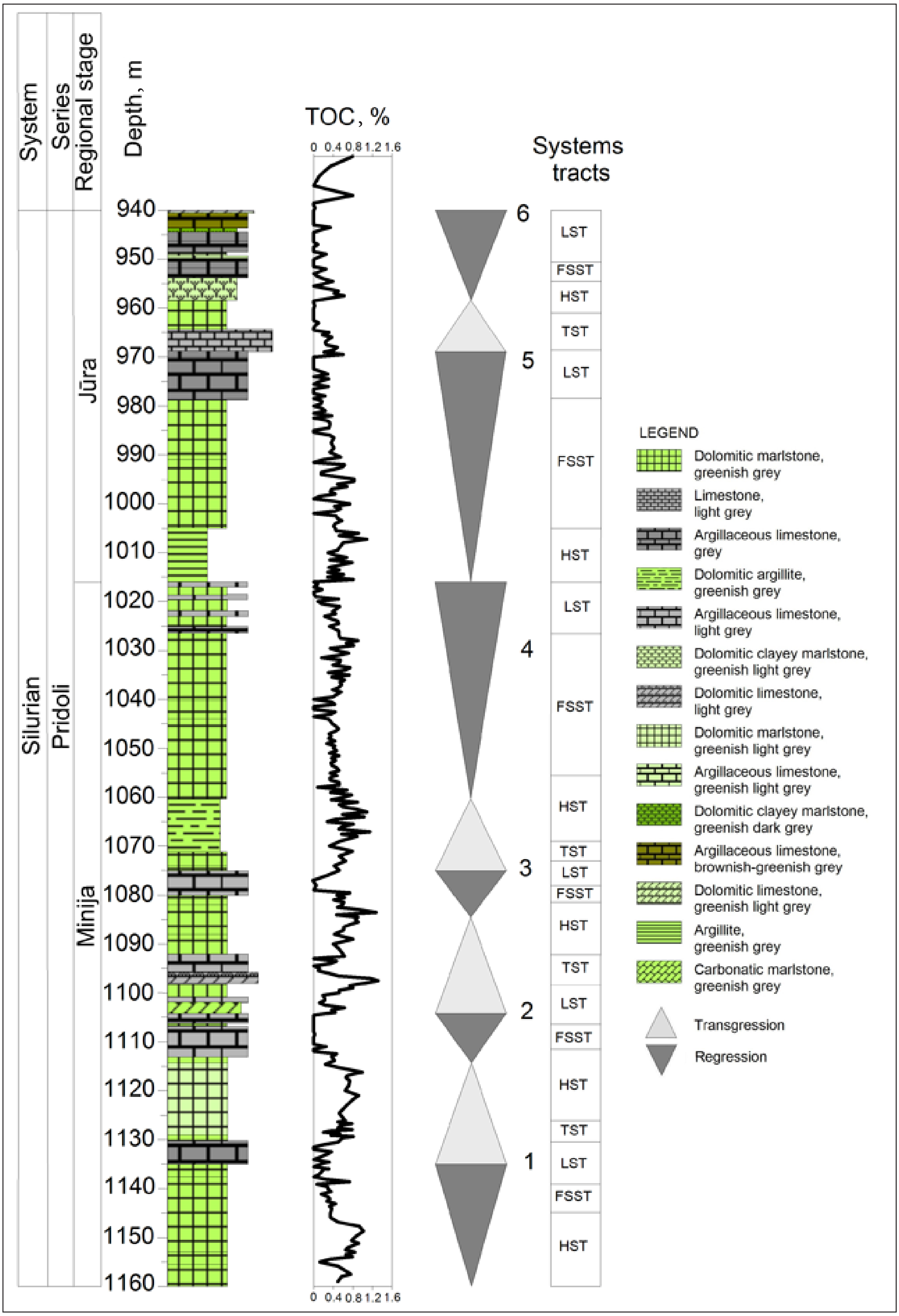

Fig. 4. Lithology, TOC trend and sequence stratigraphic interpretation of the sedimentary succession of Pridoli in the Milaičiai-103 core

The last or 6th T-R cycle was distinguished at the 958.4–940 meters depth interval. Only three system tracts were interpreted, because based on the lithological succession this sedimentary cycle should be incomplete. This cycle starts from the last HST at a depth of 958.4 m. FSST (interval 954–950 m) is represented by marlstones which are followed by more carbonaceous rocks (interval 950.4–958.4 m). The rest part of the 6th T-R cycle mostly consists of argillaceous limestone (interval 950.4–940 m) and is interpreted as a lowstand system tract.

