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# Baltoscandian Middle Ordovician brachiopod oxygen stable isotope trends: implications for palaeotemperature changes

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**Abstract.** Over the last two decades, there has been an intensive research effort focused on studying the climate fluctuations during the Ordovician period. In this study, we provide brachiopod and bulk carbonate rock stable isotopic data for oxygen (O) and carbon (C) from the Middle Ordovician succession from northern Estonia for evaluating the Middle Ordovician palaeotemperature and palaeoenvironmental history. We present $\delta^{18}O$ curves from eight northern Estonian outcrops. This new data, together with the published results, enable compiling the first complete stable oxygen isotopic curve for Middle Ordovician to early Silurian for the eastern Baltoscandian Palaeobasin. Combining the published and new $\delta^{13}C_{brac}$ and $\delta^{18}O_{brac}$ data allows us to address chemostratigraphic correlation in the Middle Ordovician. The Baltoscandian $\delta^{18}O$ data generally confirm a cooling trend from Early to Middle Ordovician documented by previous studies in different palaeobasins.

***Keywords***: *$\delta^{13}C$ and $\delta^{18}O$ chemostratigraphy; palaeotemperature; Ordovician; Baltoscandia*

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## INTRODUCTION

For a long time, the Ordovician Period was thought to be characterised predominantly by warm greenhouse climate. Over the past few decades, the Ordovician System has been in the focus of intensive palaeoenvironmental, palaeontological, and stratigraphical studies. The complexity of the environmental and faunal changes during this period is better understood today (Bergström *et al*. 2010; Goldberg *et al*. 2021). It is suggested that, during the Middle Ordovician, ocean temperatures reached levels comparable to those in modern equatorial regions (Edward *et al*. 2022). Taking into account both palaeoclimate models and new data from palaeotemperature proxies, it appears that the Ordovician icehouse conditions may have lasted for a considerable time, as supported by studies like those by Saltzman and Young (2005), Rasmussen *et al*. (2016), and Edward *et al*. (2022).

Within this dynamic paleoclimate context, the Ordovician was a period of the peaked global sea level, when vast epeiric seas engulfed much of the palaeocontinents and a remarkable proliferation of marine life, known as the Great Ordovician Biodiversification Event (GOBE), took place. During the GOBE, the marine biota in these shallow-water areas underwent significant changes that resulted in the appearance of a multitude of new species and ecological niches (Edwards, Saltzman 2016). The period was terminated by the first significant mass extinction of the Phanerozoic, known as the Late Ordovician Mass Extinction (LOME), as described by Jablonski (1991). Detailed geochemical investigations using improved palaeotemperature proxies and modelling have produced a much more complex picture of the Ordovician climate, including the recognition of several time periods possibly representing ice ages, although glaciogenic deposits older than the latest Ordovician are yet to be discovered (Trotter *et al*. 2008; Rasmussen *et al*. 2016).

Stable oxygen isotopes of biominerals that are formed in equilibrium with the surrounding water offer valuable insights into environmental parameters of the past, like ocean water temperature, precipitation and seawater chemical composition (Muehlenbachs 1998). The temperature estimates rely on the temperature-dependent fractionation equilibrium between seawater and anions ($CO_3^{2-}$) that become integrated into minerals (Grossmann, Joachimski 2020). While stable carbon isotopic curves from bioclastic material generally reflect changes in marine carbon influx, the primary data's source material is less influenced by temperature (Epstein *et al*. 1951; Brenchley *et al*. 1994; Shields *et al*. 2003). At the same time, oxygen isotope paleothermometry based on bulk carbonate and calcareous bioclasts (e.g., brachiopod shells) faces challenges due to uncertainties regarding the stable oxygen isotope composition of ambient seawater and the diagenetic changes that may have affected fossils (Grossman 2012). Although the $\delta^{18}O$ values obtained from low-Mg calcite are dependent on palaeotemperature, they can be subjected to alteration. The process of re-equilibration with pore water, even when there is a relatively small degree of exchange with pore fluids in an open system, can influence the results (Banner, Hanson 1990). Nevertheless, it is possible to obtain a high-resolution $\delta^{18}O$ trend from brachiopods, which are considered an excellent group for stable isotopic studies of the Palaeozoic because their low-Mg calcite shells are thought to be generally more resistant to diagenesis, preserving the primary isotopic signals better than high-Mg calcite shells do (Shields *et al*. 2003; Azmy *et al*. 1998).

The Baltoscandian Palaeobasin is characterised by a good preservation of the Palaeozoic sediments, due to a limited post-depositional tectonic activity and insignificant thermal alteration of the rocks. Consequently, it serves as a crucial area for the global Ordovician stable isotope chemostratigraphic studies (Ainsaar *et al*. 2010).

