Stratigraphy and facies differences of the Middle Darriwilian Isotopic Carbon Excursion (MDICE) in Baltoscandia

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Abstract. The Middle Darriwilian Isotopic Carbon Excursion (MDICE) is a global isotopic event described in sections from different palaeocontinents. Here we present new stable carbon isotopic data from carbonates of ten sections in different parts of the Baltoscandian Palaeobasin (Estonia, Latvia, Lithuania, Sweden, NW Russia). The definition of the MDICE as a chemostratigraphic unit is discussed, as well as the subdivision of its peak into two distinct peaks. The MDICE is one of the longest carbon isotopic events in the Palaeozoic. It was preceded by the L-chondritic cosmic dust flow event, which may have been responsible for cooling through the Darriwilian and the initiation of the Great Ordovician Biodiversification Event. High-resolution chemostratigraphic analyses show that the time interval between these environmental events and the base of the MDICE is up to one million years. Due to the long duration of the MDICE the modelling of this excursion should address more complex scenarios than a simple response of the carbon cycle to rapid climatic perturbations.

Key words: carbon isotopes, chemostratigraphy, Ordovician, Darriwilian, Baltoscandia.

INTRODUCTION AND GEOLOGICAL SETTING

The Middle Darriwilian Isotopic Carbon Excursion (MDICE) was first described by Ainsaar et al. (2004) in the Baltoscandian sections. Recorded in several palaeocontinents like Baltica (Ainsaar et al. 2007, 2010), Laurentia (Leslie et al. 2011; Bergström et al. 2018), Argentine Precordillera (Albanesi et al. 2013), Siberia (Ainsaar et al. 2015), South China (Schmitz et al. 2010; Munnecke et al. 2011), North China (Bang & Lee 2020) and Tarim Basin (Zhang & Munnecke 2016), it is now known as one of the three major global Ordovician carbon isotopic events (together with the Guttenberg and Hirnantian carbon isotopic excursions). The raised $\delta^{13}C$ values of the MDICE are covering the middle or upper parts of the Darriwilian Stage, but the amplitude of variation in carbon isotopic values is within the limits of 2‰ in most cases.

The chemostratigraphy of the Darriwilian Stage is relatively well studied in the sections of the Baltoscandian Palaeobasin compared to other areas of the world. Carbon isotope data from 18 outcrop and drillcore sections of Estonia, Latvia, Sweden and NW Russia have been published since 2004 (Ainsaar et al. 2010; Wu et al. 2017, and references therein). However, the stratigraphic range of the MDICE as a chemostratigraphic unit has been dealt differently (only the peak values or the limbs of the curve included) and the facies variations of the isotopic values have not been studied systematically. In this study, we present new data from ten sections in northern and southern Estonia, western Latvia, Lithuania, NW Russia (Pskov and Leningrad regions) and Sweden (Gotland and Jämtland). Data from Lithuania, Gotland and the Pskov region are first reported from these areas. Comparative analysis of all these isotopic curves helps to evaluate the chemostratigraphic potential of the characteristic intervals of the MDICE, including previous work on the subdivision of the sedimentary succession to isotopic zones (Ainsaar et al. 2010) or different peaks (Lehnert et al. 2014; Wu et al. 2015). This work allows us to track and discuss more precisely secular palaeoenvironmental changes and lateral (facies) variability of the carbon isotopic signal during the Darriwilian in the Baltoscandian Palaeobasin.

The Middle Ordovician strata in Baltoscandia comprise a nearly continuous succession of limestones and marls (Nestor & Einasto 1997). The general distribution of the Ordovician fauna and lithofacies delineates large-scale facies zones within the Baltoscandian Palaeobasin (Jaanusson 1976; Harris et al. 2004; Fig. 1). The Early Ordovician Tremadocian siliciclastic ramp environment of the Baltoscandian Palaeobasin was replaced by a cool-water carbonate ramp setting in the Floian and evolved into a temperate carbonate ramp in the Darriwilian Age (Nestor & Einasto 1997; Dronov & Rozhnov 2007). Carbonate sediments, wackestones–packstones, formed in the inner to middle ramp settings, mainly below the fair-weather wave base in northern Estonia (North Estonian Confacies by Jaanusson 1976; Estonian Shelf facies by Harris et al. 2004). This area is characterized by numerous sedimentary gaps, some of which are related to small-scale stratigraphical unconformities marking boundaries of depositional sequences (Nestor & Einasto 1997; Dronov et al. 2011). The Scandinavian Basin, including its broad embayment, the Livonian Basin in southern Estonia, western Latvia and Lithuania, was characterized by argillaceous carbonate sedimentation (mainly wackestones–mudstones) in distal ramp/basinal settings. Some limestone units are of reddish

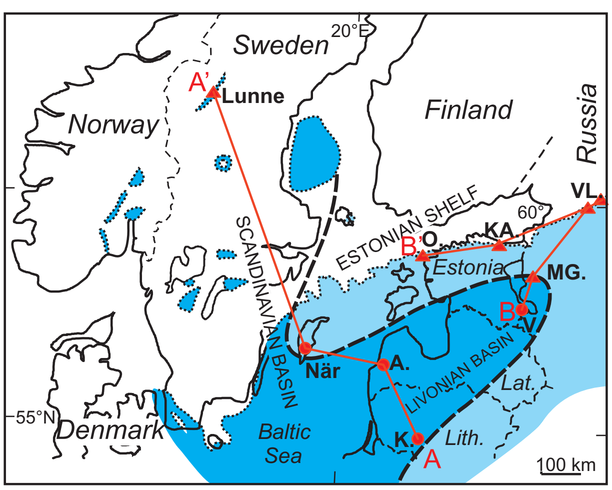

Fig. 1. Major Ordovician facies zones of Baltoscandia (modified from Jaanusson 1976 and Harris et al. 2004) and location of sections (red triangles – outcrops; red dots – drillcores) and profiles A–A' and B–B'. A., Aizpute-41; K., Kurtuvėnai-166; KA., Kunda-Aru; MG., Mishina Gora; O., Osmussaar; V., Värska-6; VL., Volkhov (western) and Lynna (eastern) outcrops. Dotted line – present-day distribution of Ordovician strata; dark blue area – basinal/distal ramp facies; light blue area – carbonate shelf/inner-middle ramp facies. Lat., Latvia; Lith., Lithuania.

