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Palaeotemperature reconstruction based on oxygen stable isotopic trends from the Ordovician-Silurian brachiopods of Baltoscandia

UNIVERSITY OF TARTU
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This dissertation is accepted for the commencement of the degree of Doctor of Philosophy in Geology at the University of Tartu on the 7th of October 2024 by the Scientific Council of the Institute of Ecology and Earth Sciences, University of Tartu.

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Commencement:	This thesis will be defended at the University of Tartu, Estonia, Chemicum (Ravila 14A), room 1019, on the 29th of November 2024 at 12.15 p.m.)

Publication of this thesis was granted by the Institute of Ecology and Earth Sciences, University of Tartu

ISSN 1406-2658 (print)
ISBN 978-9916-27-700-3 (print)
ISSN 2806-2310 (pdf)
ISBN 978-9916-27-701-0 (pdf)

University of Tartu Press
www.tyk.ee

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LIST OF ORIGINAL PUBLICATIONS

This thesis is based on the following published papers, which are referred to in the text by numbers.

Paper 1. **Gul, B**., Ainsaar, L. & Meidla, T. 2021**.** Latest Ordovician-early Silurian palaeoenvironmental changes and palaeotemperature trends indicated by stable carbon and oxygen isotopes from northern Estonia. *Estonian Journal of Earth Sciences*, 70: 196–209. https://doi.org/10.3176/earth.2021.14

Paper 2. **Gul, B**., Ainsaar, L. & Meidla, T. 2024. Baltoscandian Ordovician and Silurian brachiopod carbon and oxygen stable isotope trends: implications for palaeoenvironmental and palaeotemperature changes. *Geological Quarterly*, 68–13. http://dx.doi.org/10.7306/gq.1742

Paper 3. **Gul, B**., Ainsaar, L. & Meidla, T. 2024. Baltoscandian Middle Ordovician brachiopod oxygen stable isotope trends: implications for palaeotemperature changes. *Baltica*, 37 (2): 87–97. https://doi.org/10.5200/baltica.2024.2.1

A table showing the author's contribution to the scientific papers (' *minor contribution*; * *moderate contribution*; ** *large contribution*; *** *leading role*).

	Paper 1	**Paper 2**	**Paper 3**
Original idea	**	**	**
Study design	**	**	**
Data collection	***	***	***
Laboratory analyses	***	**	***
Analysis and interpretation	***	***	***
Manuscript writing	***	***	***

ABBREVIATIONS

GOBE	Great Ordovician Biodiversification Event
GICE	Guttenberg isotopic carbon excursion
LOME	Late Ordovician mass extinction
MDICE	Mid-Darriwilian Carbon Isotope Excursion
LDNICE	Lower Darriwilian Negative Isotopic Carbon Excursion
HICE	Hirnantian carbon isotope excursions
SST	Sea surface temperature
LA-ICP-MS	Laser ablation inductively coupled plasma mass spectrometry
QC	Quality control
VPDB	Vienna Peedee Belemnite
$\delta^{18}O$	Stable oxygen isotope, ratio of $^{18}O/^{16}O$ (parts per thousand relative to standard)
$\delta^{13}C$	Stable carbon isotope, ratio of $^{13}C/^{12}C$ (parts per thousand relative to standard)

ABSTRACT

Over the last two decades, intensive research has focused on studying the climate fluctuations during the Ordovician-Silurian period. Oxygen stable isotopic values obtained from brachiopod shells are considered a reliable proxy of palaeoclimate, providing information on temperature trends in ancient oceans. Brachiopod shells are resistant to diagenetic alteration and generally precipitate in oxygen-isotopic equilibrium with ambient seawater. This study includes brachiopod C and O stable isotopic data from the Baltoscandian Ordovician-Silurian succession to evaluate the palaeotemperature and palaeoenvironmental variability within the Estonian Shelf facies. Baltoscandia stands out as an ideal region for such studies due to the generally good preservation of Paleozoic sediments, limited post-depositional tectonic activity, and insignificant thermal alteration of rocks. The $\delta^{18}O$ values in the shell calcite of Ordovician and Silurian brachiopods range between ~−7‰ to 1‰. High $\delta^{18}O$ values, sometimes accompanied by higher $\delta^{13}C$ values, indicate cooling if the isotope signal reflects the original isotopic composition of oxygen dissolved in seawater and *vice versa*.

Combining the published and new $\delta^{18}O_{brac}$ and $\delta^{13}C_{brac}$ data enables us to compile a stable oxygen isotopic curve for the interval from Lower Ordovician (Floian) up to the topmost Silurian (Přídolí) in the Baltoscandian Palaeobasin. Multiple Ordovician-Silurian $\delta^{13}C_{brac}$ excursions identified in the Estonian Shelf correspond to the previously documented excursions in the bulk carbonate stable isotopic curves, reflecting global palaeoenvironmental history and events. The $\delta^{18}O_{brac}$ data supports warmer temperatures during early Ordovician (Floian-Dapingian) and a cooling trend into the Mid-Ordovician, also documented by previous studies in different palaeobasins, but still shows warmer temperatures during the middle Ordovician (Dapingian-Sandbian). The Hirnantian glaciation HICE episode reflects the minimum temperature during this interval, while the post-HICE data suggest a rising temperature trend. Another temperature minimum is evident in the strata corresponding to the Ireviken Event (Sheinwoodian). Our study shows that $\delta^{18}O$ values from the brachiopod Ordovician-Silurian carbonates of Baltoscandian Palaeobasin generally agree with other data and thus may be considered a reliable proxy of palaeoenvironmental changes.

1. INTRODUCTION

Estonia is the northernmost of the Baltic countries located in northeastern Europe. It lies on the eastern coast of the Baltic Sea and covers an area of 45,227 km^2. It has been a significant region for global studies on Ordovician and Silurian faunas and palaeoenvironments. It is considered an ideal region for such studies due to the generally good preservation of Paleozoic sediments due to limited post-depositional tectonic activity and insignificant thermal alteration of the rocks. Consequently, it is a crucial area for the global Ordovician chemostratigraphic correlation (Ainsaar et al., 2010).

Brachiopods are considered to be one of the most suitable groups for stable isotopic studies of the Paleozoic Era as the low-Mg calcite shells are more resilient to diagenesis than high-Mg calcite shells or carbonate cement, thus retaining the primary marine isotopic signals much better (Azmy et al., 1998). The $\delta^{18}O$ values obtained from low-Mg calcite may undergo alteration and re-equilibration with pore water, even with minimal pore fluid exchange in an open system (Banner & Hanson, 1990). In order to improve the accuracy of $\delta^{18}O$ –based palaeotemperature estimates, mineral phases that are more resistant to diagenesis are preferred (Edward et al., 2022).

Stable oxygen isotopes from biogenic materials are believed to have precipitated in equilibrium with ambient waters and provide valuable insights into environmental parameters of the past, like precipitation, ocean water temperature, and seawater chemical composition (Muehlenbachs, 1998 and references therein). The temperature estimates rely on the temperature-dependent fractionation equilibrium between seawater and anions ($CO3^{2-}$) that become integrated into minerals. Although stable carbon isotopic curves obtained from biogenic material generally reflect the change in the marine carbon influx, the source material of primary data may not be strongly influenced by temperature (Epstein et al., 1951; Shields et al., 2003; Brenchley et al., 2003). During the Ordovician and Silurian periods, a significant challenge in reliable oxygen isotope palaeothermometry arises from the ambiguity surrounding ambient seawater's stable oxygen isotope composition and the diagenesis of fossils (Grossman, 2012).

During the Ordovician and Silurian periods, substantial climatic changes occurred. The Ordovician period was characterized by a period of peaked global sea level, when vast epeiric seas engulfed much of the palaeocontinents and a substantial increase in marine biodiversity designated as the Great Ordovician Biodiversification Event (GOBE), that brought along the rise of a complex Paleozoic marine ecosystem. During the Great Ordovician Biodiversification Event (GOBE), significant changes occurred in the shallow-water areas' marine biota, leading to numerous new species and ecological niches (Edwards & Saltzman, 2016). Rapid sea-level fluctuations and numerous positive carbon isotope ($\delta^{13}C$) excursions have been documented as a background. The Ordovician Period was terminated by a major marine extinction event (termed the Hirnantian event), the loss of 85% of marine animals (Sheehan, 2001; Trotter et al., 2008;

Bartlett et al., 2018), followed by a slow biotic recovery (Munnecke et al., 2010). The extinction is regarded as a result of an abrupt climate change (the Hirnantian Glaciation) that caused ice-sheet formation over most of Gondwana and a global sea-level decline; the regions that were previously submerged marine shelves were exposed as $\delta^{13}C$ -enriched carbonates due to sea-level fall (Brenchley et al., 2001; Trotter et al., 2008).

For a long time, the generally accepted scenario of palaeoenvironmental changes for this region has been based on the assumption that the plate tectonic drift of Baltica led to a temperature rise as it shifted from the southern high temperate zone to the tropical zone, which led to increased sedimentation rate of carbonates (e.g., Nestor & Einasto, 1997). The Ordovician–Silurian Baltoscandian Palaeobasin was an epicontinental basin primarily characterized by carbonate sedimentation. During its drift northward, the area experienced substantial climatic changes, reaching the low southern latitudes near the equator (Cocks & Torsvik 2005). For a significant period, researchers believed that a warm, greenhouse climate primarily defined the Ordovician Period, which concluded with a brief glaciation of the southern regions of the supercontinent Gondwana during the transition from Ordovician into the Silurian (Shields et al., 2003). Over the past few decades, the Ordovician System has been the focus of intensive palaeoenvironmental, palaeontological, and stratigraphical studies. The complexity of the environmental and faunal changes during this period is today better understood as a result of this research (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). According to Trotter et al. (2008), higher sections exhibit a cooling trend that brings sea surface temperature (SST) values into a more reasonable range, reaching 28–32 °C by the Middle Ordovician, even though the possibility of tropical SST surpassing 40 °C in the earliest Ordovician looks unlikely. Several cooling phases are suggested by an analysis utilizing conodont-based $\delta^{18}O_{phos}$ from Estonia, including a quick temperature drop during the early Sandbian and a milder cooling from the late Sandbian to the Katian (Männik et al., 2021). Trotter et al. (2008) developed a rather controversial model that contradicts previous models (Servais et al., 2009; Veizer et al., 1999), but its Mid-Ordovician temperature values are comparable to modern ocean temperatures. This conflicts with the warming assumption that has been generally accepted for many decades. In a recent paper, Thiagarajan et al. (2024) analyzed and interpreted clumped isotope results from Estonian Ordovician sections and showed that SST might have been about 10 °C lower than it was previously suggested by $\delta^{18}O_{brac}$ analyses, having still a cooling trend towards the end-Ordovician glacial event.