The current study presents new oxygen and carbon isotope data based on brachiopod and bulk carbonate samples from the Middle Ordovician of northern Estonia (Fig. 1). Particularly in the context of the mid-Ordovician oxygen isotope trend, this interval has been somewhat neglected, probably due to remarkable perturbations in the $\delta^{18}O$ record during the Ordovician (Shields *et al*. 2003; Veizer, Prokoph 2015; Fig. 3). The objective of the present study was to analyze the Middle Ordovician oxygen and carbon stable isotopic records in the regional type area of the eastern Baltic Ordovician succession (northern Estonia) and complement the palaeotemperature records from the Baltoscandian region. This area has been extensively studied in terms of biostratigraphy, sedimentology, and event stratigraphy and is serving as one of the world key areas for the Ordovician studies. This abundant geological data allows comprehensive contextualisation of the isotope data within the regional palaeoenvironmental record.

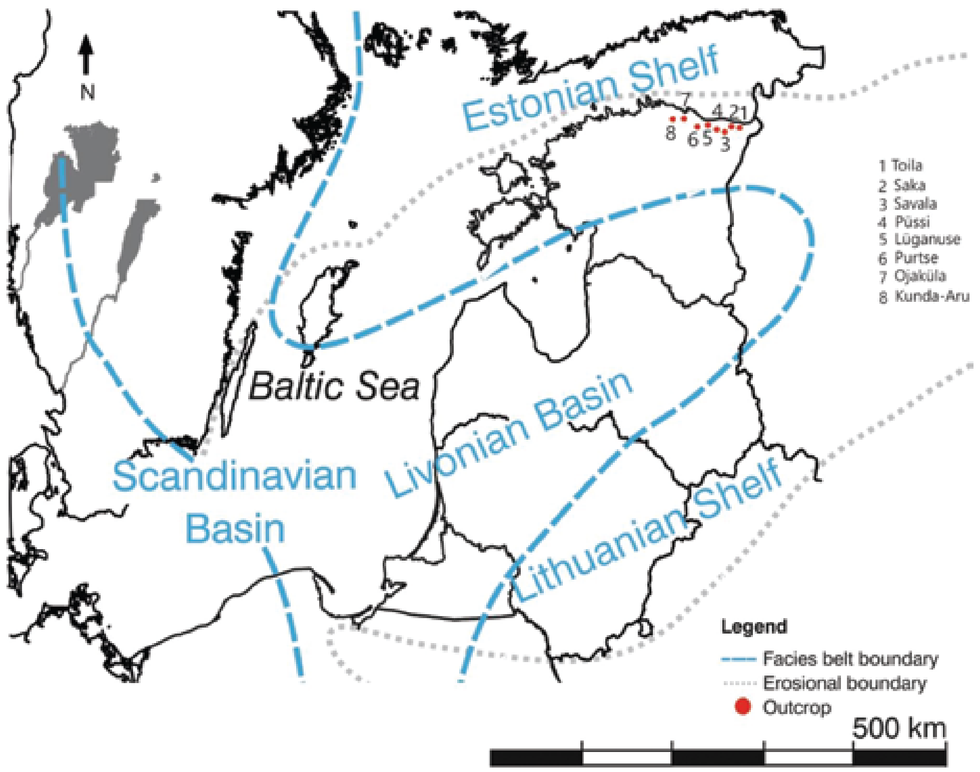


**Fig. 1** The geological map of Estonia (modified from Harris et al. 2004) and locations of outcrops



## MATERIALS AND METHODS

A total of 50 brachiopod and 30 bulk rock samples were collected for this study from eight outcrops in north-eastern Estonia (Fig. 2), spanning across the Middle Ordovician (Dapingian to Sandbian, the Volkhov to Kukruse regional stages (RS)) (Fig. 3). Samples were not collected bed by bed for stable isotopic analysis. In the stratigraphic order, the Toila section (Lat. 59.429603, Long. 27.490083), where the Volkhov is represented by the Toila Formation (Fm), is composed of glauconite-rich limestone. The Saka section (Lat. 59.441158, Long. 27.215056) (Kunda and Aseri RS) spans approximately 9 meters of dolomitized oolitic and glauconitic limestones of the Sillaoru, Loobu, and Kandle Fms that are notable for their abundant cephalopods, trilobites, brachiopods and other shelly faunas. The Loobu and Kandle formations are also visible in the Purtse outcrop (Lat. 59.411389, Long. 27.002222), and the oolitic limestones of the Kandle Fm are also well exposed in the Ojaküla outcrop (Lat. 59.478447, Long. 26.481289) located about 4 km southwest of Kunda, west of the highway, in the Ojaküla village. The Kunda-Aru quarry located east of Haljala-Kunda highway, approximately 5 km south of Kunda (Lat. 59.444063, Long. 26.479414), consists of the Väo Formation, light grey pure massive limestone. The Püssi quarry (Lat. 59.360278, Long. 27.049167) consists of alternating limestones of argillaceous limestone of the Kõrgekallas Fm (Uhaku RS). The Lüganuse quarry (Lat. 59.387525, Long. 59.387525) also consists of the Kõrgekallas Fm.

The Savala quarry (Kukruse RS) (Lat. 59.319442, Long. 27.009725) is located where the Viivikonna Fm, argillaceous bioclastic limestone with interbeds of kukersite (oil shale) and marl, crops out.