or mixed grey-reddish colour (the Kriukai, Baldone, Segerstad, Stirnas, Holen and Lanna formations) within the generally greenish-grey Ordovician succession (Fig. 2). The biostratigraphic correlation of the units across the facies belts is mainly based on microfossils, such as chitinozoans (Nõlvak & Grahn 1993) and conodonts (Viira & Männik 1997; Viira et al. 2001).

MATERIAL AND METHODS

Altogether 446 whole-rock samples, taken with a mean interval of 0.3 m from six outcrop and four drillcore sections, were analysed (see supplementary online data at https://doi.org/10.23679/502). The sections represent a wide area and different facies zones of the Baltoscandian Palaeobasin (Fig. 1). The samples for isotopic analysis were collected from carbonate rocks avoiding obvious veins or burrows. The powdered material from the Kurtuvėnai-166 (Lithuania), Aizpute-41 (Latvia) and Värska-6 (southern Estonia) drillcore sections, and the Osmussaar outcrop section (northern Estonia) was analysed for carbonate carbon stable isotopic composition using a Thermo Fisher Scientific Delta V Advantage mass spectrometer in the Department of Geology, University of Tartu. Material from the När drillcore section (Gotland, Sweden), and the Lunne (Jämtland, Sweden), Mishina Gora (Pskov District, Russia), Volkhov and Lynna (Leningrad District, Russia) and Kunda-Aru (northern Estonia) outcrop sections was analysed by the Thermo Fisher Scientific Delta V Advantage mass spectrometer in the Department of Geology, Tallinn University of Technology. Carbon isotopic results are reported, using the usual δ-notation, as per mil deviation from the VPDB standard. The accuracy of the analyses is in the order of $\sigma = 0.05$‰.

DARRIWILIAN CARBON ISOTOPE STRATIGRAPHY

Geological sections from the distal ramp/basinal facies (Scandinavian Basin) Kurtuvėnai, Aizpute, När, Lunne, Värska and Mishina Gora represent the most complete sedimentary successions in the respective areas, with well-expressed carbon isotopic curves (Figs 3, 4). The Dapingian part of the succession (Volkhov Regional Stage) is characterized by scattered $\delta^{13}C$ values between 0.5‰ and 1‰ with no clear trend (Baltic Carbon Isotopic Zone BC1; Ainsaar et al. 2010). This segment ends with the rising limb of the MDICE. The curve low point in the lowermost part of the Darriwilian Stage has been named the Lower Darriwilian Negative Isotopic Carbon Excursion (LDNICE) by Lehnert et al. (2014). The rising limb of the MDICE, described as Zone BC2 by Ainsaar