During the Darriwilian, substantial transformations occurred within Ordovician ecosystems, marked by a gradual cooling process that led to a significant decrease in SST at low latitudes, similar to recent equatorial regions (Trotter et al., 2008). The Middle Ordovician succession (Floian–Sandbian) consists of cool-water limestones, with changes in carbonate deposition reflecting a change from cold-water to tropical sedimentation in the Late Ordovician (early Katian).

This shift was followed by significant biotic and environmental changes, driven by the onset of glacial conditions at high latitudes and a drop in ocean temperatures in Estonia and surrounding regions near the end of the Ordovician (Cocks & Torsvik 2005; Dronovet al. 2011). Recent insights indicate that the transition from a greenhouse to an icehouse climate might have occurred considerably earlier than previously suggested, and the Darriwilian continental ice sheets influenced global sea levels (Rasmussen et al., 2016). 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 in 2005, Rasmussen et al. in 2016 and Edward et al. in 2022.

According to Saltzman & Young, 2005 and Goldman et al., 2020, the Guttenberg isotopic carbon excursion (GICE) phenomenon has been historically interpreted as proof of an extended late Ordovician glaciation, commencing during the uppermost Sandbian–lower Katian period. A brief cooling phase, evident from $\delta^{18}O$ values, has been linked to the GICE and tentatively related to the onset of Ordovician icehouse conditions (Rosenau et al., 2012). However, a detailed investigation of both previous and recently collected conodont $\delta^{18}O$ data from Laurentia, spanning the Sandbian-Katian border through the GICE interval, exhibits an inconsistent warming trend throughout the late Sandbian–early Katian period, shows no evidence of cooling (Quinton et al., 2018). A $\delta^{18}O_{phos}$ study of the Sandbian–Katian time interval suggests a slight rise in temperature and a gradual cooling during the Late Katian, followed by an abrupt temperature drop during the latest Ordovician (Hirnantian) and the glacially driven mass extinction (Buggisch et al., 2010).

The beginning and duration of the Late Ordovician mass extinction (LOME), as well as its possible triggers and mechanisms, are hotly debated in recent publications (Hammarlund et al., 2012; Bond & Grasby, 2020; Zhang et al., 2022 and references therein). Several papers have also questioned the direct relationships between LOME and the Hirnantian Glaciation (Bond & Grasby, 2020; Hints et al., 2023, and references therein).

According to Männik et al. 2021, oxygen isotope data of conodont suggests sea surface temperature (SST) fluctuations reveal a cooling trend through the early Late Ordovician in Baltica. At the same time, the global temperature trends revealed from multiple proxies show cooling towards the end-Ordovician (Grossman & Joachimski, 2020). After the late Ordovician – early Silurian glaciation, multiple small-scale climate cycles demonstrate a general warming trend until the mid-Llandovery (early-mid Telychian), then a progressive cooling trend until the late Llandovery (Grossmann et al., 2020). Wenlock $\delta^{18}O_{phos}$ excursions coincided with the Ireviken biotic event (Lehnert et al., 2010; Trotter et al., 2016).

The specific objectives of this research were:

- To determine the climatic and environmental changes during the Ordovician-Silurian periods from brachiopod stable isotopic data in the Baltoscandian palaeobasin.
- To evaluate the stratigraphic correlation of $\delta^{13}C$ and $\delta^{18}O$ excursions and integrate new $\delta^{18}O$ data from brachiopod shells with the results of previous studies.
- To reconstruct the tentative palaeotemperature curve based on new and published $\delta^{18}O$ data from brachiopod shells spanning from the Lower Ordovician (Floian) up to Přidoli Epoch in the Baltoscandian region.

This study aims to test the following hypotheses:

- Brachiopod calcitic shells can be reliably used and reflect palaeotemperatures, establishing it as a viable proxy for palaeotemperature analysis.
- Several distinct cooling phases are characteristic of the Ordovician climate, including a rapid temperature decline during the early Late Ordovician.
- The palaeotemperature data from the Baltoscandian Palaeobasin are consistent with the global cooling trends suggested by other studies.

2. GEOLOGICAL SETTING

Estonia is situated in the north-western part of the East-European Platform. Estonian sedimentary strata in Estonia, positioned on the southern slope of the Fennoscandian Shield where crystalline basement rocks are overlain with nearly unaffected and un-metamorphosed sedimentary rocks, mostly contain fossils that are well-preserved and only minor dolomitization and declining southwards at about 3–4 meters per kilometer. The Estonian Quaternary deposits overlay the Neoproterozoic (Ediacaran) and Paleozoic (Cambrian, Ordovician, Silurian, Devonian) sedimentary rocks. Neoproterozoic and Paleozoic lie on the top of crystalline Paleoproterozoic basement rocks (Nestor & Einasto, 1997).

The Ordovician–Silurian Baltoscandian Palaeobasin represents an epicontinental basin that was primarily characterized by carbonate sedimentation, consisting mainly of shallow water carbonates – dolomite, limestone, and marlstone with clay interlayers. The lower Ordovician sequence consists of terrigenous sediments – silty sandstone, clayey sandstones, and graptolite argillite. Generally, the clay content proportion in Ordovician and Silurian rocks increases southwards or south-westerly (Nestor & Einasto, 1997).

During the earliest Cambrian, Baltica underwent a rifting process, separating the continent of Gondwana, opening the Tornquist Sea to the southwest, and effectively dividing Baltica and Gondwana. Baltica drifted southwest from mid-Cambrian to Middle Ordovician, and this period was associated with counter-clockwise rotation (Torsvik & Rehnström, 2003). During the Middle Ordovician, Baltica moved from high southerly to intermediate latitudes and proceeded toward the palaeoequator all through the Ordovician (Cocks & Torsvik, 2005; Torsvik et al., 2011). The Baltic palaeocontinent experienced relative tectonic stability until the Mid-Ordovician and was bounded by the Tornquist Sea to the southwest and the Iapetus Ocean to the northwest. As the microcontinent Avalonia approached Baltica, volcanic activity commenced. This became apparent in the Sandbian (early Late Ordovician) period, when subduction beneath Avalonia started and a complex of bentonites appeared on Baltica (Huff et al., 1992; Torsvik & Rehnström, 2003).

Based on the rock patterns and faunal distribution along the facies gradient, from shallow-water to deeper basinal environments, three main facies belts have been distinguished in the Baltoscandian basin during Ordovician (Fig. 1). The North Estonian Shelf and Lithuanian Shelf Facies Belt (the Estonian and Lithuanian basins by Harris et al., 2004) were the shallowest parts of the palaeobasin and were characterized mainly by carbonate rocks. The Central Baltoscandian Facies Belt (the Scandinavian Basin by Harris et al., 2004) stretched from modern southern Estonia to Latvia and Sweden, representing deeper shelf conditions and being characterized by widespread argillaceous limestones and mudstones. The Scanian Facies Belt in Southern Scandinavia (the Scanian Basin by Harris et al., 2004) covers the deepest part of the basin. It is characterized by the wide distribution of graptolitic black shales (Kaljo et al., 2007).

During the Silurian period, Estonia experienced predominantly shallow water sedimentary conditions. The facies alterations of the Silurian rocks and the Mid-Estonian and South-Estonian confacies belts have been eminent. The West-Estonian Archipelago's islands and the western and central regions of mainland Estonia are encompassed by the Mid-Estonian Confacies Belt, which is distinguished by various dolomites and limestones. In contrast, most of the rocks of the South-Estonian Confacies Belt are marlstones. The composition of sediments, particularly the clay content, reflects the sea level changes of the Silurian Basin (Nestor & Einasto, 1997).

The general stratigraphy of the Ordovician and Silurian systems in Baltoscandia is presented in Fig. 2. Regional stages are the primary unit in Estonian Paleozoic chronostratigraphic classification, defined historically based on fauna and characteristic lithology rather than boundaries (Männik et al., 2021: Meidla et al., 2023; Hints et al., 2023 and references therein).