Statistical analysis

The statistical analysis revealed consistent and expected patterns of variation in TOC to relation in different system tracts which were distinguished using the lithological criteria (Tables 1 and 2). It was determined that the highest concentrations of TOC are observed in HST settings (expected concentration is estimated to be 0.53%). Second highest concentrations are determined in TST settings (0.38%) which are significantly lower than in HST settings (Table 1). The lowest concentrations were estimated in the FSST (0.26%) and the LST (0.23%) settings, and they are, as was determined, statistically indistinguishable from each other with respect to this variable. It also should be noted that TST settings show higher variability in the expected concentration of organic carbon in comparison to other system tracts. HST shows the second highest level of variability in TOC concentrations, and FSST and LST consistently show the lowest levels of variability (Table 2).

Table 1. **Table showing the fixed effects of system tracts constituting 4th-order sedimentary cycles on the concentrations of TOC in the samples (total 401 samples) of the Milaičiai-103 core. Equality of means was tested using the two-sided Student's t-test comparing the most distinct group (in this case FSST*) to other groups**

System tract	Estimate (TOC*, %)	SE (TOC, %)	p
HST	0.53	0.085	<0.01
TST	0.38	0.107	<0.2
FSST*	0.26	0.066	<0.001
LST	0.23	0.07	>0.5

* TOC – total organic carbon.

Table 2. **Table showing random (between-group) effects of different system tracts on TOC**

System tract	Variance (TOC, %)	Standard deviation (TOC, %)
HST	0.036	0.190
TST	0.054	0.232
FSST	0.023	0.150
LST	0.023	0.152

DISCUSSION AND CONCLUSIONS

The sequence stratigraphy interpretation of lithological succession revealed six 4th-order sedimentary cycles: four in the Minija Formation and two in the Jūra Formation. The forth cycle, which ends the Minija Regional stage, is interpreted to be incomplete (or very condensed). This interpretation is congruent with the previously revealed paleoclimatic patterns of sea temperature change, which pointed to significant cooling and is associated with the regression in the Middle of the Pridoli (Žigaitė et al., 2010).

It should be noted that lithological variability was higher and the lengths of sedimentary cycles were significantly shorter at the beginning and at the end of the Pridoli due to progradational tendencies. The middle part of the studied succession is distinctly aggradational (with the exception of the boundary between 4th and 5th cycles), because it is dominated by the same dolomitic marlstone lithofacies. This difference in the sequence stratigraphic architecture could be related to possible tectonic shifts in the generation of accommodation space and the generation of sediments.

The revealed pattern of total organic carbon preservation in differing system tracts showed that the highest amount of carbon is expected at highstands and transgressive phases of 4th-order sea level cycles. This pattern conforms to the classical model of deposition of organic matter in relation to the sequence stratigraphic architecture (Miall, 2010). Though, it is interesting to note that during the falling stage phases of cycles there is a significantly lowered amount of TOC in the samples than during the transgressions, similar to that observed in LST's. This observation points to possible depositional and or climatic asymmetries which perhaps occurred during different stages of sedimentary cycles in the observed time span. Alternatively it could be an artefact of a low number of replicates (sedimentary cycles) which were used for the estimation of system tracts on the preservation of TOC.

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ORGANINĖS ANGLIES IŠSAUGOJIMAS MILAIČIŲ-103 GRĘŽINIO (VAKARŲ LIETUVA) PRŽIDOLIO (VIRŠUTINIS SILŪRAS) PJŪVYJE

S a n t r a u k a

Pržidolio aukštas lietuviškuose Baltijos sedimentacinio baseino pjūviuose pasižymi ypač dideliais storiais ir stratigrafiniu pilnumu. Šiame darbe sekų stratigrafijos perspektyva nagrinėjamas organinės medžiagos koncentracijos pasiskirstymas Milaičių-103 pržidolio pjūvyje. Minijos regioninis aukštas, remiantis sekų stratigrafine analize, yra padalytas į keturis sedimentacinius 4-ojo laipsnio ciklus (1–4 ciklai), paskutinis iš jų interpretuotas kaip nepilnas. Jūros regioninis aukštas yra padalytas į dar du ciklus (5 ir 6 ciklai). Išskirti sedimentaciniai ciklai buvo padalyti į keturis santykinio jūros lygio metraščių (angl. *system tracts*) tipus: žemo jūros lygio, kylančio jūros lygio, aukšto jūros lygio ir krintančio jūros lygio. Naudojantis apibendrintų tiesinių mišriųjų modelių metodika nustatyta, kad didžiausios organinės anglies koncentracijos sutinkamos aukšto jūros lygio metraščiuose (0,53 %) ir šiek tiek mažesnės – kylančio jūros lygio metraščiuose (0,38 %). Mažiausios organinės anglies koncentracijos tikėtinos krintančio jūros lygio (0,26 %) ir žemo jūros lygio (0,23 %) metraščiuose.

Raktažodžiai: silūras, pržidolis, organinė anglis, sekų stratigrafija, Baltijos silūro sedimentacinis baseinas