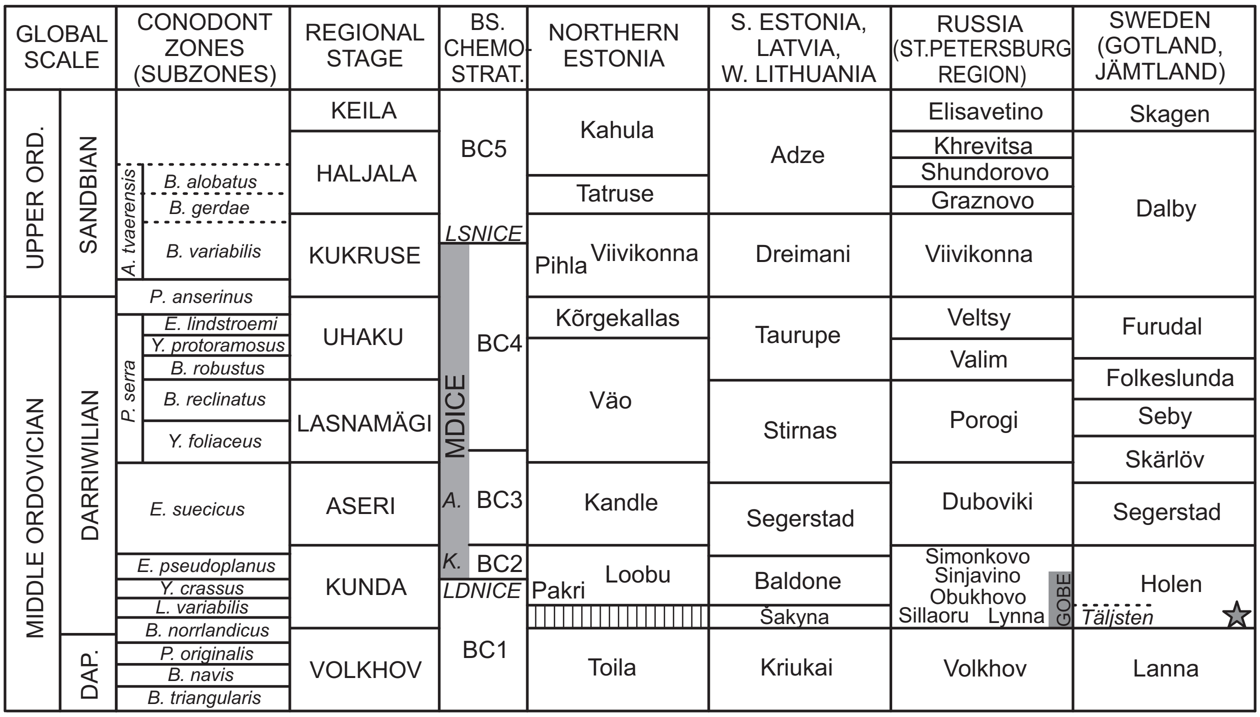

Fig. 2. Dapingian, Darriwilian and Sandbian stratigraphy of Baltoscandia (correlation of formations modified from Nõlvak & Grahn 1993, Dronov 2005 and Meidla et al. 2014). Baltoscandian (BS) carbon isotope chemostratigraphy according to Ainsaar et al. (2010). DAP., Dapingian; A., K., MDICE Aseri and Kunda peaks, respectively; LDNICE, Lower Darriwilian Negative Isotopic Carbon Excursion; LSNICE, Lower Sandbian Negative Isotopic Carbon Excursion. The grey rectangle 'GOBE' marks the onset of the Global Ordovician Biodiversification Event based on brachiopod data from NW Russia, and related cooling interval (Rasmussen et al. 2016); the star marks the interval of L chondrite meteorites in Sweden (Lindskog et al. 2017).

et al. (2010), is covering stratigraphically most of the Kunda Regional Stage and is characterized by an increase of 1–1.5‰ in δ^{13}C values in the sections of the distal ramp facies. The plateau of the MDICE (Zone BC3) has δ^{13}C values between 1.5‰ and 2‰ and roughly corresponds to the Aseri Regional Stage in Baltoscandia (Ainsaar et al. 2007, 2010). This plateau-like peak of the MDICE is followed by a long falling limb (Zone BC4) which is terminated by a low in the curve (the Upper Kukruse Low by Kaljo et al. 2007; Lower Sandbian Negative Isotopic Carbon Excursion, LSNICE, by Bauert et al. 2014) with δ^{13}C values around 0‰ in the uppermost part of the Kukruse Regional Stage.

The MDICE can be defined *sensu lato* as an interval between these two low points in the isotopic curves, the LDNICE and the LSNICE. Therefore, the MDICE is covering stratigraphically the Kunda, Aseri, Lasnamägi, Uhaku and Kukruse regional stages in Baltoscandia, corresponding to the *Eoplacognathus pseudoplanus*, *E. suecicus*, *Pygodus serra* and *P. anserinus* conodont biozones (Fig. 2). Considering the latest zircon U–Pb datings from sections in Sweden (Lindskog et al. 2017), the MDICE started at about 467 Ma, reached its maximum at 465–463 Ma in the *E. suecicus* conodont Biozone and gradually returned to the δ^{13}C base values at about 457 Ma (earliest Sandbian; Ainsaar et al. 2010; Wu et al. 2017). With the duration of ~10 million years, it is apparently one of the longest carbon isotopic events in the Palaeozoic.

Some authors have tried to subdivide the MDICE peak into several peaks, which could have chemostratigraphic value. The MDICE main peak plateau has also been named the Aseri peak, MDICE-A (Ainsaar & Meidla 2016), corresponding to the *E. suecicus* conodont Biozone (Ainsaar et al. 2007; Wu et al. 2017). This peak is preceded in several Baltoscandian sections by a lower peak (MDICE peak 1 by Lehnert et al. 2014; the Kunda peak, MDICE-K by Ainsaar & Meidla 2016) in the Kunda Regional Stage. In the studied sections, the MDICE-K peak is best visible in the interval of the Baldone Formation of the Aizpute and Värska core sections (Figs 3, 4). It has also been well recognized in the Tartu (Bauert at al. 2014), Mehikoorma, Ruhnu, Gullhögen, Kärgarde (Ainsaar et al. 2010), Mora, Solberga and Tingskullen (Lehnert et al. 2014) sections and is tied to the upper part of the *E. pseudoplanus* conodont Biozone (the *M. ozarkodella* conodont Biozone; Wu et al. 2017).