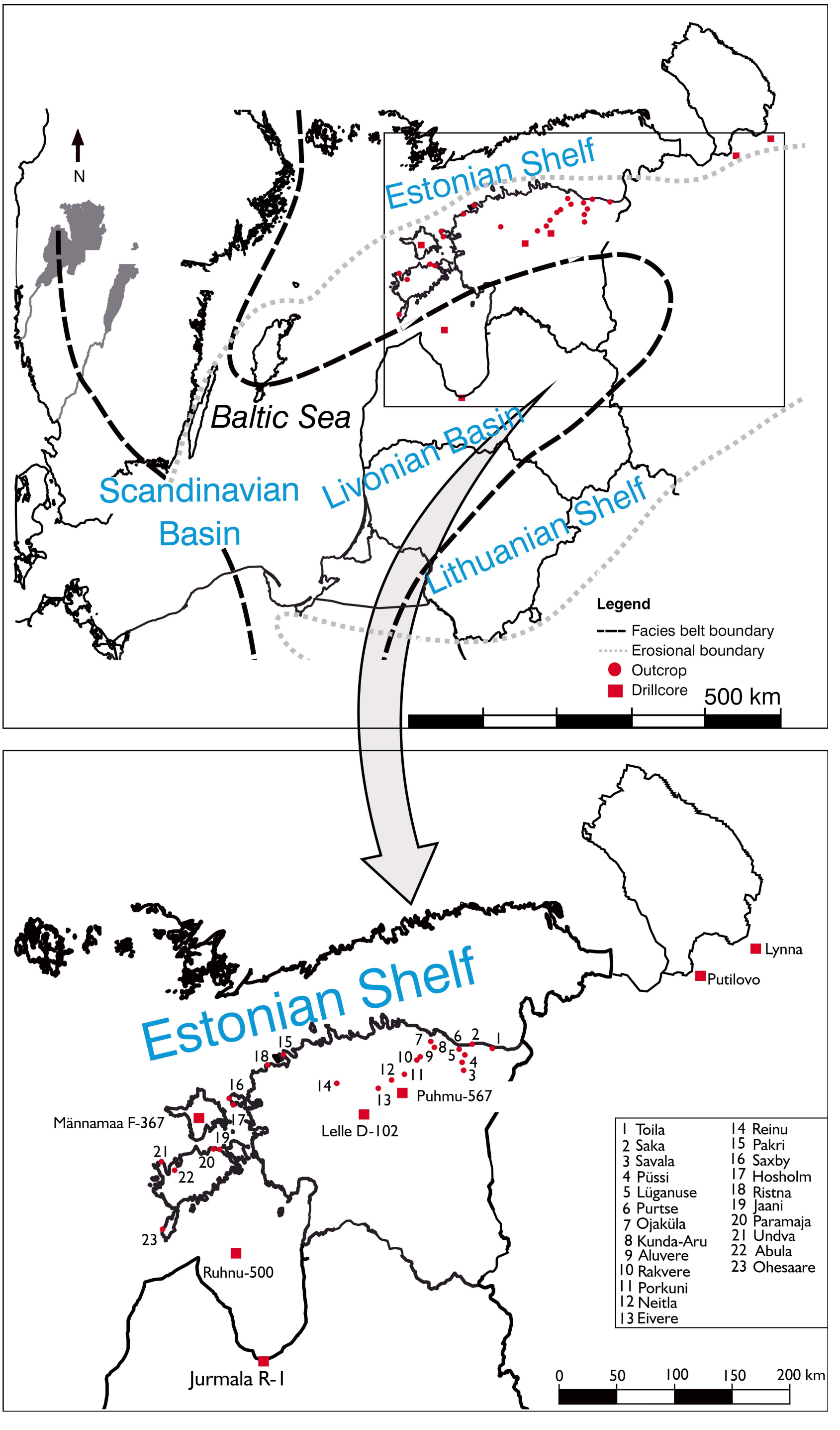

Fig. 1 Locality map showing the outcrops and drillcore sites of Ordovician and Silurian rocks in the Baltic region and schematic configuration of the Baltoscandian basin (modified from Harris et al., 2004).

3. MATERIAL AND METHODS

3.1. Drillcore and outcrop sections sampled for this study

For this study, 23 outcrop and seven drillcore sections covering the stratigraphic interval from the Middle Ordovician to Silurian were described and sampled. Brachiopod shells were collected and separated from samples. One hundred twelve brachiopod samples were prepared and analyzed for stable carbon and oxygen isotopic composition. The geological sections used in this study are as follows (Fig. 1). Supplementary Materials in **Paper 1**, **Paper 2**, and **Paper 3**.

Eivere quarry (Järva County, Lat. 58.977553, Long. 25.57685) features lithologically distinctive argillaceous nodular wackestones-packstones that represent an open marine tropical carbonate shelf (Varbola Formation, 4.2 m) and shallow-water high-energy bioclastic carbonates (Tamsalu Formation, Tammiku Member, 4.8 m; Fig. 2) of the Juuru RS. The grey to greenish-grey limestones of the Varbola Formation alternate with thin, wavy layers of greenish-grey marls. Varbola Fm is highly fossiliferous, containing numerous stromatoporoids, corals, and brachiopods. The Tammiku Member, the Tamsalu Formation, is known for its massive occurrence of *Borealis borealis* and its prevalence of stylolites. Twenty-three samples were collected from the Eivere quarry. (See **Paper 1**)

Reinu quarry (Rapla County, Lat. 59.087299, Long. 24.73768) exposes distinctive lithological units in slightly different thickness (the Varbola Formation 6.85 m and the Tamsalu Formation, Tammiku Member 2.15 m). Twenty-five samples were collected from the Juuru RS interval of the Reinu quarry. (See **Paper 1**)

Neitla section is located 5 km east of Järva-Madise (Järva County, Lat. 59.102247, Long. 25.762486). It exposes 1.6 m of the shoal to open shelf carbonates of the Tõrevere and Kamariku members (Ärina Formation, Porkuni RS) and the basal part of the Varbola Formation (Fig. 2). (See **Paper 1**)

Lelle D-102 drill site is situated at the Rapla–Türi highway intersection with the road to Lelle in central Estonia (Lat. 58.842497, Long. 24.984431). Transitional facies from shallow to deeper shelf are distinctive features of this section. The core penetrates the succession from the Llandovery down to the Cambrian and exhibits strata with varying shelf settings. A total of 122 samples at an average of three per meter were collected from the Lelle drill core at a depth of 61.3–104.6 m, representing the interval of the Pirgu to Raikküla RS. The Ärina Formation in this section comprises only the Röa, Vohilaid, and Kamariku members (Fig. 2). (See **Paper 1**)

Männamaa F-367 borehole is situated in the central part of the Island of Hiiumaa (Lat. 58.83821, Long. 22.628508). 20 samples were collected from the interval of 29.5–46.7 m representing the Varbola and Tamsalu formations, in addition to the previously published isotope data (Ainsaar & Meidla, 2008), (Fig. 2). (See **Paper 1**)

Toila section (Lat. 59.429603, Long. 27.490083) exposes the Volkhov RS, represented by the Toila Formation, composed of glauconite-rich limestone. Eight samples were collected. (See **Paper 3**)

Saka section (Lat. 59.441158, Long. 27.215056) (Darriwilian, Kunda and Aseri RS) 13 samples were collected from approximately 9 meters of dolomitized oolitic and glauconitic limestones of the Sillaoru, Loobu, and Kandle Formations that are notable for their abundant cephalopods, trilobites, brachiopods and other shelly faunas. The oolitic limestones of the Kandle Formation are well exposed. (See **Paper 3**)

Purtse outcrop (Lat. 59.411389 Long. 27.002222) consists of dolomitized oolitic and glauconitic limestones of the Loobu and Kandle Formations. Four samples were collected from the Purtse outcrop. (See **Paper 3**)

Ojaküla outcrop (Lat. 59.478447 Long. 26.481289), located about 4 km southwest of Kunda, west of the highway, in the Ojaküla village, exposes oolitic limestones of the Kandle Formation. Only one brachiopod sample was collected. (See **Paper 3**)

Kunda-Aru quarry, located east of Haljala-Kunda highway, approximately 5 km south of Kunda (Lat. 59.444063 Long. 26.479414), comprises the Väo Formation, light grey pure massive limestone. Six samples were collected. (See **Paper 3**)

Püssi quarry (Lat. 59.360278 Long. 27.049167) consists of alternating limestones and argillaceous limestones of the Kõrgekallas Fm (upper Darriwilian, Uhaku RS). Two samples were collected. (**See Paper 3**)

Lüganuse quarry (Lat. 59.387525 Long. 59.387525) also exposes the Kõrgekallas Formation. Three samples were collected. (See **Paper 3**)

Savala quarry (Lat. 59.319442 Long. 27.009725) where the Viivikonna Fm, argillaceous bioclastic limestone with intercalation of kukersite (oil shale) and marl, crops out. One sample was collected. (See **Paper 3**)

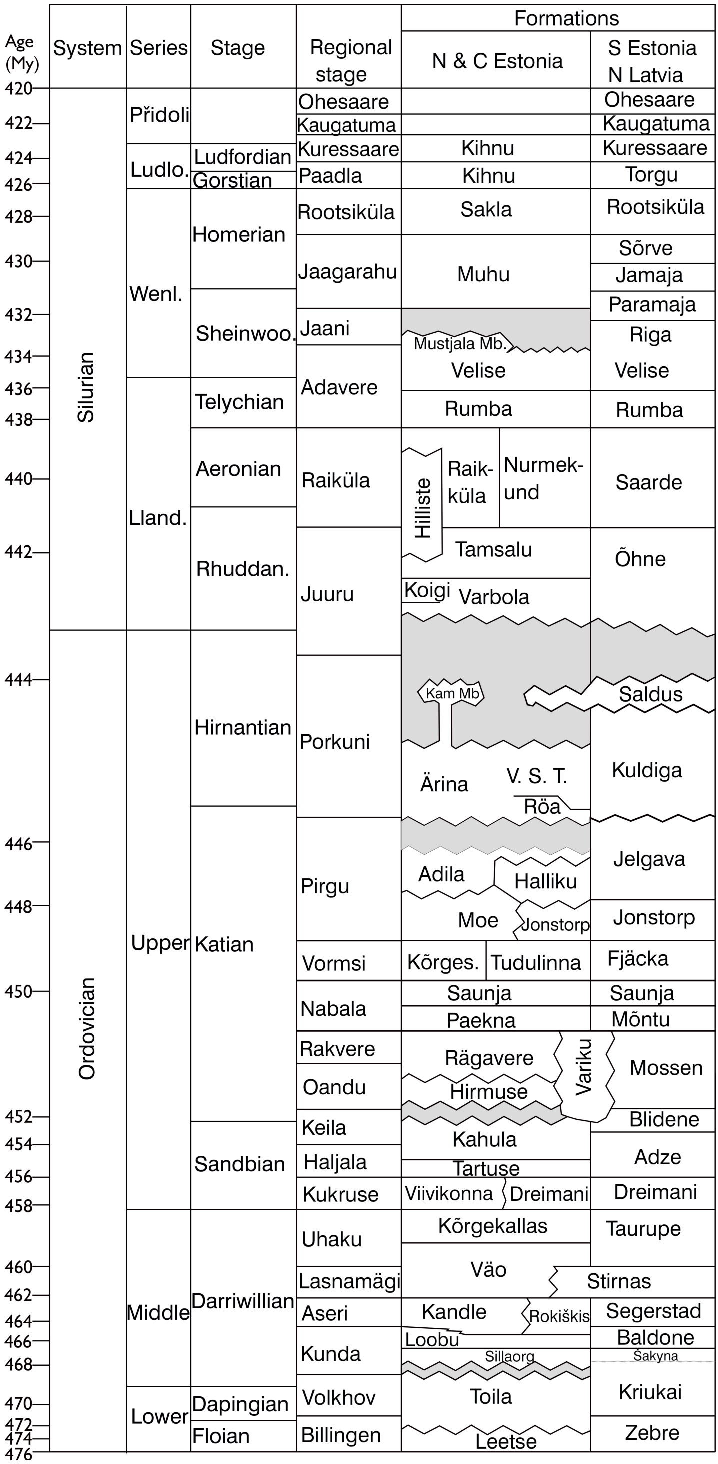

Fig. 2 Stratigraphy of Ordovician-Silurian strata of the Baltoscandian region (modified from Männik, 2014; Meidla, 2014; Truuver & Meidla, 2015).