Brachiopods collected in outcrops were carefully removed from the limestone matrix and cleaned. For stable isotope analyses, brachiopod shell powder was obtained by micro-drilling avoiding cement and rock matrix. The size of the brachiopod fragments was generally too small for identifying the species, genera or even families. The powdered material was analysed for stable isotopes (oxygen and carbon) using a Thermo Scientific Delta V Advance continuous flow isotope ratio mass spectrometer at the Department of Geology, University of Tartu. Delta V advantage (continuous flow) + GasBench II samples were dissolved (reaction time > 8 hours) in $H_3PO_4$ (99%) at 25°C. About 0.5 mg of the powdered samples were used. The results are reported as the δ notation in per mil relative to Peedee belemnite (VPDB) for both oxygen and carbon, and reproducibility of the results is generally better than ±0.1‰ and ±0.2‰ for carbon and oxygen (respectively). The international laboratory standards (from IAEA) IAEA-60, NBS 18, and LSVEC were used. For palaeotemperature estimates, we calculated temperatures from the $\delta^{18}O$brac values using the formula $T°C = 17.3750–4.2535\ (\delta c–\delta w) + 0.1473\ (\delta c–\delta w)^2$, assuming possible preservation of original marine carbonate isotopic composition formed in seawater with $\delta^{18}O$ value – 1‰ (Brand *et al*. 2019).

Trace element concentration measurements were performed with laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) using an Agilent 8800 quadrupole ICP-MS coupled to a Cetac LSX-213 G2+ laser with HelEx II fast-washout two-volume large-format cell and a "Squid" signal smoothing device. Helium (at a combined flow rate of 0.8 l/min) was used as a carrier gas in the laser and was mixed with argon (0.9 l/min) downstream of the cell. Elemental concentrations were calculated from raw spectrometry data using $^{43}Ca$ as an internal standard element, assuming stoichiometric calcite Ca concentration of 40.04%, using Iolite 3.62 software