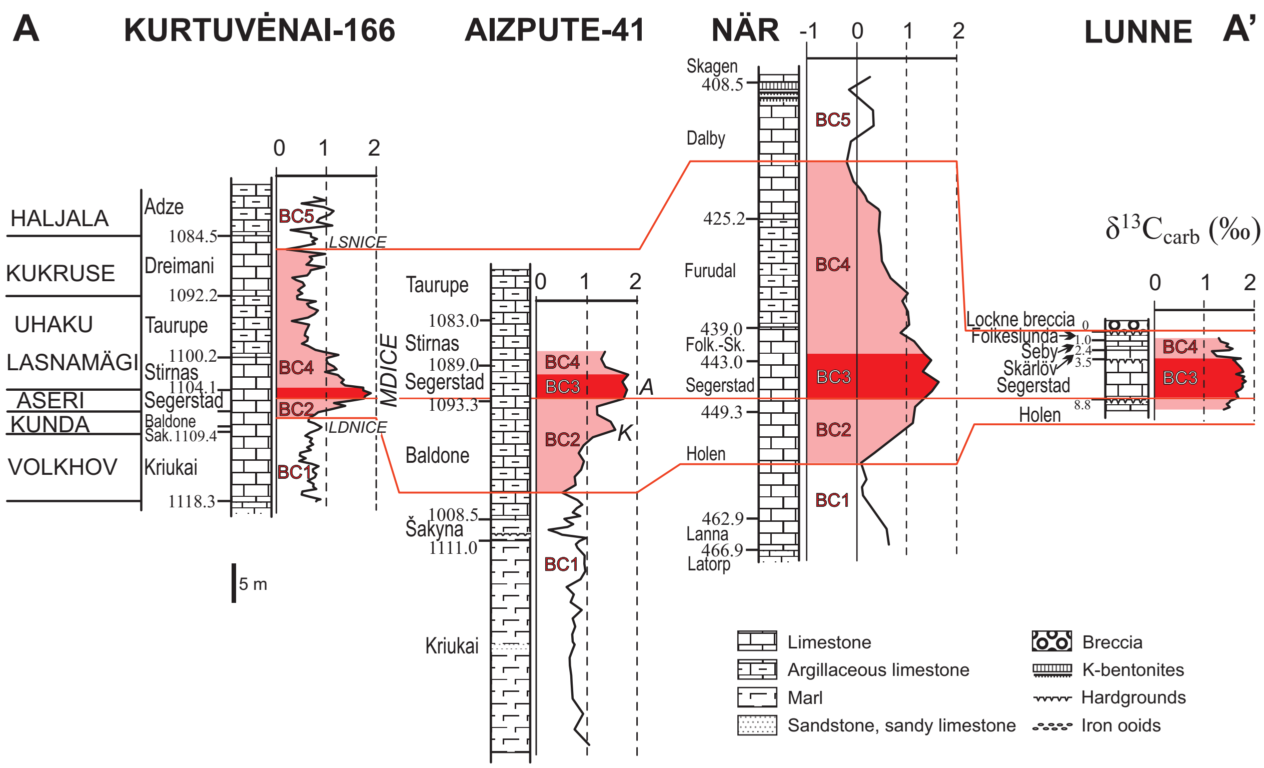

Fig. 3. Chemostratigraphic correlation of sections along profile A–A’ based on $\delta^{13}C$ curves. For location of the profile see Fig. 1, for abbreviations Fig. 2.

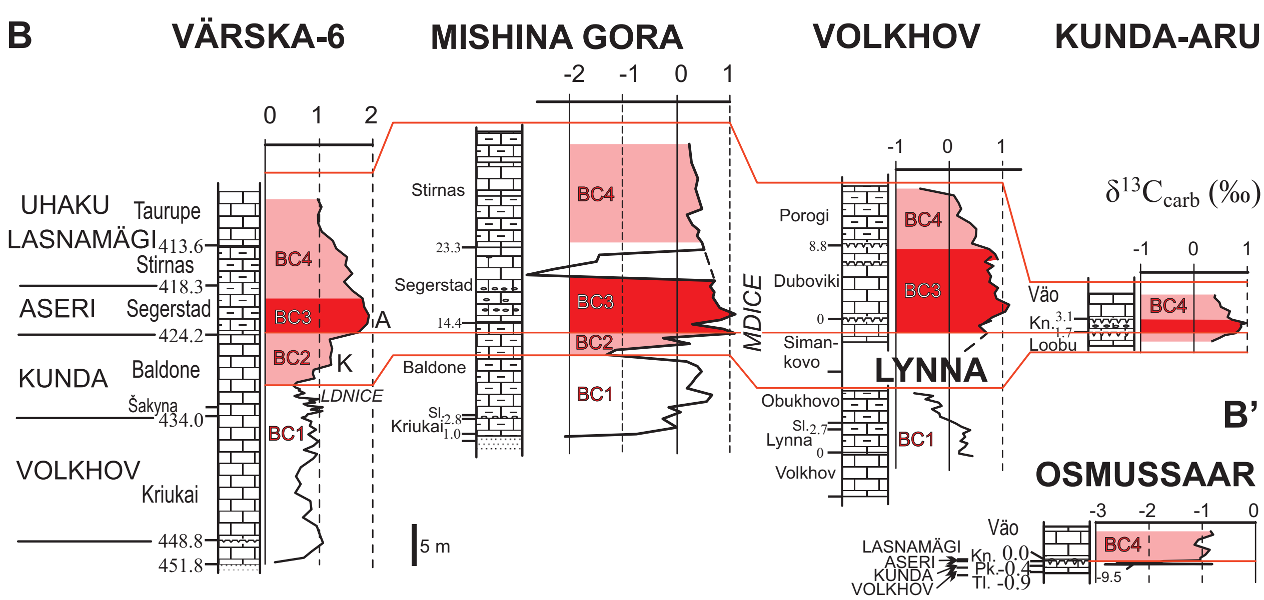

Fig. 4. Chemostratigraphic correlation of sections along profile B–B’. Sl., Sillaoru; Kn., Kandle; Pk., Pakri; Tl., Toila. For location of the profile see Fig. 1, for legend Fig. 3.

The MDICE-A peak is positioned in all studied sections of the Scandinavian Basin (distal ramp/basinal facies) in the Segerstad Formation. Still, the peak has been described higher than the Segerstad Formation in some earlier studies, e.g. in the Skarlöv Formation (Tingskullen, Wu et al. 2017; Kargärde, Ainsaar et al. 2010) or Stirnas Formation (Mehikoorma, Ainsaar et al. 2010). This confirms the diachronous character of these Ordovician local stratigraphic units, defined mainly by rock colour (e.g., reddish-brown limestone of the Segerstad Formation defined by Jaanusson & Mutvei 1953 and later also introduced in the Baltic states – see Männil & Meidla 1994). The MDICE-A peak interval of the curves has been described by Lehnert et al. (2014) as separate MDICE peaks 2 and 3 in several sections of Sweden. However, these peaks cannot be followed in other parts of Baltoscandia and can be regarded here as parts of the main MDICE-A peak.