3.2. Sample preparations and analytical methods

Brachiopods collected in outcrops fragment size ~3–10 mm. The state of the shells and fragments was generally inadequate for identifying specific families or genera due to their poor condition. Very few complete brachiopod specimens were found as a whole. Drill cores were carefully removed from the limestone matrix and cleaned. For stable isotope analyses, brachiopod shell powder was obtained by micro-drilling, avoiding cement and matrix material from outcrop sections. The powdered material was analyzed 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 sample was used. The results are reported as 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 $\delta^{18}O_{brac}$ values using the formula T°C = 17.3750–4.2535 (δc-δw) +0.1473 $(\delta c\text{-}\delta w)^2$, assuming possible preservation of original marine carbonate isotopic composition formed in seawater with $\delta^{18}O$ value –1‰ (Brand et al., 2019). (See **Paper 1**, **Paper 2** and **Paper 3**)

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 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 CaCO3) was used as a matrix-matched quality control (QC) standard. During analysis, calibration and QC standards in 3 replicates were ablated after every nine analytical spots. Before analysis, ICP-MS settings were tuned on NIST610 to achieve a ThO/Th ratio of < 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 6ms. The following laser parameters were used for all analyses: 100 μm round spot, repetition rate 5 Hz, shot count 250, 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. (see **Paper 2** and **Paper 3**)

4. RESULTS

The $\delta^{13}C$ and $\delta^{18}O$ values for Ordovician and Silurian brachiopods used in this study range between ~–2.6 to +7.6 ‰ and –7 to 1‰ respectively (Figs. 5 and 6). While individual values are dispersed throughout the successions, the principal trends are evident and can be discussed based on the averaged curve.

4.1 Chemical preservation and trace elements of the brachiopod shells

The carbonate rocks and fossils analyzed in the prior study exhibit remarkable preservation throughout the majority of the study sites in Estonia. This preservation is attributed to minimal tectonic activity and limited regional burial diagenesis (Azmy et al., 1998). Petrographic analyses from previous studies indicate minimal dolomitization and recrystallization (as summarized by Azmy et al., 1998). The overall characteristics of isotopic variations through time are retained.

Diagenetic changes in carbonate isotopic composition can be assessed by analyzing the $\delta^{13}C$–$\delta^{18}O$ cross-plot of brachiopod shell material. According to Jacobsen and Kaufman (1999), the relationship between $\delta^{13}C$ and $\delta^{18}O$ values depicted in this plot indicates the degree of meteoric diagenesis. However, the cross-plot of carbon and oxygen isotopic data of randomly selected samples in our study shows no clear covariation between the $\delta^{13}C$ and $\delta^{18}O$ values (Reinu $R^2 = 0.0646$, Eivere $R^2 = 0.2479$, Lelle $R^2 = 0.0385$, Ristna $R^2 = 0.6518$, Saxby $R^2 = 0.5676$, Ohesaare $R^2 = 0.1657$, Pakri $R^2 = 0.9378$, Porkuni $R^2=1$, Abula $R^2 = 0.1075$, Paramaja $R^2 = 0.0029$, Jaani $R^2 = 1$, Undva $R^2 = 0.7423$, 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 3. (**Paper 1, 2 and 3**) The values exhibit a close clustering without any notable extreme negative points on either axis, suggesting that the preservation of the analyzed material is relatively good. Regarding correlation, the Püssi, Jaani, and Porkuni sections show excellent preservation ($R^2 = 1$). Nevertheless, it still cannot be ruled out that some samples may have been subject to some secondary influence, potentially affecting the primary signal.

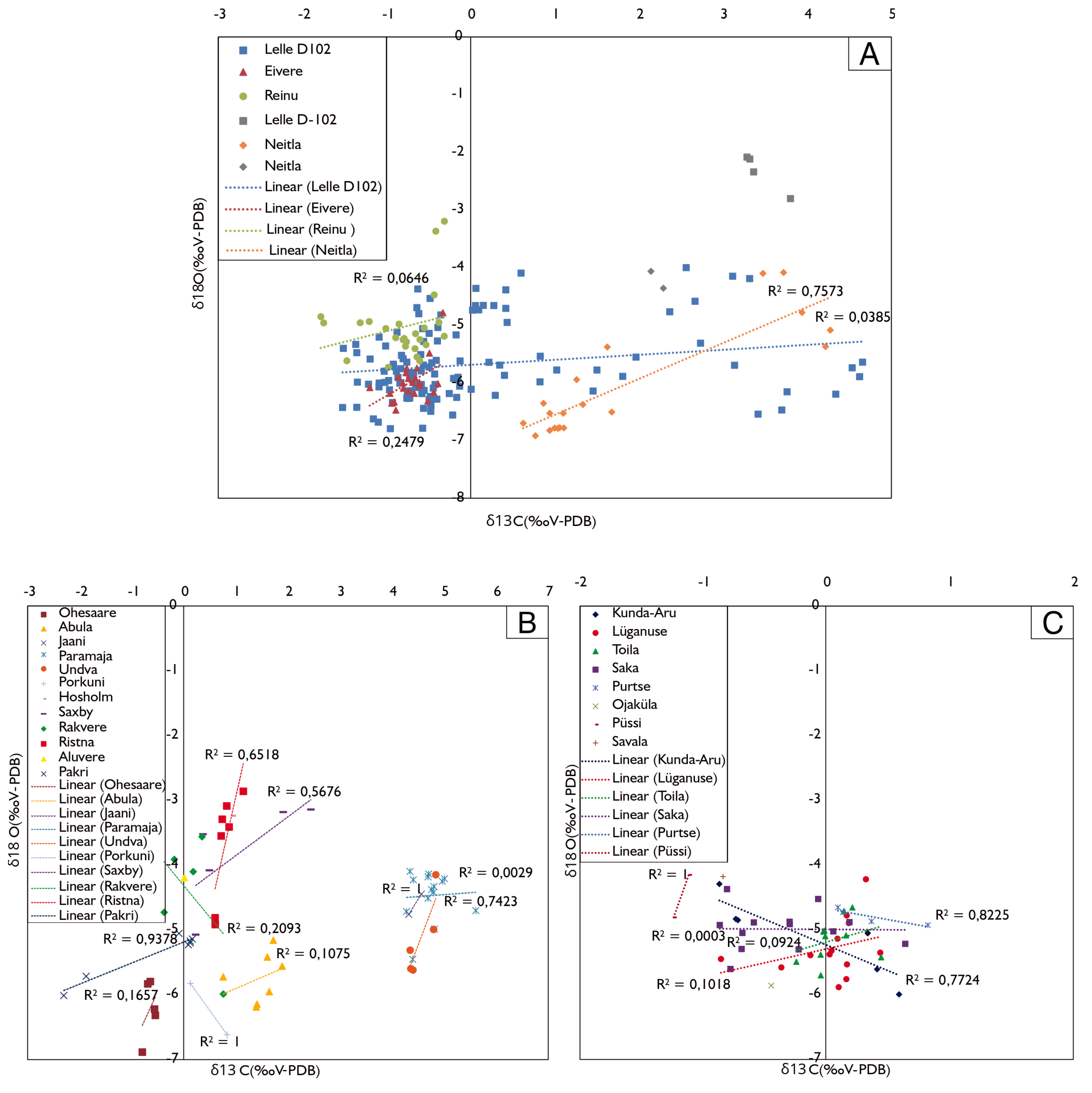

Fig. 3 Oxygen vs carbon isotopic composition measured from brachiopod shell material in the stratigraphic units studied. $\delta^{13}C$–$\delta^{18}O$ cross-plot illustrates the isotopic data from the shells and the correlation factor (R^2). Solid symbols represent different sections, and dotted lines indicate the R^2 values. The data from the randomly selected samples show no clear covariation between the $\delta^{13}C$ and $\delta^{18}O$ values. A see **Paper 1**, B see **Paper 2**, C see **Paper 3**.

Brachiopod shells have also been widely used to assess the extent of diagenetic alteration of rocks, with strontium (Sr) and manganese (Mn) abundance ratios serving as the key indicators (Brand & Veizer, 1980). Comparison between the trace element contents of Ordovician brachiopods from this study and modern brachiopods shows that the Sr abundances range from 359 to 2159 ppm, although concentrations as low as 200 ppm have been documented for modern brachiopods (Veizer et al., 1999; Immenhauser et al., 2002). The manganese abundances range below the detection limit up to 200 ppm, except for one brachiopod shell from the Purtse section with the Mn value lying out of the normal range (831 ppm, see Fig. 4) (see **Paper 2** and **Paper 3**). These results indicate that their preserved values are near the primary isotopic values and consistent with the range found in primary isotopic composition (Veizer et al., 1999).

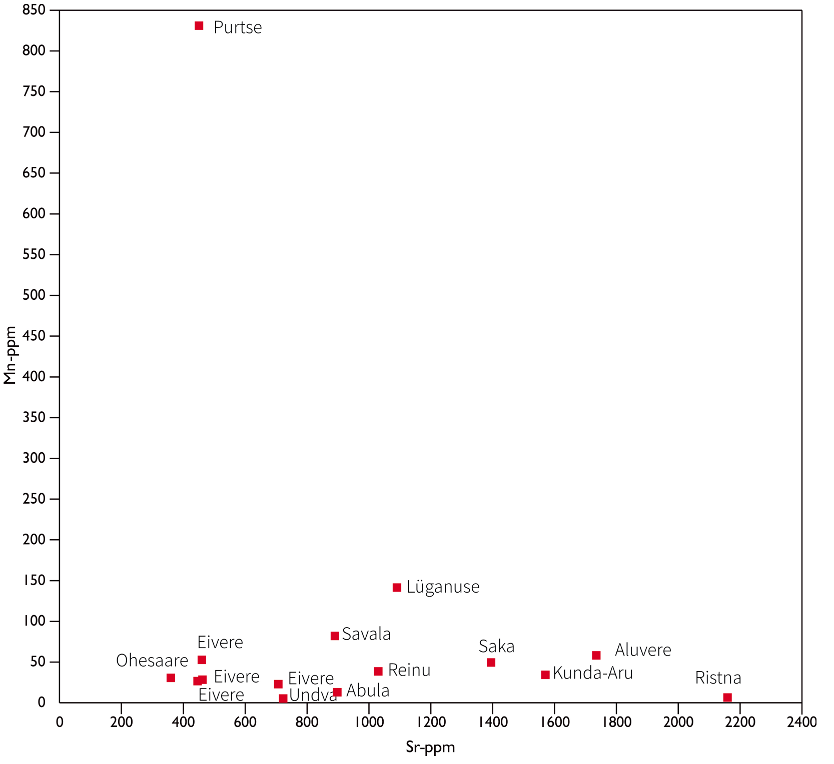

Fig. 4 Strontium and manganese abundances in the brachiopod shells used in this study (modified from **Paper 2** and **Paper 3**).