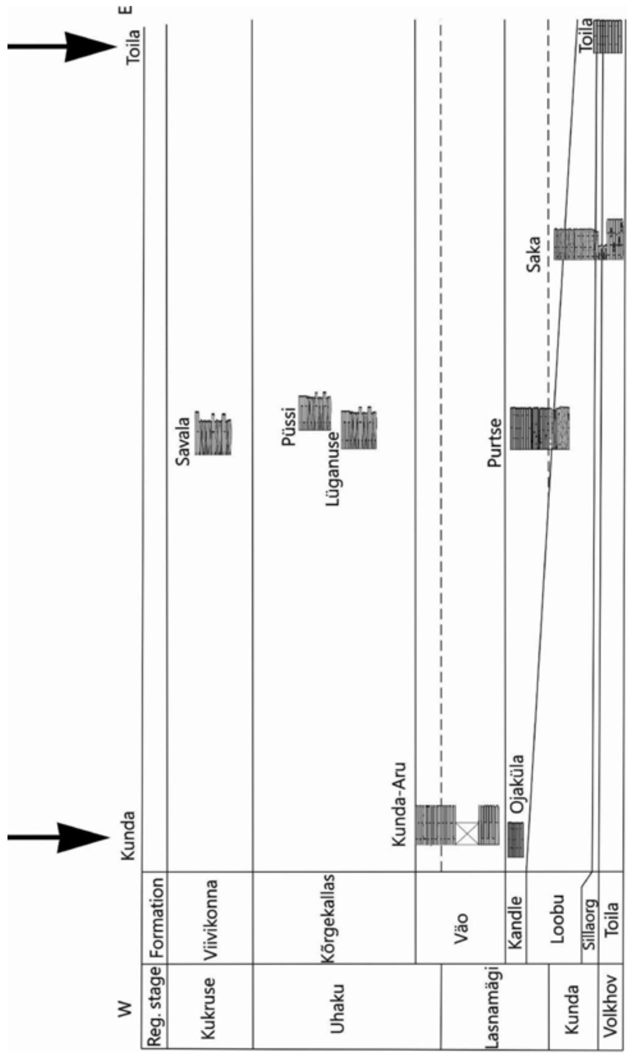

**Fig. 2** Location of the studied sections along the W–E transect and their stratigraphic position

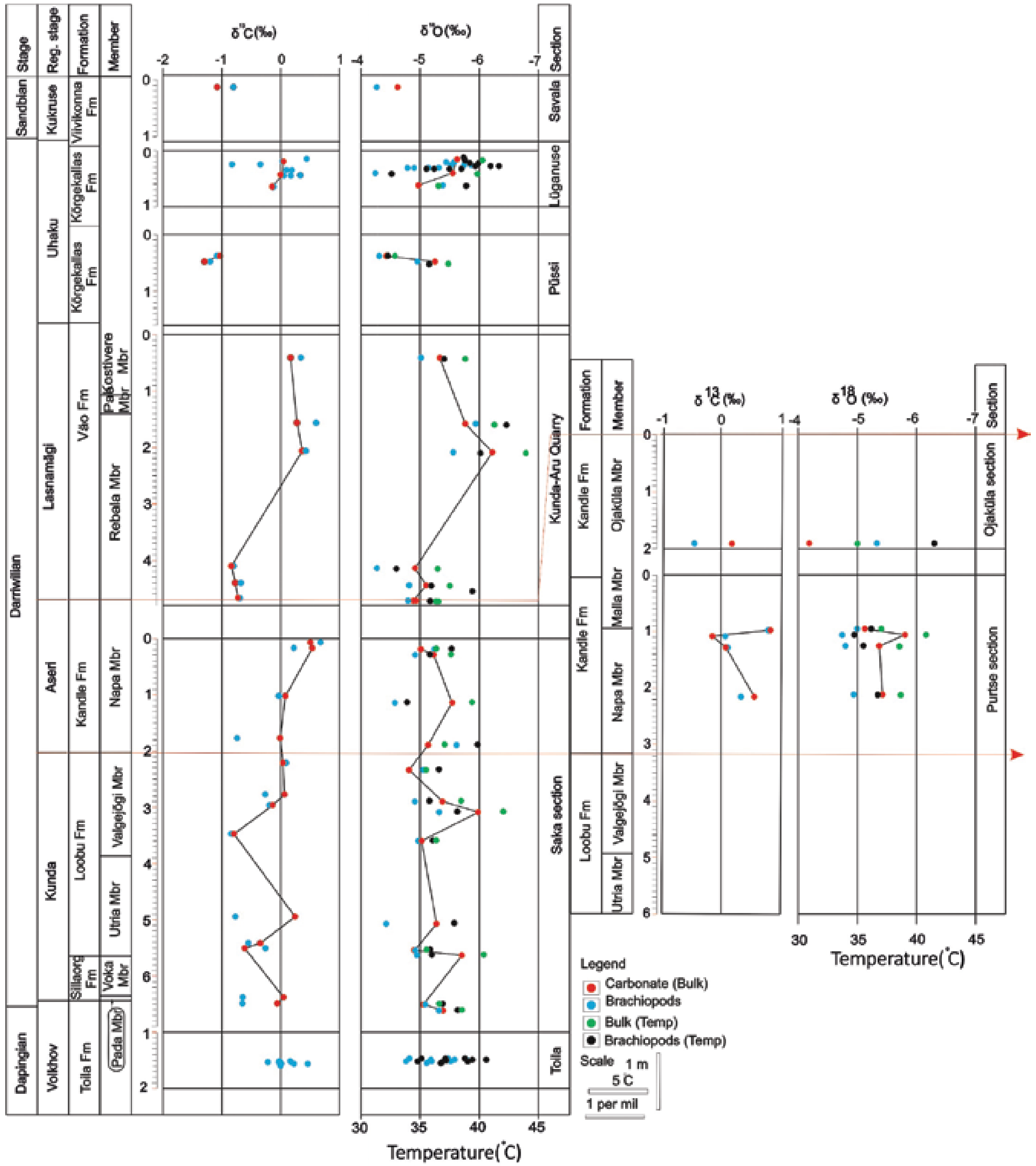


**Fig. 3** Composite figure showing carbon and oxygen isotope (bulk and brachiopods) compositions during middle Ordovician (Dapingian–Sandbian). The temperature is based on oxygen isotope (bulk and brachiopods). Temperatures are calculated from brachiopods data by a formula of Brand *et al*. (2019), assuming a possible preservation of original marine carbonate isotopic composition formed in sea water with $\delta^{18}O$ value –1‰

package and Trace Elements DRS (Paton *et al*. 2011; Woodhead *et al*. 2007). USGS GSD-1G, with reference values from Jochum *et al*. (2011) was used as a primary calibration standard. USGS MACS-3 (synthetic $CaCO_3$) was used as a matrix-matched quality control (QC) standard. During analysis, calibration and QC standards in 3 replicates were ablated after every 9 analytical spots. Before analysis, the ICP-MS setting was tuned on NIST610 to achieve the ThO/Th ratio < 0.25%. The following masses were measured: $^{24}Mg$, $^{27}Al$, $^{29}Si$, $^{31}P$, $^{43}Ca$ with dwell time of 6 ms and $^{55}Mn$, $^{57}Fe$, $^{88}Sr$, $^{89}Y$, $^{137}Ba$, $^{139}La$, $^{140}Ce$, $^{141}Pr$, $^{146}Nd$,



$^{147}Sm$, $^{153}Eu$, $^{157}Gd$, $^{165}Ho$, $^{206}Pb$, $^{238}U$ with dwell time of 6 ms. Laser parameters used for all analyses were as follows: 100 µm round spot, 5 Hz repetition rate, 250 shot count, and fluence of 3.5 J/cm². During ablation, the first 20 s were recorded as gas blank and 10 s were added to the end of ablation for washout.

## RESULTS

### Carbon and oxygen isotopes

The $\delta^{13}C$ values were mostly scattered in the range from 0.5‰ to 1‰. The $\delta^{13}C$ values varied between 0.5‰ to 1‰ in the Toila Fm but showed lower values (< 0‰) in the Loobu Fm followed by a slight increase in the lower part of the Kandle Fm (from -0.9‰ to 0.6‰) in the Saka section (Fig. 3). Slightly higher values (up to 1‰) were also recorded from the Kandle Fm in the Purtse section. A subsequent decrease of values was recorded higher up in the succession, in the Lüganuse, Püssi and Savala section.