The Darriwilian sections representing the middle and inner ramp facies (the Estonian Shelf) of Baltoscandian Palaeobasin can be correlated by carbon isotope chemostratigraphy with the sections from the deeper marine facies, but not always without additional biostratigraphic control (Ainsaar et al. 2010). The MDICE-A peak and curve lows below and above the MDICE can be better recognized in the easternmost sections (Kunda-Aru, Volkhov River) than in NW Estonia (Osmussaar; Fig. 4), although the $\delta^{13}C$ values and amplitude of the excursion are significantly lower within the Estonian Shelf than in the sections in the deeper part of the basin (Fig. 3). The northwestern part of Estonia represents the shallowest part of the palaeobasin (Nestor & Einasto 1997) and therefore the relatively thin carbonate units there are separated by numerous stratigraphic gaps, making the isotopic curves discontinuous and the true peaks more difficult to observe. The $\delta^{13}C$ values in some parts of the outcrop sections are also obviously diagenetically depleted, from –2‰ to –3‰ (Osmussaar, Mishina Gora; Fig. 4), which complicates the chemostratigraphic correlation. Anomalously negative $\delta^{13}C$ values in the Segerstad Formation of the Mishina Gora section (Fig. 4) may be related to occasional recrystallization of fractured carbonate rocks followed by the dislocation and deformation of all the sedimentary strata in this Late Palaeozoic circular structure area (Dronov 2004; Komatsu et al. 2019). The MDICE-K peak cannot be distinguished in the sections within the shallower part of the shelf.

FACIES DIFFERENCES IN THE STABLE CARBON ISOTOPIC COMPOSITION

The Baltoscandian isotopic data show clear differences in Darriwilian–Sandbian $\delta^{13}C$ values between the major facies zones, defined by lithological and faunal differences (Jaanusson 1976; Nestor & Einasto 1997). The MDICE pre-excursion, peak/plateau and post-excursion $\delta^{13}C$ values in the Estonian Shelf facies (e.g., in Kunda-Aru, Volkhov; Fig. 4) are all 0.5–1‰ lower and in northwestern Estonia (Osmussaar) even 1.5–2‰ lower than in the sections from deeper in the Scandinavian Basin. A similar depletion trend in $\delta^{13}C_{carb}$ values towards the shallower facies has been described in the Baltoscandian Basin by Saltzman & Edwards (2017) and Lindskog et al. (2019). The aquafacies differences reflected in $\delta^{13}C$ carbonate bulk-rock values in Ordovician carbonate basins have also been recorded in previous studies from North America (Holmden et al. 1998; Panchuk et al. 2006; Saltzman & Edwards 2017).

Several processes related to sedimentary facies differences might explain this phenomenon. Sections in the proximal nearshore parts of the palaeobasin are obviously stratigraphically incomplete, because of gaps caused by sea-level fluctuations and condensed deposition due to limited accommodation space. These gaps may cut off some of the intervals of peak isotopic values. This may partly be the case in the Osmussaar section where the gaps are more significant, but the respective beds with the MDICE-A interval (the Aseri Regional Stage and *E. suecicus* conodont Biozone; e.g., Viira et al. 2001) are apparently present within the rest of the Estonian Shelf.

The depletion of carbonates in ^{13}C in the sections is a common phenomenon close to the hardground surfaces and is commonly linked to subaerial exposure events (incl. meteoric diagenesis) or bacterially-mediated early subsurface cementation (e.g., Dickson et al. 2008). The Darriwilian sections of the shallowest part of the Baltoscandian Basin (e.g., Osmussaar) contain numerous well-developed pyritized hardgrounds and generally lower $\delta^{13}C$ values of carbonates in this area could be explained by discontinuous sedimentation. Indeed, there are some samples with $\delta^{13}C$ values of –2‰ to –3‰ close to the hardground surfaces in the Osmussaar section. However, the other moderately depleted (–1‰ to +1‰) parts of the carbonate succession in the shallow-marine facies areas (Osmussaar, Kunda-Aru, Volkhov) show no direct relationship between lowered $\delta^{13}C$ values and hardground surfaces in the sections, but the whole $\delta^{13}C$ curves are slightly shifted towards negative values instead, depending on their position in the facies profile. The most probable explanation for these facies-dependent nearshore depletion trends could be an influence of local input of isotopically light carbon from various sources to the shallow restricted platform, due to the oxidation of organic matter in land or in water (Saltzman & Edwards 2017; Lindskog et al. 2019).

ORIGIN OF THE MDICE

The MDICE differs from the other Lower Palaeozoic global carbon isotopic excursions in several features. Firstly, based on the biostratigraphic correlations (e.g., Ainsaar et al. 2010) and the latest volcanogenic zircon datings (Lindskog et al. 2017), the time-equivalent of the excursion is altogether up to 10 million years, i.e. 3–5 times longer than the SPICE, GICE, HICE, Ireviken and other prominent carbon isotopic excursions. Secondly, with 2‰ relative $\delta^{13}C$ change it represents a much smaller positive excursion than other global isotopic events. Thirdly, the MDICE covers several sedimentary sequences in Baltoscandia and shows no obvious correlation with short-term global sea-level fluctuations (Ainsaar et al. 2007).

Several authors (Rasmussen et al. 2016; Wu et al. 2017) have pointed at the causal link between the MDICE event and the global biodiversity rise of marine benthic fauna (the Great Ordovician Biodiversification Event – GOBE, Webby et al. 2004). The GOBE has been attributed to the global cooling (Trotter et al. 2008) and the MDICE has been suggested to be related to the increased primary productivity associated with this environmental event (Rasmussen et al. 2016; Wu et al. 2017). According to Schmitz et al. (2008, 2019), the mid-Ordovician (Darriwilian) cooling or glaciation together with sea-level fall was initiated by extraordinary L-chondritic cosmic fall and dust. Recently, on the basis of the nitrogen isotopic data from the Sino-Korean Block, Bang & Lee (2020) suggested that the global MDICE event may be an environmental response to changing seawater circulation associated with global sea-level rise in the Middle Ordovician.