4.2 Carbon isotope record ($\delta^{13}C$)

The $\delta^{13}C_{bulk}$ values within the Ordovician Baltoscandian succession typically display a gradual increase from the Floian to the Hirnantian ages. The Floian-Darriwilian $\delta^{13}C_{brac}$ values are characterized by an increasing-upwards trend on average from –1 to 0‰ (Fig. 5). The shift towards an increase in $\delta^{13}C_{brac}$ during the middle Ordovician, Darriwilian- Sandbian is evident from 0.5‰ to 1‰ but shows lower values (<0‰) in the Loobu Fm followed by a slight increase (from –0.9‰ to 0.6‰) in the Saka section. Slightly higher values (up to 1‰) are recorded also from the Purtse section (Fig. 5). A subsequent decrease of values is recorded higher up in the succession in the Lüganuse, Püssi, and Savala sections. Conversely, the Sandbian-Katian $\delta^{13}C_{brac}$ values vary generally between 1‰ and 2‰, but the resolution is too low to recognize the well-known isotopic excursions revealed in the bulk carbon data (e.g., Ainsaar et al., 2020).

The pre-HICE $\delta^{13}C$ values from bulk material are typically between –0.5‰ and +1‰ in the Estonian Shelf area (Ainsaar et al. 2015). Carbonates from the Hirnantian age (Porkuni Regional Stage in Estonia and the adjacent areas) have elevated $\delta^{13}C$ values that peak at +7‰, which corresponds to the HICE (Brenchley, 2004; Meidla et al., 2014). The results from bulk rock samples in the Lelle drill core typically show a positive excursion that is similar to those seen in the Tartu 453, Ruhnu 500, Männamaa, and Jurmala R-1 cores (Ainsaar et al., 2010, 2015; Bauert et al., 2014). The $\delta^{13}C$ isotopic curve shows a continuous rise from 0.8‰ to 4.7‰ in Katian-Hirnantian. The Ordovician succession is terminated by an abrupt increase in the $\delta^{13}C_{brac}$ values up to +5–7‰ in the Hirnantian Stage (the HICE peak). Higher up, the values decline to 0‰ at the top of the Varbola Formation (Eivere quarry). The falling limb of the HICE curve is marked by $\delta^{13}C_{brac}$ values returning to ~–1 to 0‰ in the topmost Ordovician.

Secular trends in the $\delta^{13}C_{brac}$ values in the Silurian part of the succession may be divided into three intervals. A large positive $\delta^{13}C$ shift is recorded throughout the early Silurian (Rhuddanian-Aeronian interval) where $\delta^{13}C$ values gradually decrease up to +1‰ (Fig. 5). The second, Aeronian-Telychian interval is characterized by stable values around +1‰. This is followed by a continuous increase in the $\delta^{13}C_{brac}$ values up to +3.5‰ in the Sheinwoodian interval, reflecting the global Ireviken Event (Munnecke et al., 2010). There is no brachiopod data in our dataset collected from Homerian to Ludfordian, mainly due to wide distribution of marginal marine carbonates in the Baltic outcrops that are nearly barren of brachiopods. The $\delta^{13}C_{brac}$ values in the mid-Přidoli interval are the lowest for the Silurian in this region (–0.7‰; Fig. 5).

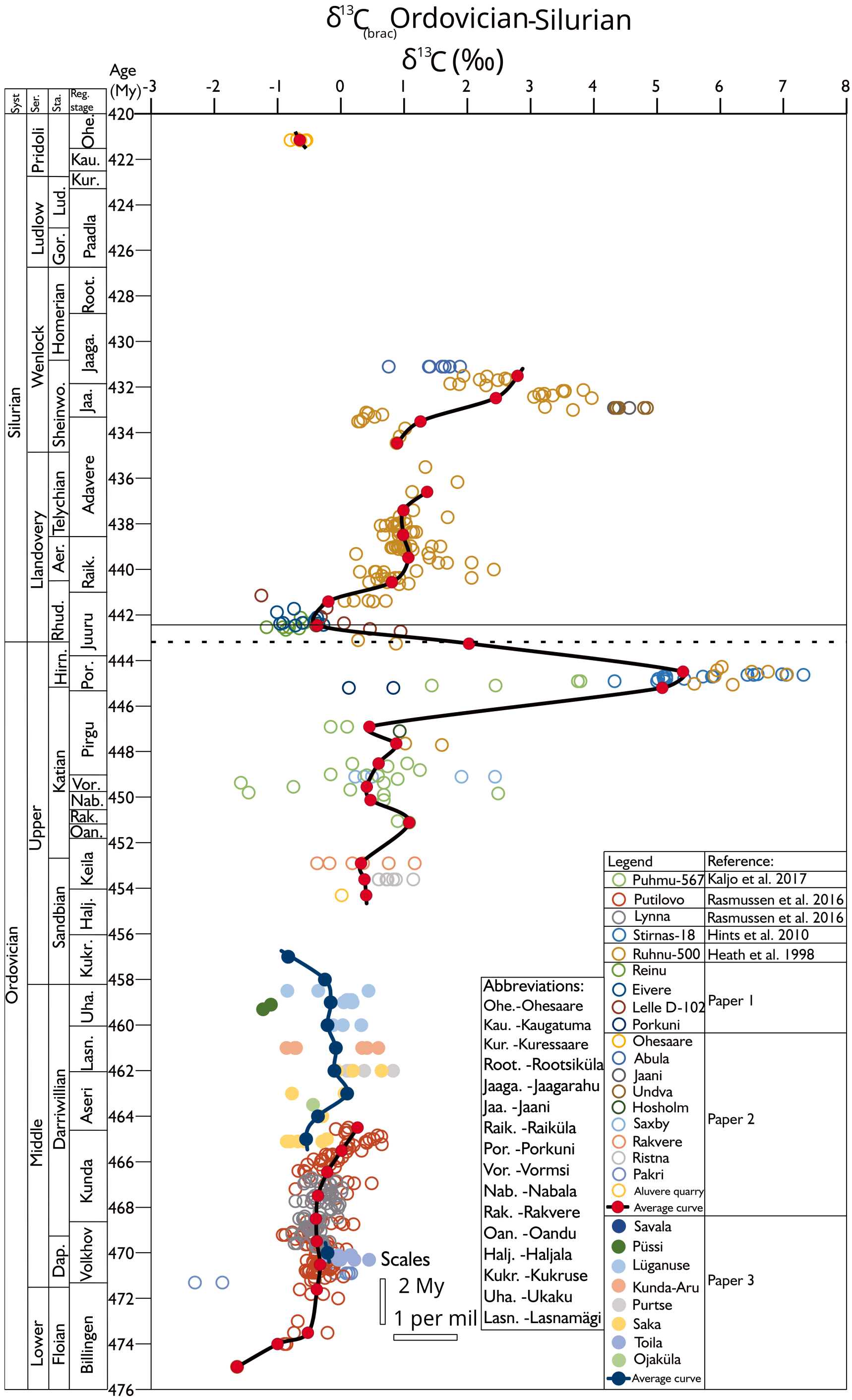

Fig. 5 Summary figure showing the carbon isotope (brachiopod) trend through the early Ordovician – late Silurian interval. The average curve comprises two-million-year segments with a centered moving average computed every 0.5 Myr.

4.3 Oxygen isotope record ($\delta^{18}O$)

In the Ordovician Baltoscandian succession, the $\delta^{18}O_{brac}$ values generally increase from the Floian to the Hirnantian. These values increase gradually from –6 to –5‰ in the Floian-Darriwilian interval but are more scattered in the Sandbian-Katian interval (between –6 and –3‰), lacking apparent trends or peaks (Fig. 6). The shift towards an increase in $\delta^{18}O$ during the middle Ordovician (Floian-Darriwilian) is evident in results brachiopods samples. Some minor fluctuations of $\delta^{18}O$ values in the studied sections may be attributed to numerous gaps in the succession in most early Middle Ordovician units. In most instances, the isotopic composition of brachiopod shells deviates from $\delta^{18}O$ values of the bulk rock in previous studies (see **Paper 1**) by less than 1‰, where brachiopod shells usually exhibit a slightly higher stable isotopic ratio. $\delta^{18}O_{brac}$ values increase from approximately –5‰ to –4‰ in the Katian (e.g., Shields et al., 2003) and between –2‰ and 0‰ in the Hirnantian before returning to pre-shift values (Brenchley et al., 1994).)

The Hirnantian $\delta^{18}O_{brac}$ values range between –5.6‰ and –4.2‰. The Hirnantian $\delta^{18}O$ averaged brachiopod values indicate a sharp increase from roughly –4 to –2‰, with a maximum coinciding with the Hirnantian glaciation event (Fig. 6), before returning to the pre-shift plateau in the basal Llandovery beds. The sharp decline in $\delta^{18}O_{brac}$ values marks a stratigraphic gap at the boundary of this area's Porkuni and Juuru regional stages (Kaljo et al., 2001).

The average $\delta^{18}O_{brac}$ values in the Silurian indicate a slight rise in the upper Rhuddanian (Llandovery) followed by a continuous decline up to the Telychian-Sheinwoodian boundary, in the range of ~–5.5 to –4.5‰. The average value of $\delta^{18}O_{brac}$ increases to –3.5‰ during the mid-Sheinwoodian. The $\delta^{18}O_{brac}$ values in the Přidoli are ~–6‰ (Fig. 6).