A shift towards increase in $\delta^{18}O$ during the middle Ordovician was evident in both bulk and brachiopod values. The $\delta^{18}O$ values in the bulk rock samples from the studied sections ranged from ca –6.5‰ to –4‰ (Fig. 3). Greater deviations from unaltered $\delta^{18}O$ values were recorded in the Saka section. In the Loobu Fm, the values ranged between –6‰ and –5.2‰. with a change towards higher values in the topmost part of the Fm. The $\delta^{18}O$ values show a decrease in the lower part of the Väo Fm. Some of smaller fluctuations of $\delta^{18}O$ values in the studied sections may be related to gaps in the succession that are numerous in most early Middle Ordovician units. In the majority of cases, the isotopic composition of brachiopod shells differed from the $\delta^{18}O$ values of the bulk rock by less than 1‰, whilst brachiopod shells fragments values were usually characterised by a slightly higher stable isotopic ratio in the range between –1.2 and 0.5‰.

### Trace elements and chemical preservation

The carbonate rocks and fossils examined in the earlier studies exhibit excellent preservation across most of the studied localities in Estonia (Azmy *et al*. 1998). This is due to low tectonic activity and limited impact of burial diagenesis in the area (Nestor, Einasto 1997).

The $\delta^{13}C$–$\delta^{18}O$ cross-plot of brachiopod shell material can be used for evaluation of diagenetic changes in carbonate isotopic composition. According to Jacobsen and Kaufman (1999), the relationship between $\delta^{13}C$ and $\delta^{18}O$ values in this plot reveals the extent of meteoric diagenesis. The cross-plot of carbon and oxygen isotopic data of selected samples in our study shows no correlation between the $\delta^{13}C$ and $\delta^{18}O$ values (Lüganuse $R^2$ = 0.1018, Purtse $R^2$ = 0.8225, Kunda-Aru $R^2$ = 0.7724, Toila $R^2$ = 0.0924, Saka $R^2$ = 0.0003, Püssi $R^2$ = 1, see Fig. 4). The values are closely clustered without any extreme negative points on either axis, which suggests that the preservation of the shells is relatively good. In term of correlation, the Püssi section shows a very good preservation ($R^2$ = 1). Nevertheless, it still can't be completely ruled out that some secondary influence may have affected the primary signal from occasional samples.

Brachiopod shells have also been widely used to estimate the extent of diagenetic alteration of rocks, with the strontium (Sr) and manganese (Mn) abun-