The interval of the cosmic dust and meteorite fall event occurs in Baltoscandia at or close to the Täljsten Bed in the lower part of the Holen Limestone, which is correlated with the Šakyna Formation in East Baltic sections. These units are biostratigraphically positioned near the boundary of the *L. variabilis* and *Y. crassus* conodont biozones (Eriksson et al. 2012; Schmitz et al. 2019). The precise correlation of the base of the MDICE (the LDNICE) shows that this stratigraphic level is clearly situated 2–5 m higher than the Täljsten–Šakyna interval in the deeper part of the Baltoscandian Palaeobasin (Figs 2, 3). Therefore, considering the slow deposition rates of the Darriwilian carbonates in Baltoscandia (Lindskog et al. 2017), the MDICE isotopic excursion began up to one million years later than the extraterrestrial dust flow, the suggested Darriwilian glacial event and the GOBE. It could principally be possible that the isotopic composition of seawater dissolved inorganic carbon in the shelf seas responded to the perturbation of the global ocean–atmosphere system with some delay and there is a causal relationship between the MDICE and the triggers of the GOBE (Rasmussen et al. 2016). Still, the modelling of the MDICE as an unusually long-lasting isotopic event should address more complex scenarios than a simple delayed response of the carbon cycle to rapid climatic perturbations and additional multiproxy geochemical, sedimentological and palaeontological evidence should also be considered.

CONCLUSIONS

The global Middle Darriwilian Isotopic Carbon Excursion (MDICE) can be defined as an interval of raised $\delta^{13}C$ values between the Lower Darriwilian Negative Isotopic Carbon Excursion (LDNICE) and Lower Sandbian Negative Isotopic Carbon Excursion (LSNICE). Two distinct peaks can be distinguished in sections all over the Baltoscandian Basin: the main peak MDICE-A (Aseri) and the preceeding MDICE-K (Kunda) peak. With the duration of ~10 million years the MDICE is one of the longest carbon isotopic events in the Palaeozoic. This event was preceded by the L-chondritic cosmic dust flow, which might be responsible for global Darriwilian cooling and the initiation of the Great Ordovician Biodiversification Event (GOBE). However, the time interval between these environmental events and the base of the MDICE is up to one million years. Therefore, the modelling of the long-lasting MDICE isotopic change should address more complex scenarios than a simple response of the carbon cycle to rapid climatic perturbations.

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Supplementary online data

Supplementary material can be found in the table at https://doi.org/10.23679/502. It contains bulk rock $\delta^{13}C$ and $\delta^{18}O$ data from Darriwilian carbonates of Baltoscandia.

REFERENCES

Ainsaar, L. & Meidla, T. 2016. Middle Darriwilian Isotopic Carbon Excursion (MDICE) in Baltoscandia as response for global changes. In *International Geoscience Programme Project 591 – Closing Meeting, The Early to Middle Paleozoic Revolution, Ghent University, Belgium, 6–9 July 2016. Abstracts* (Gurdebeke, P., De Weirdt, J., Vandenbroucke, T. R. A. & Cramer, B. D., eds), p. 20. Ghent University, Ghent.

Ainsaar, L., Meidla, T. & Tinn, O. 2004. Middle and Upper Ordovician stable isotope stratigraphy across the facies belts in the East Baltic. In *WOGOGOB-2004 Conference Materials* (Hints, O. & Ainsaar, L., eds), pp. 11–12. Tartu University Press, Tartu.

Ainsaar, L., Meidla, T., Tinn, O., Martma, T. & Dronov, A. 2007. Darriwilian (Middle Ordovician) carbon isotope stratigraphy in Baltoscandia. *Acta Palaeontologica Sinica*, **46 (Suppl.)**, 1–8.

Ainsaar, L., Kaljo, D., Martma, T., Meidla, T., Männik, P., Nõlvak, J. & Tinn, O. 2010. Middle and Upper Ordovician carbon isotope chemostratigraphy in Baltoscandia: A correlation standard and clues to environmental history. *Palaeogeography, Palaeoclimatology, Palaeoecology*, **294**, 189–201.

Ainsaar, L., Männik, P., Dronov, A. V., Izokh, O. P., Meidla, T. & Tinn, O. 2015. Carbon isotope chemostratigraphy and conodonts of the Middle–Upper Ordovician succession in the Tungus Basin, Siberian Craton. *Palaeoworld*, **24**, 123–135.

Albanesi, G. L., Bergström, S. M., Schmitz, B., Serra, F., Feltes, N. A., Voldman, G. G. & Ortega, G. 2013. Darriwilian (Middle Ordovician) $\delta^{13}C_{carb}$ chemostratigraphy in the Precordillera of Argentina: Documentation of the middle Darriwilian Isotope Carbon Excursion (MDICE) and its use for intercontinental correlation. *Palaeogeography, Palaeoclimatology, Palaeoecology*, **389**, 48–63.

Bang, S. & Lee, Y. I. 2020. Darriwilian carbon isotope stratigraphy in the Taebaeksan Basin, Korea and its implications for Middle Ordovician paleoceanography. *Palaeogeography, Palaeoclimatology, Palaeoecology*, **541**, 109534.

Bauert, H., Ainsaar, L., Põldsaar, K. & Sepp, S. 2014. $\delta^{13}C$ chemostratigraphy of the Middle and Upper Ordovician succession in the Tartu-453 drillcore, southern Estonia, and the significance of the HICE. *Estonian Journal of Earth Sciences*, **63**, 195–200.

Bergström, S. M., Schmitz, B., Liu, H. P., Terfelt, F. & McKay, R. M. 2018. High-resolution $\delta^{13}C_{org}$ chemostratigraphy links the Decorah impact structure and Winneshiek Konservat-Lagerstätte to the Darriwilian (Middle Ordovician) global peak influx of meteorites. *Lethaia*, **51**, 504–512.

Dickson, J. A. D., Wood, R. A., Bu Al Rougha, H. & Shebl, H. 2008. Sulphate reduction associated with hardgrounds: Lithification afterburn! *Sedimentary Geology*, **205**, 34–39.

Dronov, A. V. 2004. Razrez ordovikskikh otlozhenii Mishinogorskogo kar´yera [A section of Ordovician deposits of the Mishina Gora quarry]. In *Ordovikskoe Plato. K 100-letiyu so dnya rozhdeniya B. P. Asatkina* [*Ordovician Plateau. On the 100 Years Anniversary of B. P. Asatkin*] (Dronov, A. V., ed.), pp. 68–85. Voentechinizdat, Moscow [in Russian].