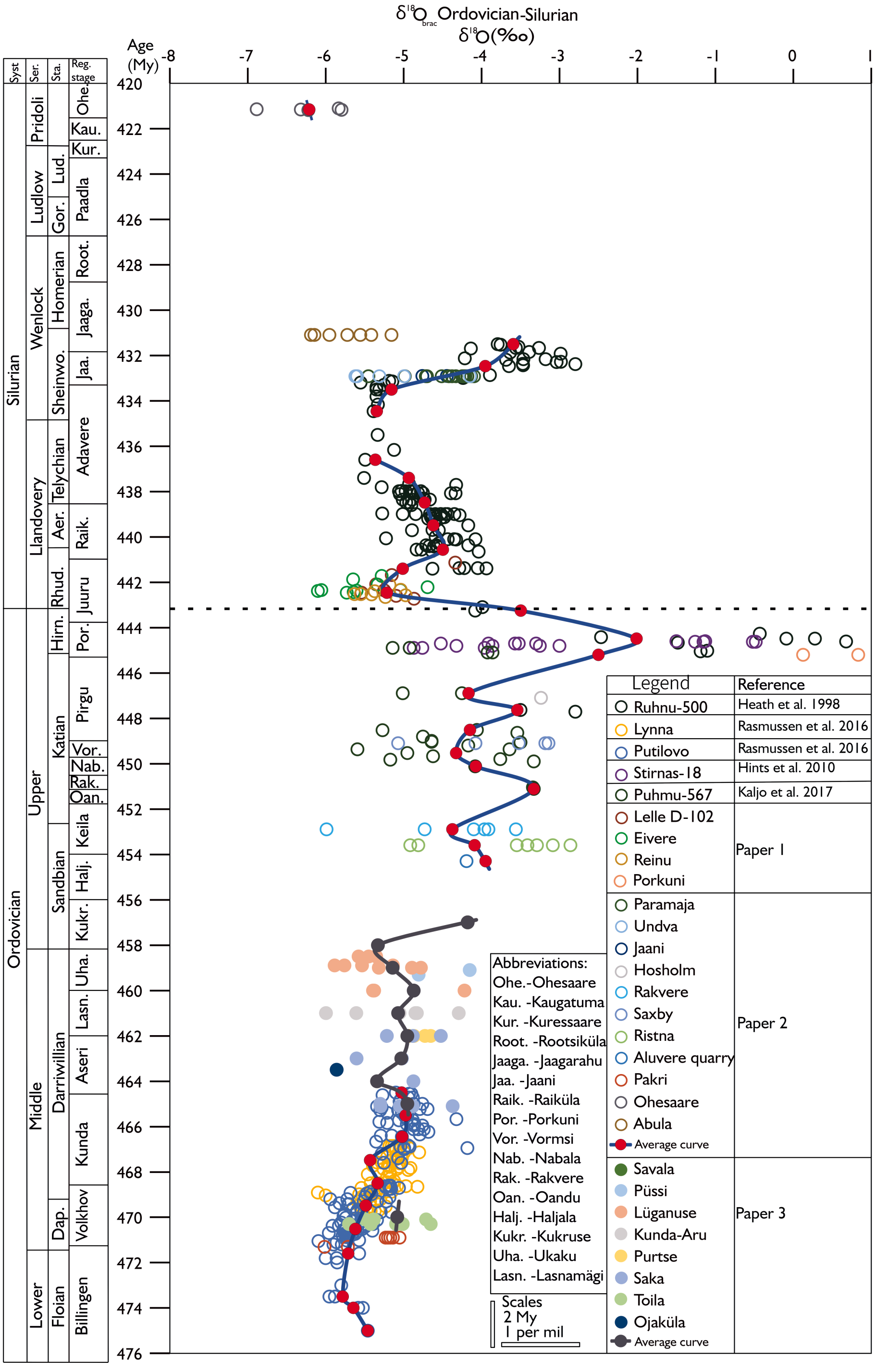

Fig. 6 Summary figure showing oxygen isotope compositions of brachiopods from the early Ordovician – late Silurian interval. The average curve comprises two-million-year centered segments with a moving average computed every 0.5 Myr.

5. DISCUSSION

In recent decades, the Ordovician and Silurian succession in Baltoscandia has gathered considerable attention from researchers due to the numerous remarkable fluctuations in carbon isotopes ($\delta^{13}C$) that are well-documented, primarily in the bulk carbonate record (Kaljo et al., 2007; Ainsaar et al., 2010). These fluctuations are interpreted as global or regional environmental change indicators and have been extensively utilized in regional stratigraphy. Numerous positive $\delta^{13}C$ excursions during the Ordovician period have been identified in various borehole core sections in the Baltoscandian area (Kaljo et al., 2007; Ainsaar et al., 2010). Except for the HICE and the Ireviken Excursion, where the $\delta^{13}C$ values reached up to +7‰, all other excursions show $\delta^{13}C$ values of only between –1 and +2 ‰. The Ordovician $\delta^{13}C$ excursions demonstrate correlation across the Baltoscandian Palaeobasin, with some extending across different palaeocontinents (such as the HICE and the Ireviken Excursion).

The carbon isotopic curve derived from brachiopod data generally aligns with curves based on bulk carbonate data (Heath et al., 1988; Hints et al., 2010; Männik et al., 2015; Rasmussen et al., 2016; Kaljo et al., 2017; Meidla et al., 2020; **Paper 1**; **Paper 2**). The difference recorded between the bulk rock and brachiopod carbon isotopic values is *ca* 0‰ and 2‰, respectively. Discrepancies between local and regional values of $\delta^{13}C_{brac}$ may arise from differences in depositional environments, tectonic regimes, or the influence of diagenesis on carbonate material.

The increase in $\delta^{13}C_{brac}$ values during the Floian–Dapingian interval is similar to what was observed in an Ordovician dataset from of the same region (Ainsaar et al., 2010). Prior research indicates that during the Dapingian the $\delta^{13}C_{brac}$ values are sporadically varying in the range of 0.5‰ to 1‰, displaying no distinct trend (the Baltic Carbon Isotopic Zone BC1 according to Ainsaar et al. 2010). The $\delta^{13}C_{brac}$ curve from the Darriwilian interval of Baltoscandian sections also includes a notable event called the Mid-Darriwilian Carbon Isotope Excursion (MDICE). This MDICE has been observed in Baltoscandian and globally in data collected from bulk carbonate samples (Rasmussen et al., 2016). The mid-Darriwilian Excursion (MDICE) occurs within the interval of the Kunda, Aseri, and Lasnamägi RSs over the entire region (Meidla et al., 2004; Ainsaar et al., 2007). The ascending limb of the MDICE, categorized as Zone BC2 in the classification of Ainsaar et al. (2010), spans a significant portion of the Kunda Regional Stage. The increase of $\delta^{13}C_{brac}$ values on the assumed level of Mid-Darriwilian Carbon Isotope Excursion (MDICE) remains minor in the studied succession, thus suggesting a gap equivalent to the highest values of the MDICE excursion in lower ramp sections, as previously documented by Ainsaar et al. (2010). In contrast to those from Baltoscandia, both the Argentinian and North American successions usually show noticeably lower $\delta^{13}C_{carb}$ values for the MDICE interval (Lindskog et al., 2019). These variations are probably caused by local processes (such as sediment reworking, slow seawater circulation, and organic matter remineralization) in addition to global disruption of the carbon cycle (e.g., Saltzman and Edwards, 2017). The low carbon isotopic curve within the lowermost part of the

Darriwilian Stage has been designated as the Lower Darriwilian Negative Isotopic Carbon Excursion (LDNICE) (Lehnert et al., 2014). However, this excursion is not documented in our dataset, likely due to a very condensed thickness of the whole Darriwilian, which reaches about 2 m.

The widely recognized HICE $\delta^{13}C_{bulk}$ excursion has been reported globally from different palaeocontinents (Kaljo et al., 2001). The precise start and end points of the HICE remain somewhat ambiguous. Within the *Metabolograptus extraordinarius* Zone, there is a gradual rise in $\delta^{13}C_{brac}$ values from the baseline, which corresponds to the time of glaciation in the early Hirnantian, e.g., Wangjiawan North Section (Chen et al., 2006; Gorjan et al., 2012). According to Brenchley et al., 2003, the difference in the highest $\delta^{13}C$ values of the HICE has been tentatively attributed to variation in depositional environments and diagenetic alteration or to the presence of unconformities. Plausible alternative explanations include the aquafacies effect proposed by Ainsaar et al. (2020) or impacts from a stratified water column (Bickert et al., 1997). Previous studies have recognized elevated $\delta^{13}C$ values in the Hirnantian in Estonia and adjacent areas, corresponding to the HICE rising to a peak of up to +7‰ (Ainsaar et al., 2010; **Paper 1**). In more complete sections, the rising and falling limbs of the HICE curves display a similarity, i.e., both are gradual, as observed in other Baltic sections studied using bulk rock samples, e.g., the Jurmala core (Ainsaar et al., 2010) as well as in coeval sections from several palaeocontinents e.g. south China (Chen et al., 2006; Ling et al., 2007), North America (Bergström et al., 2010) and elsewhere. The average $\delta^{13}C_{brac}$ curve generally agrees with the trends described, and the absence of data points in the Porkuni-Juuru regional stage transition interval is remarkable (Fig. 5) because of the gaps and the scarcity of fauna in this transition.

The potential of stable oxygen isotopic composition of sedimentary materials to indicate palaeotemperatures has been acknowledged for a long time (Urey, 1947). The majority of $\delta^{18}O_{brac}$ values in the present study lie within the range of approximately –7 to –0.5‰, generally suggesting a modest amount of change due to the degree of alteration by meteoric diagenesis. This Ordovician $\delta^{18}O$ dataset from Baltoscandia aligns with the established pattern of increasing $\delta^{18}O_{brac}$ values with decreasing age, as documented in previous studies (Trotter et al., 2008; Grossman & Joachimski, 2020). $\delta^{18}O_{brac}$ values decrease by 2‰ from the Hirnantian to the latest Llandovery (roughly –3‰ to –5‰), which is followed by an increase in late Silurian, e.g., Grossmann & Joachimski (2020). The $\delta^{18}O_{brac}$ trends indicate several glaciation and periods of deglaciation throughout the Ordovician-Silurian period (Brenchley et al., 1994). Since temperature is a fundamental component that regulates changes in oxygen isotopes, most of the $\delta^{18}O_{brac}$ shifts are interpreted as resulting from sea surface water temperature (Trotter et al., 2016).

In this study, the brachiopod calcite temperature values were calculated using the formula developed by Brand et al. (2019). This calculation assumes the potential preservation of the original marine carbonate isotopic composition, initially formed in seawater with a $\delta^{18}O$ value of –1‰.