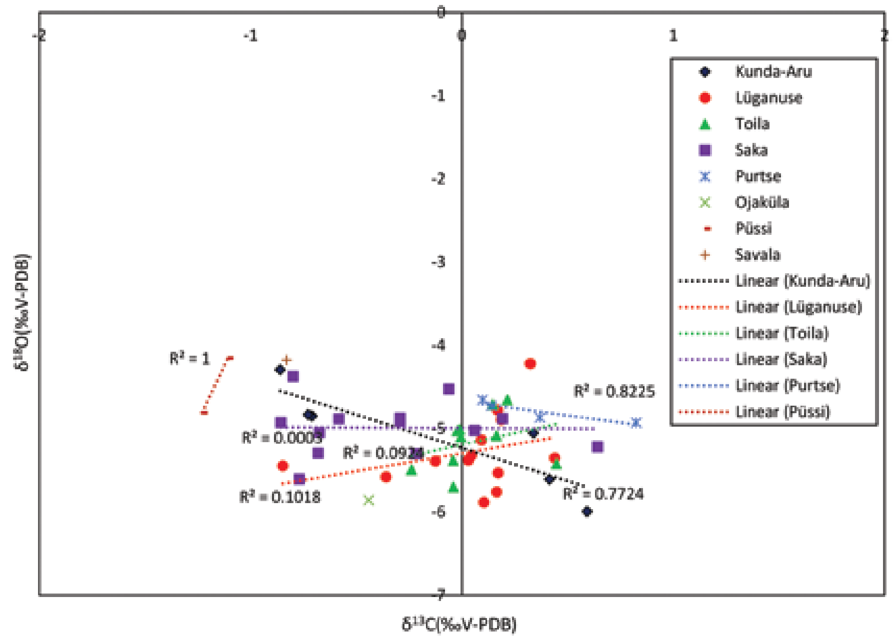


**Fig. 4** Ratio between oxygen *vs*. carbon isotopic composition in the studied stratigraphic units

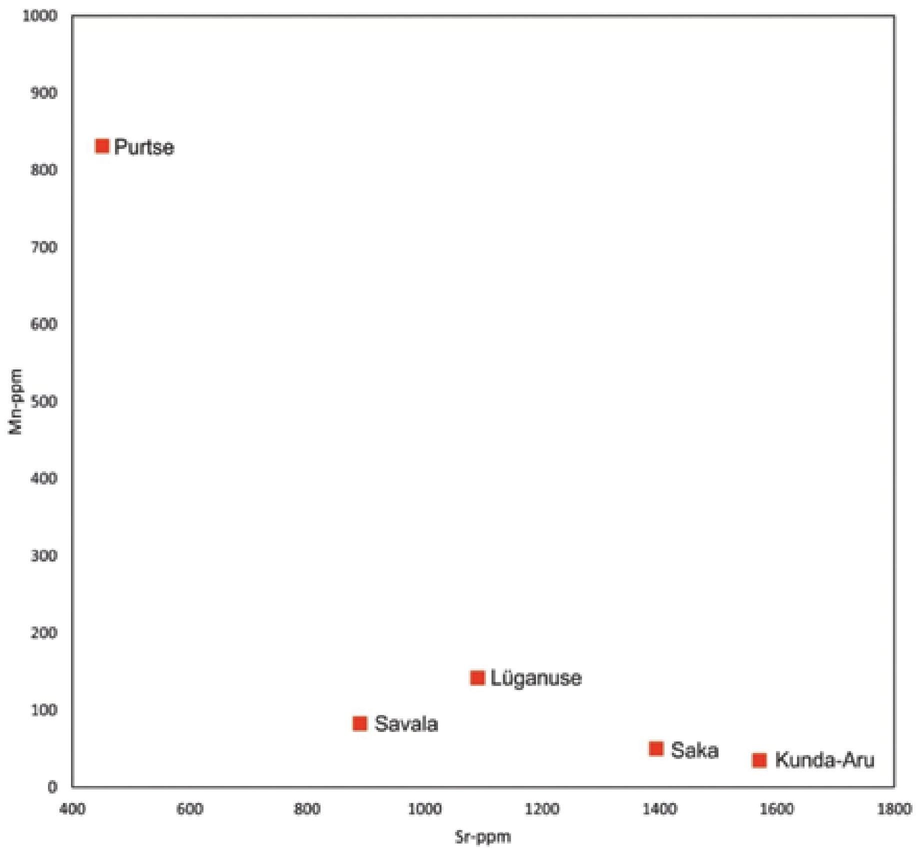


**Fig. 5** Strontium and manganese abundances from the brachiopod shells used in this study

dance ratio serving as a key indicator (Brand, Veizer 1980). A comparison between the trace element contents of Ordovician brachiopods from this study and modern brachiopods (Fig. 5) shows that most of our samples fall within the predicted ranges for unaltered brachiopods, with Sr = 500 to 2000 ppm and Mn = < 200 ppm (Morrison, Brand 1986) except for one brachiopod shell from the Purtse section with the Mn value lying out of the normal range (831 ppm, see Fig. 5). Other values align with the range observed in modern low-Mg calcite shells (Veizer *et al*. 1999, Immenhauser *et al*. 2002), showing the retained values being close to their primary isotopic composition.

## DISCUSSION

Carbonate rocks typically preserve syndepositional carbon isotopic values even during diagenetic recrystallization and low-grade metamorphism (Valley, O'Neil 1984; Hood *et al*. 2018). This information is crucial for reconstructing environmental changes and palaeoclimate records (Brenchley *et al*. 2003). Although our carbon isotope data are not extensive enough for a thorough analysis of the relatively short $\delta^{13}$C excursions during the Ordovician period, they still allow us to identify long-term trends in the data.

Previous studies show that during the Dapingian (Volkhov Age), the $\delta^{13}$C values are sporadically varying in the range of 0.5‰ to 1‰, displaying no distinct trend . In the current study, excursion is not recorded in the sections of the Toila Fm, probably because it is very condensed, as the thickness of the whole Darriwilian reaches about 2 m. The mid-Darriwilian Excursion (MDICE) occurs in the interval of the Kunda, Aseri and Lasnamägi RSs over the whole region (Meidla *et al*. 2004; Ainsaar *et al*. 2007). This phase is characterised by a rise of 1–1.5‰ in $\delta^{13}$C values, and this is specifically evident in sections featuring distal ramp facies. The increase of $\delta^{13}$C values on the assumed level of MDICE is still minor in the studied succession, and this is suggesting a gap which is equivalent to the highest values of MDICE excursion in lower ramp sections, like shown already by Ainsaar *et al*. (2010). Both Argentinian and North American successions typically show distinctly lower $\delta^{13}C_{carb}$ values for the MDICE interval compared to those from Baltoscandia (Lindskog *et al*. 2019), and these differences are likely due to local processes (e.g., organic matter remineralization, sluggish seawater circulation, sediment reworking) that are superimposed upon a global perturbation of the carbon cycle (e.g., Saltzman, Edwards 2017).

The MDICE (Mid-Darriwilian Isotopic Carbon Excursion) exhibits distinct characteristics that set it apart from other global carbon isotopic excursions in the Lower Paleozoic era. It represents a relatively smaller but remarkably long-lasting positive excursion with a $\delta^{13}$C change of 2‰, which is in contrast to the more substantial shifts observed in other global isotopic events. Moreover, the MDICE is present across multiple sedimentary sequences in the Baltoscandia region and doesn't display any apparent correlation with short-term global sea level fluctuations (Ainsaar *et al*. 2007). Several researchers, including Rasmussen *et al.* (2016) and Wu *et al*. (2017), have suggested a potential causal link between the MDICE event and the global rise in biodiversity among marine benthic fauna. 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). In the eastern Baltic sections, the most rapid diversity rise regarded as GOBE seems to be confined to the Volkhov and Kunda regional stages that represent a prologue of the MDICE isotopic event. This diversity rise is followed, somewhat controversially, by the turnover among the shelly faunas, notably bryozoans, trilobites and brachiopods, but also among conodonts. This event at the Kunda-Aseri transition is termed the Öland Turnover and it coincides well with the start of the prolonged MDICE (Meidla *et al*. 2023).