Dronov, A. 2005. Ordovician of St. Petersburg Region. In *Cambrian and Ordovician of St. Petersburg Region. 6th Baltic Stratigraphical Conference, August 23–25, 2005, Guidebook of the Pre-conference Field Trip* (Dronov, A., Tolmacheva, T., Raevskaya, E. & Nestell, M., eds), pp. 5–9. Baltic Stratigraphic Association, St. Petersburg.

Dronov, A. & Rozhnov, S. 2007. Climatic changes in the Baltoscandian basin during the Ordovician: sedimentological and palaeontological aspects. *Acta Palaeontologica Sinica*, **46 (Suppl.)**, 108–113.

Dronov, A. V., Ainsaar, L., Kaljo, D., Meidla, T., Saadre, T. & Einasto, R. 2011. Ordovician of Baltoscandia: facies, sequences and sea-level changes. In *Ordovician of the World* (Gutierrez-Marco, J. C., Rabano, I. & Garcia-Bellido, D., eds), pp. 143–150. Instituto Geologico y Minero de España, Madrid.

Eriksson, M. E., Lindskog, A., Calner, M., Mellgren, J. I. S, Bergström, S. M., Terfelt, F. & Schmitz, B. 2012. Biotic dynamics and carbonate microfacies of the conspicuous Darriwilian (Middle Ordovician) 'Täljsten' interval, south-central Sweden. *Palaeogeography, Palaeoclimatology, Palaeoecology*, **367–368**, 89–103.

Harris, M. T., Sheehan, P. M., Ainsaar, L., Hints, L., Männik, P., Nõlvak, J. & Rubel, M. 2004. Upper Ordovician sequences of western Estonia. *Palaeogeography, Palaeoclimatology, Palaeoecology*, **210**, 135–148.

Holmden, C., Creaser, R. A., Muehlenbachs, K., Leslie, S. A. & Bergström, S. M. 1998. Isotopic evidence for geochemical decoupling between ancient epeiric seas and bordering oceans: Implications for secular curves. *Geology*, **26**, 567–570.

Jaanusson, V. 1976. Faunal dynamics in the Middle Ordovician (Viruan) of Balto-Scandia. In *The Ordovician System: Proceedings of a Palaeontological Association Symposium, Birmingham, September 1974* (Bassett, M. G., ed.), pp. 301–326. University of Wales Press, Cardiff.

Jaanusson, V. & Mutvei, H. 1953. Stratigraphie und Lithologie der unterordovizischen *Platyurus*-Stufe im Siljan Gebiet, Dalarna. *Bulletin of the Geological Institute of Uppsala*, **35**, 7–34.

Kaljo, D., Martma, T. & Saadre, T. 2007. Post-Hunnebergian Ordovician carbon isotope trend in Baltoscandia, its environmental implications and some similarities with that of Nevada. *Palaeogeography, Palaeoclimatology, Palaeoecology*, **245**, 138–155.

Komatsu, G., Coletta, A., Battagliere, M. & Virelli, M. 2019. Mishina Gora, Russia. In *Encyclopedic Atlas of Terrestrial Impact Craters* (Flamini, E., Di Martino, M. & Coletta, A., eds), pp. 183–184. Springer, Cham.

Lehnert, O., Meinhold, G., Wu, R. C., Calner, M. & Joachimski, M. M. 2014. $\delta^{13}C$ chemostratigraphy in the upper Tremadocian through lower Katian (Ordovician) carbonate succession of the Siljan district, central Sweden. *Estonian Journal of Earth Sciences*, **63**, 277–286.

Leslie, S. A., Saltzman, M. R., Bergström, S. M., Repetski, J. E., Howard, A. & Seward, A. M. 2011. Conodont biostratigraphy and stable isotope stratigraphy across the Ordovician Knox/Beekmantown unconformity in the Central Appalachians. In *Ordovician of the World* (Gutierrez-Marco, J. C., Rabano, I. & Garcia-Bellido, D., eds), pp. 301–308. Instituto Geologico y Minero de España, Madrid.

Lindskog, A., Costa, M. M., Rasmussen, C. M. Ø., Connelly, J. N. & Eriksson, M. E. 2017. Refined Ordovician timescale reveals no link between asteroid breakup and biodiversification. *Nature Communications*, **8**, 14066.

Lindskog, A., Eriksson, M. E., Bergström, S. M. & Young, S. A. 2019. Lower–Middle Ordovician carbon and oxygen isotope chemostratigraphy at Hällekis, Sweden: implications for regional to global correlation and paleoenvironmental development. *Lethaia*, **52**, 204–219.

Männil, R. & Meidla, T. 1994. The Ordovician System of the East European Platform (Estonia, Latvia, Lithuania, Byelorussia, parts of Russia, Ukraine and Moldova). In *The Ordovician System of the East European Platform and Tuva (Southeastern Russia): Correlation Charts and Explanatory Notes* (Webby, B. D., Ross, R. J. & Zhen, Y. Y., eds), *IUGS Publication*, **28**, 1–52.

Meidla, T., Ainsaar, L. & Hints, O. 2014. The Ordovician System in Estonia. In *4th Annual Meeting of IGCP 591, Estonia, 10–19 June 2014. Abstracts and Field Guide* (Bauert, H., Hints, O., Meidla, T. & Männik, P., eds), pp. 116–122. Tartu.

Munnecke, A., Zhang, Y., Liu, X. & Cheng, J. 2011. Stable carbon isotope stratigraphy in the Ordovician of South China. *Palaeogeography, Palaeoclimatology, Palaeoecology*, **307**, 17–43.