The question of whether and to what extent the overall $\delta^{18}O$ trends could be explained in terms of palaeotemperatures is complex and has no straightforward answer. Secular variation in $\delta^{18}O$ may be affected by several factors beyond sea water temperature, including other factors, like salinity, the isotopic composition of seawater and mud composition, diagenetic alteration, vital effects, etc. (Munnecke et al., 2010; Swart, 2015). Some of these factors (e.g., isotopic composition of seawater, minute variations in salinity, the source location of mud) are difficult to assess, while trends in some others could be inferred from the analysis of properties of rocks and facies gradients. Brachiopods are likely the most plausible source of temperature information among calcareous fossils, and the existence of the secondary layer in Baltoscandian brachiopod shells indicates that vital effects are unlikely or minor. The secondary layer is more likely to develop in or near isotopic equilibrium with ambient seawater, unlike the primary shell layer (Ullmann et al., 2017). Notably, the results from our study show a more substantial alignment with modern temperatures and appear closer to them compared to values obtained from bulk material in earlier research. It is essential 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. The curve could be slightly shifted at some intervals if the seawater composition changed through time (e.g., during glacial episodes).

The temperature calculated from brachiopods from the Floian-Dapingian stages ranges from ~36 to 43 °C and from ~33 °C to 42 °C in the Dapingian–early Sandbian (Fig 7). Some of these values appear notably high and may seem unrealistic, but this is a well-documented problem. Some authors propose that primary seawater $\delta^{18}O$ values might have varied during this period (see, for example, Grossmann et al., 2020 and Trotter et al., 2008). The idea of excessively high minimum water temperatures is unlikely, as protein molecules cannot withstand prolonged temperature stress beyond 37 °C (Shields et al., 2003). Considering adjustments, our maximum temperature of ~40 °C, after adjusting for $\delta^{18}O_{seawater}$ errors and an analytical range of ±3 °C, is basically near the top limit of modern tropical temperatures. Well-preserved samples nevertheless show near-primary long-term $\delta^{18}O$ trends, even though Darriwilian seawater $\delta^{18}O$ values from Baltoscandia records imply that diagenesis may have impacted parts of the primary $\delta^{18}O$ ratios (Edward et al., 2022). A decline in the temperature values can be observed during the Darriwilian and Sandbian, bringing the temperature values down into the interval of 30 and 38 °C, which is not significantly different from modern tropical temperatures, considering possible error, ±3 °C. Temperature fluctuations ranging from 25 to 37 °C were calculated for the pre-Hirnantian Upper Ordovician brachiopods (Fig 7). The low $\delta^{18}O_{seawater}$ values contrast with suggested similarity to modern $\delta^{18}O_{seawater}$ values; the $\delta^{18}O$ values have risen by approximately 8‰ from the early Paleozoic to the present (Thiagarajan et al., 2024), emphasizing the necessity of reevaluating temperature records using oxygen isotope data. The results may suggest a possible connection between the long-term increase in the oxygen isotope composition of marine sedimentary rocks and global water interactions.

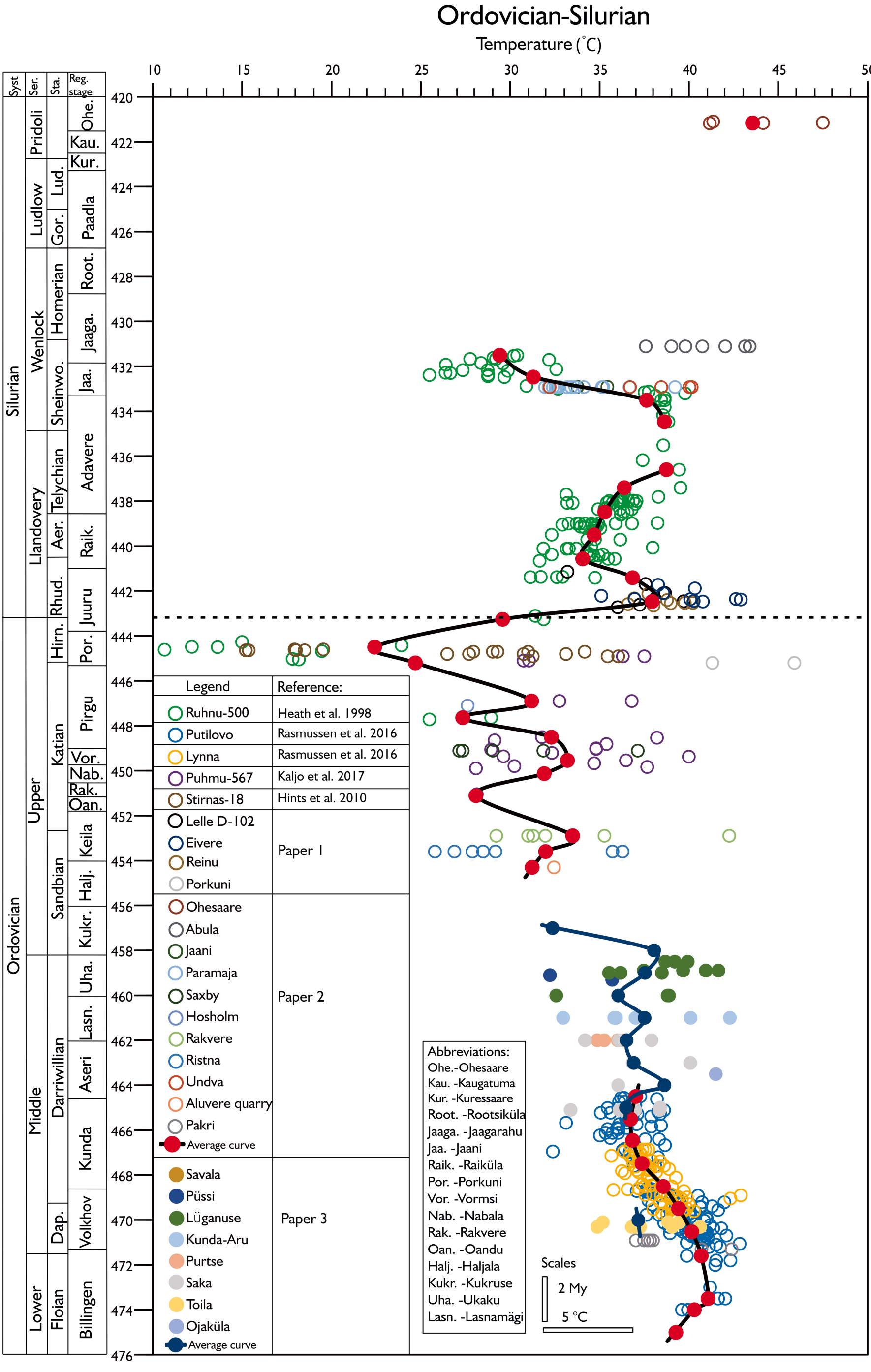

Fig. 7 Summary figure showing temperature based on oxygen isotope data. Temperatures are calculated from brachiopod data by the formula of Brand et al. (2019), assuming possible preservation of original marine carbonate isotopic composition formed in sea water of $\delta^{18}O$ value –1‰.

With the onset of the HICE, the temperature drops to 27 °C in the strata, corresponding to low sea level and a global regression. Shortly after that, an abrupt fall in the temperature to approximately 22 °C is observed in our averaged dataset, corresponding to the Hirnantian Glaciation. This trend aligns with widely accepted Hirnantian scenarios (Brenchley et al., 2003; Trotter et al., 2008; Finnegan et al., 2011). However, the large ice-volume component, which was clearly significant during the Hirnantian, may have affected the isotopic composition of seawater, making estimating the true temperature range difficult. The Hirnantian cooling phase coincided with a regional extinction (e.g., Meidla et al., 2020 and references therein).

The post-HICE temperature calculations reveal a two-step increase. Temperatures derived from brachiopods from the Rhuddanian Epoch mostly fall within the range of approximately 31 to 38 °C, with few exceptions, potentially resulting from altered bioclasts (see **Paper 1**). In the overlying strata (Aeronian and Telychian), temperatures range between ~30 and 38 °C (Fig. 7), not far from modern tropical temperatures. The temperature values derived from brachiopod calcite in the Sheinwoodian Age are notably lower, ranging between approximately 25 and 32 °C, thus corresponding to the Ireviken ICE. The temperatures calculated for the Přidoli (Ohesaare) Epoch range between approximately 39 and 43 °C, slightly surpassing modern values. The brachiopod calcite temperature values in Přidoli seem to better agree with the warming scenario of the late Silurian, where temperature values are rising as lower Ordovician. Our compiled data indicates a warming trend in the early Silurian (Llandovery), followed by a return to colder temperatures in the Sheinwoodian Age and a return to a warmer climate during the Přidoli Epoch (Grossman & Joachimski, 2020).

Our $\delta^{18}O_{brac}$ dataset suggests a steady cooling trend for the Middle Ordovician, which is nearly consistent with the trends proposed by Trotter et al. (2008) and Grossman & Joachimski (2020). Following the relatively warm late Katian, an abrupt worldwide climate cooling in the Hirnantian is evident in all comparative studies (Fig. 8) (Trotter et al., 2008; Grossman and Joachimski, (2020); Männik et al., 2021). The temperatures recorded from the Ordovician and Silurian are consistent with those derived from conodont apatite, considering the low-temperature values associated with the Hirnantian and early Silurian. Over the past decade, Trotter et al. (2008) and Finnegan et al. (2011) have reconstructed temperature trends for the Ordovician-Silurian periods based on clumped isotope palaeothermometry and $\delta^{18}O_{apatite}$. The results are comparable to those derived from $\delta^{18}O_{brac}$ and $\delta^{18}O_{bulk}$ values by Brenchley et al. (2003) and are consistent with the results from the Hirnantian interval. The early Silurian temperature values from the current study and Grossman & Joachimski (2020) are nearly consistent with the Middle to Late Silurian ranges, except for the Rhuddanian temperature values reflecting climatic instability prior to the return to equatorial temperatures corresponding to the present in the Wenlock (Fig. 8).