The question of if and to what degree the overall $\delta^{18}$O trends could be interpreted in the context of palaeotemperatures, has no simple and straightforward answer. Secular variation in $\delta^{18}$O may be influenced not only by sea water temperature but also by a multitude of other factors, like the isotopic composition of sea water, salinity, source and composition of mud, vital effects, diagenetic alteration, etc. (Munnecke *et al*. 2010). Some of these factors (e.g. isotopic composition of sea water, smaller changes in salinity, source areas of mud) are difficult to evaluate, whilst trends in some others could be assumed from the analysis of rock properties and facies gradients. Brachiopods are likely the most reliable source of temperature information among calcareous fossils, and the presence of the secondary layer in Baltoscandian brachiopod shells suggests that vital effects are unlikely or minor. The secondary layer is more likely formed in or near isotopic equilibrium with ambient sea water, whilst the primary shell layer is not (Ullmann *et al*. 2017).

In this study, we have calculated the palaeotemperature values using the formula developed by Brand *et al*. (2019). This calculation assumes the potential preservation of the original marine carbonate isotopic composition, which initially formed in seawater with a $\delta^{18}$O value of –1‰. Notably, the results obtained in our study demonstrate a stronger agreement with modern temperatures and appear to be closer to them when compared to values derived from the bulk material in earlier research. It is worth noting that if we were to consider alterations in the seawater $\delta^{18}$O during cooling episodes, even a relatively small change of 1‰ could exert a significant impact, leading to temperature variations of up to 4°C. Consequently, the temperature curve might exhibit slight shifts during certain intervals if the composition of seawater experienced changes over time, such as during glacial episodes.

The overall $\delta^{18}$O trends from earlier studies are similar to the results of the present study, showing an increasing $\delta^{18}$O trend in the Middle Ordovician. Both brachiopod and bulk $\delta^{18}$O values increase throughout the middle Ordovician. In the current study, the $\delta^{18}$O profile values lie mostly between –6.3‰ and –4.29‰ (Fig. 3).

The temperature calculated from brachiopods and bulk material for Dapingian – early Sandbian stages range from ~ 33°C up to 42°C (Fig. 3). Some of these values are clearly too high and seem to be unrealistic but this is a well-known problem (see Grossmann, Joachimski 2020; Trotter *et al*. 2008). The notion of exceedingly high minimum water temperatures is implausible, as protein molecules cannot endure the sustained temperature stress beyond 37°C (Shields *et al*. 2003). According to Trotter *et al*. (2008) the ancient seawater $\delta^{18}$O values may have been notably distinct during this period. Despite the indication that diagenesis might have influenced Darriwilian seawater $\delta^{18}$O values from Baltoscandia, the well-preserved samples are still revealing the near-primary long-time $\delta^{18}$O trends (Edward *et al*. 2022). Considering adjustments for $\delta^{18}$O seawater errors and an analytical range of ±3°C, our maximum temperature of approximately 42°C falls very close to the upper threshold of contemporary tropical temperatures (Fig. 3).

Our new data fill in most of the Mid-Ordovician gap in the carbonate-based palaeotemperature record from the eastern Baltoscandian region (Meidla *et al*. 2023; Gul *et al*. 2024), confirming a cooling trend throughout the Middle Ordovician. For a long time, a rising palaeotemperature trend has been anticipated for Baltica, based on the depositional history of the palaeobasin (Nestor, Einasto 1997) and rapid plate tectonic drift towards the low southern latitudes. Our data and other recent studies (Rasmussen *et al*. 2016; Edward *et al*. 2022; Männik *et al*. 2022) confirm that the global cooling trend was seemingly overruling the anticipated warming (Meidla *et al*. 2023). The composite curve (Fig. 6) suggests a temperature decrease of about 8°C from early Dapingian up to early Sandbian and is roughly comparable to the palaeotemperature data derived from $\delta^{18}O_{brach}$ and $\delta^{18}O_{bulk}$ values by Goldberg *et al*. (2021). Even if the absolute temperature values obtained from our data may contain some uncertainty, it is still noteworthy that the observed trends closely correspond to the generally accepted temperature and climatic scenarios of the Ordovician