Nestor, H. & Einasto, R. 1997. Ordovician and Silurian carbonate sedimentation basin. In *Geology and Mineral Resources of Estonia* (Raukas, A. & Teedumäe, A., eds), pp. 192–204. Estonian Academy Publishers, Tallinn.

Nõlvak, J. & Grahn, Y. 1993. Ordovician chitinozoan zones of Baltoscandia. *Review on Palaeobotany and Palynology*, **79**, 245–269.

Panchuk, K. M., Holmden, C. E. & Leslie, S. A. 2006. Local controls on carbon cycling in the Ordovician midcontinent region of North America, with implications for carbon isotope secular curves. *Journal of Sedimentary Research*, **76**, 200–211.

Rasmussen, C. M. Ø., Ullmann, C. V., Jakobsen, K. G., Lindskog, A., Hansen, J., Hansen, T., Eriksson, M. E., Dronov, A., Frei, R., Korte, C., Nielsen, A. T. & Harper, D. A. T. 2016. Onset of main Phanerozoic marine radiation sparked by emerging Mid Ordovician icehouse. *Scientific Reports*, **6**, 18884.

Saltzman, M. R. & Edwards, C. T. 2017. Gradients in the carbon isotopic composition of Ordovician shallow water carbonates: A potential pitfall in estimates of ancient CO_2 and O_2. *Earth and Planetary Science Letters*, **464**, 46–54.

Schmitz, B., Harper, D. A. T., Peucker-Ehrenbrink, B., Stouge, S., Alwmark, C., Cronholm, A., Bergström, S. M., Tassinari, M. & Xiaofeng, W. F. 2008. Asteroid breakup linked to the Great Ordovician Biodiversification Event. *Nature Geoscience*, **1**, 49–53.

Schmitz, B., Bergström, S. M. & Wang, X. F. 2010. The middle Darriwilian (Ordovician) $\delta^{13}C$ excursion (MDICE) discovered in the Yangtze Platform succession in China: implications of its first recorded occurrences outside Baltoscandia. *Journal of the Geological Society*, **167**, 249–259.

Schmitz, B., Farley, K. A., Goderis, S., Heck, P. R., Bergström, S. M., Boschi, S., Claeys, P., Debaille, V., Dronov, A., van Ginneken, M., Harper, D. A. T, Iqbal, F., Friberg, J., Liao, S., Martin, E., Meier, M. M. M., Peucker-Ehrenbrink, B., Soens, B., Wieler, R. & Terfelt, F. 2019. An extraterrestrial trigger for the mid-Ordovician ice age: Dust from the breakup of the L-chondrite parent body. *Science Advances*, **5**, eaax4184.

Trotter, J. A., Williams, I. S., Barnes, C. R., Lecuyer, C. & Nicoll, R. S. 2008. Did cooling oceans trigger Ordovician biodiversification? Evidence from conodont thermometry. *Science*, **321**, 550–554.

Viira, V. & Männik, P. 1997. Conodonts. In *Geology and Mineral Resources of Estonia* (Raukas, A. & Teedumäe, A., eds), pp. 241–244. Estonian Academy Publishers, Tallinn.

Viira, V., Löfgren, A., Mägi, S. & Wickström, J. 2001. An Early to Middle Ordovician succession of conodont faunas at Mäekalda, northern Estonia. *Geological Magazine*, **138**, 699–718.

Webby, B. D., Paris, F., Droser, M. L. & Percival, I. G. (eds). 2004. *The Great Ordovician Biodiversification Event*. Columbia University Press, New York, 484 pp.

Wu, R., Calner, M., Lehnert, O., Peterffy, O. & Joachimski, M. M. 2015. Lower–Middle Ordovician $\delta^{13}C$ chemostratigraphy of western Baltica (Jämtland, Sweden). *Palaeoworld*, **24**, 110–122.

Wu, R., Calner, M. & Lehnert, O. 2017. Integrated conodont biostratigraphy and carbon isotope chemostratigraphy in the Lower–Middle Ordovician of southern Sweden reveals a complete record of the MDICE. *Geological Magazine*, **154**, 334–353.

Zhang, Y. & Munnecke, A. 2016. Ordovician stable carbon isotope stratigraphy in the Tarim Basin, NW China. *Palaeogeography, Palaeoclimatology, Palaeoecology*, **458**, 154–175.

Kesk-Darriwili süsiniku isotoopekskursiooni (MDICE) stratigraafia ja fatsiaalne muutlikkus Baltoskandias

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Kesk-Darriwili süsiniku isotoopekskursioon (MDICE) on globaalne isotoopsündmus, mida on kirjeldatud mitme erineva paleokontinendi läbilõigetes. Artiklis on kirjeldatud süsiniku isotoopkoostise muutusi kümnes Kesk-Ordoviitsiumi läbilõikes Baltoskandia paleobasseini eri piirkondadest (Eesti, Läti, Leedu, Rootsi, Loode-Venemaa). On täpsustatud MDICE isotoopsündmuse definitsiooni ja selle alamjaotust erinevateks isotoopkõvera tippudeks. MDICE on üks kestuselt pikemaajalisi globaalseid süsiniku isotoopkoostise muutusi Paleosoikumis. Sellele eelnes L-kondriitse kosmilise tolmuvoolu sündmus, mida on peetud nii Darriwili-aegse kliima jahenemise kui ka globaalse merelise elurikkuse tõususündmuse (GOBE) põhjustajaks. Läbilõigete kõrge resolutsiooniga kemostratigraafiline analüüs näitab, et eelnimetatud keskkonnasündmuste ja MDICE alguse vahele jääb umbes ühe miljoni aastane ajalõik. Erakordselt pikaajalise kestuse ja eelmainitud ajalise distantsi tõttu tuleks MDICE põhjuste modelleerimisel kasutada komplekssemaid stsenaariume kui isotoopkoostise muutuse lihtne vastus kiiretele kliimamuutustele.