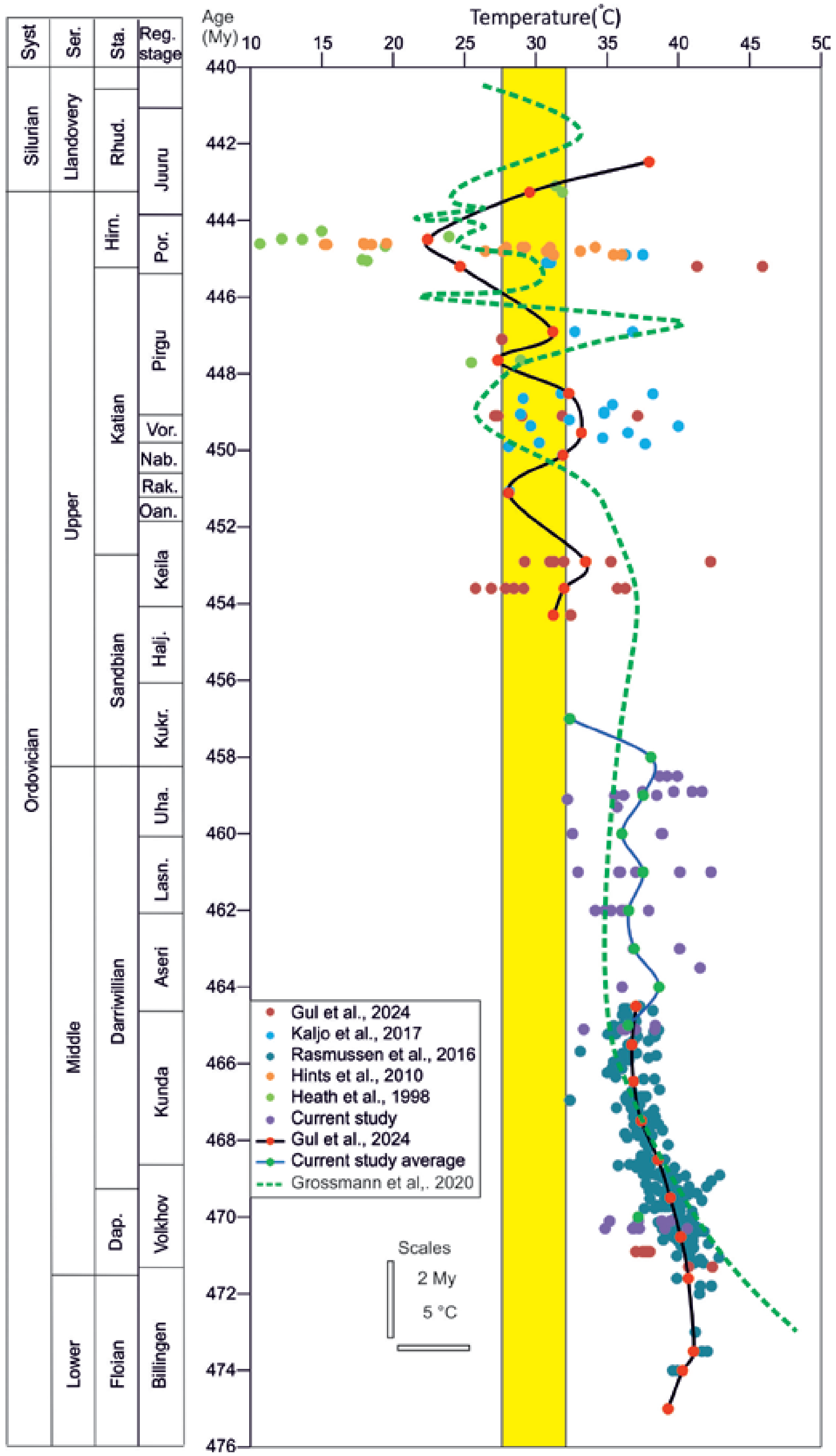


**Fig. 6** Calculated oxygen isotopic temperatures of this and previous studies compared with the Ordovician brachiopods (calcite) curve by Grossmann *et al*. (2020), assuming seawater $\delta^{18}O$ of –1‰. Average curves are calculated by regional stages. Abbreviations: Halj. – Haljala, Kukr. – Kukruse, Uha. – Uhaku, Lasn. – Lasnamägi. The yellow band highlighted denotes the present-day tropical sea surface temperatures following Trotter *et al*. (2008)



Period, supporting the cooling trend demonstrated by Grossmann and Joachimski (2020) (Fig. 6).

## CONCLUSIONS

The oxygen isotope composition of the bulk carbonate and brachiopods shell material reveals a consistent trend throughout the Dapingian-Sandbian with $\delta^{18}O$ values progressively becoming heavier. The results of our study agree with ideas of a warmer Dapingian-Darriwilian and cooler early Sandbian. During this specific time interval, temperatures exhibited an average decrease of about 8°C. However, it's important to note that on the background of this cooling trend the temperatures display some variability. When we compare our data to the geochemical and sedimentological information published from other locations, it strongly indicates that the cooling evidence is not due to local environmental disturbances but more likely mirrors the global climate trend. While the accuracy of the absolute temperature values derived from our data may contain some uncertainty, it is noticeable that the observed trends are closely aligned with global temperature and climatic patterns from other studies.

### Supplementary online data

Supplementary material online can be found at https://doi.org/10.23673/re-457. It contains the list of brachiopod samples, together with analytical results (stable carbon and oxygen isotope ratios).

## ACKNOWLEDGEMENT

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