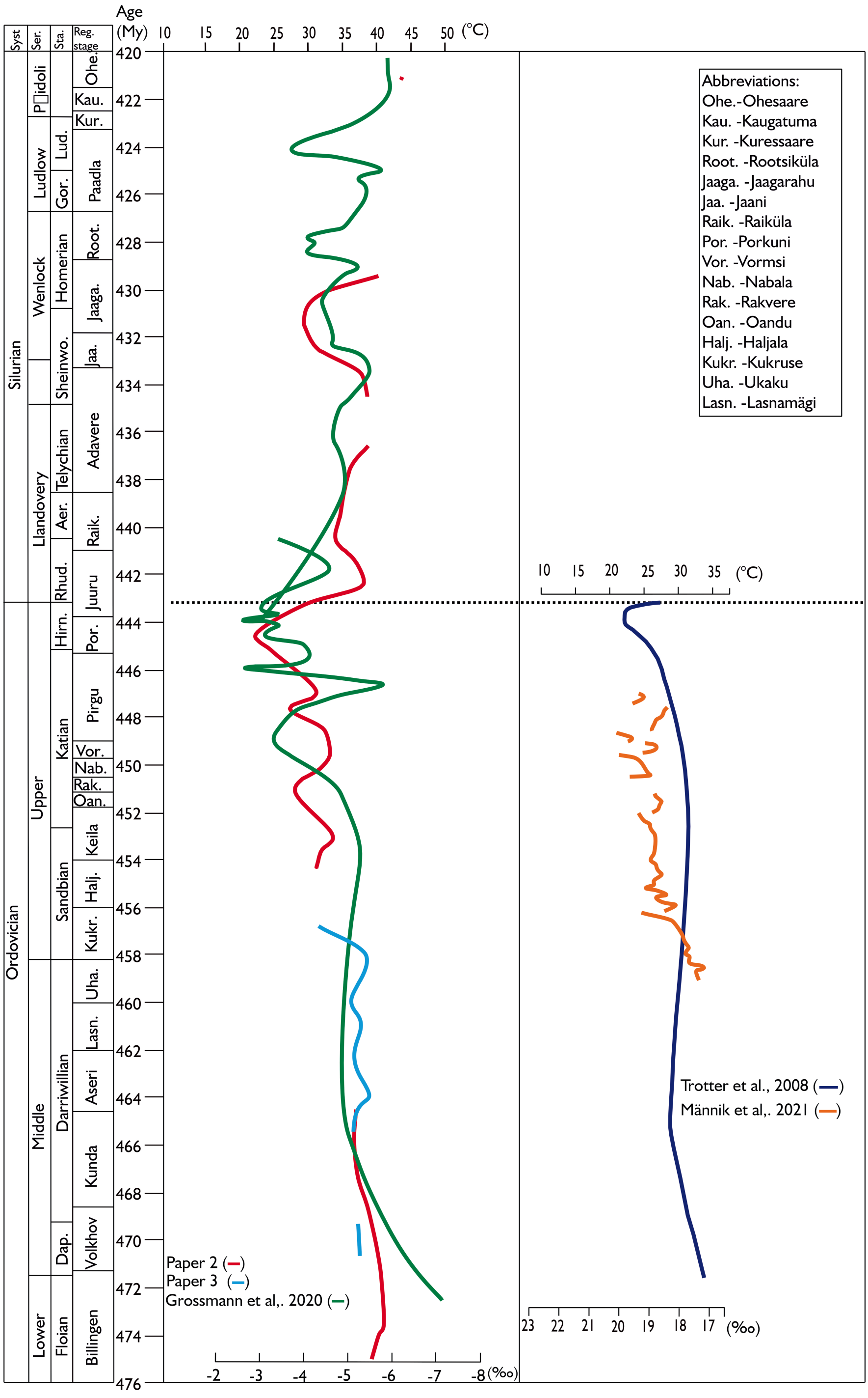

Fig. 8 Oxygen isotopic temperatures comparison of Ordovician-Silurian brachiopods (calcite) (Grossmann et al. 2020) and conodonts (phosphate) (from Männik et al., 2021 and Trotter et al., 2008) assuming seawater $\delta^{18}O$ of –1‰.

According to Männik et al., 2021, conodont-based $\delta^{18}O_{phos}$ studies from Estonia suggest that the pre-Hirnantian Late Ordovician period experienced a general cooling trend. This general trend also includes a more rapid climate cooling in the early Sandbian and a less intense cooling from the late Sandbian through the Katian. Temperature data from conodont-$\delta^{18}O_{phos}$ in Kukruse RS (lower Sandbian) marks an interval of the almost continuous cooling trend from 31–24 °C (Männik et al., 2021), reflecting the similar temperature drop ranging between 39–32 °C in the current study, with a difference of about 7 °C respectively. The fall in temperature continues until the end of Kukruse RS (mid-Sandbian). The middle Sandbian (late Kukruse RS) period corresponds to a regressive stage in basin development and a major Ordovician sea level lowstand (Nielsen, 2004). The temperature rise can be observed in the middle of Keila RS (upper Sandbian), followed by a fall in the low Katian, which shows a similar temperature trend in the current study. These findings are consistent with previous studies of a colder Late Ordovician climate preceding the Hirnantian (e.g., **Paper 1** and **Paper 2**). Our data and other recent studies (Männik et al., 2022) confirm that the global cooling trend seemingly overruled the expected warming trend (Meidla et al., 2023). The composite curve (Fig. 8) suggests a temperature decrease of about 9 °C from early Dapingian to early Sandbian. It is roughly comparable to the palaeotemperature data derived from $\delta^{18}O_{brac}$ and $\delta^{18}O_{bulk}$ values by Goldberg et al., 2021.

Some studies contend that there is no evidence of glaciation before the Hirnantian, and the Katian is marked by stable, generally warm climatic conditions (e.g., Shields et al., 2003). However, these studies do not entirely exclude the possibility of a cooler episode or glaciation during the earlier Sandbian Age. Even if the prevailing view supports a warm climate, there may still have been transient cooling events that could have led to glaciation, indicating a more complex climatic history than previously understood. Our data suggests that the late Darriwilian to earliest Sandbian was not very cold. On the contrary, it was a comparatively warm period compared to the following Late Ordovician Epoch. On the other hand, there was a sharp cooling in the early Sandbian, which peaked during the Late Kukruse. This agrees with conodont data from the same area (Männik et al., 2021).

For a considerable time, the idea of a gradual 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. However, our findings and other recent studies (Edward et al., 2022; Männik et al., 2022) support the notion that the global cooling trend appears to have surpassed the predicted warming (Meidla et al., 2023), overruled the influence arising from the latitudinal change. This is also in agreement with conodont data from the same area.

Our findings provide significant insights into the primary temperature trends in the carbonate-based palaeotemperature record from the eastern Baltoscandian region (Meidla et al., 2023; **Paper 2**), confirming a cooling trend throughout the Ordovician. Additionally, they indicate a temperature increase at the beginning of the Silurian, followed by an abrupt decline and a subsequent rise in the upper Silurian. Even if the absolute temperature values calculated from our data may not be precise and contain some uncertainty, the observed trends are still in good agreement with widely accepted temperature and climatic scenarios. For analyzing finer-scale climatic variability, more densely collected samples, ideally from fossil-rich drill cores, would be required for several intervals through the Ordovician-Silurian.

6. CONCLUSIONS

The current study evaluates stable isotopic data from brachiopods from the Ordovician and Silurian periods, focusing on the environmental and climatic changes in the Baltoscandian Palaeobasin during these times. Oxygen stable isotopic values obtained from brachiopod shells are considered a reliable proxy of palaeoclimate, providing information on temperature trends in ancient oceans. Using this approach, this study reconstructs a comprehensive palaeotemperature record for the Baltoscandian Palaeobasin. Our study expands upon earlier studies that showed brachiopod calcite's potential as a temperature proxy. The Ordovician and Silurian periods, marked by significant geological and biological events, provide a critical context for understanding long-term climate dynamics. The Baltoscandian Palaeobasin, with its well-preserved sedimentary sequences, is an ideal location for such a study.

1. The results indicate that the carbon and oxygen stable isotopic composition of Paleozoic brachiopods can be tentatively used for palaeoenvironmental interpretation. Although the absolute temperature values calculated from our data may not be precise, the observed trends are largely consistent with known global temperature and climatic trends. This alignment supports the reliability of brachiopod isotopic data in reconstructing past environmental conditions.

2. Multiple major $\delta^{13}C_{brac}$ excursions found in the Ordovician-Silurian on the Estonian Shelf are consistent with previously documented excursions in bulk carbonate stable isotopic curves. The increase in $\delta^{13}C_{brac}$ values during the Floian–Dapingian interval is similar to what was observed in an Ordovician dataset from the same region. The $\delta^{13}C_{brac}$ curve from the Darriwilian interval of Baltoscandian sections also includes a notable event called the Mid-Darriwilian Carbon Isotope Excursion (MDICE). This MDICE has been observed in Baltoscandian and globally in data collected from bulk carbonate samples. The widely recognized HICE δ^{13}Cbulk excursion has been reported globally from different palaeocontinents. Previous studies have recognized elevated δ^{13}C bulk and brachiopod values in the Hirnantian in Estonia and surrounding areas, corresponding to the HICE values rising to a peak of up to +7‰. Higher up in the section, the global Ireviken ICE Event was recognized and correlated with the Jaani regional stage in Estonia. Our average $\delta^{13}C_{brac}$ curve generally agrees with the trends of δ^{13}C from Baltoscandia and globally.

3. The oxygen isotope composition of fossil brachiopods reveals a general secular trend from the Early to Late Ordovician towards heavier δ^{18}O values. The $\delta^{18}O_{brac}$ data from Baltoscandia indicate warmer temperatures during the Early Ordovician (Floian), followed by a cooling trend towards the Middle Ordovician (Dapingian-Darriwilian) and cooler early Sandbian. During this epoch, average temperatures dropped by roughly 8 °C, indicating that the gradual cooling evidence is most likely a reflection of the global climate trend rather than caused by local environmental disturbances. The results of our

study agree with oxygen isotopic data from conodont phosphate and previous isotope studies in Laurentia and other palaeocontinents.

4. Following the relatively warm late Katian, a sharp global climate cooling in the Hirnantian is evident in all comparative studies. The Hirnantian glaciation HICE episode corresponds to a minimum temperature confined to the upper section of the Ärina Formation in the Porkuni Regional Stage. The post-HICE data suggest $\delta^{18}O_{brac}$ values start decreasing and a rising temperature trend during early Silurian. Another temperature minimum is evident in the strata reflecting the Ireviken Event, correlated with the Jaani Regional Stage in Estonia. The results of our study agree with oxygen isotopic studies of bulk and brachiopods.
5. Despite the plate tectonic drift of Baltica from higher southern palaeolatitudes to the tropical realm during the Ordovician-Silurian periods, the absolute temperature values calculated from our data reflect global temperature and climatic trends. This means that regional palaeoenvironmental changes in Baltoscandia were influenced by broader, global climatic shifts, suggesting a complex interplay between local and global factors in shaping the palaeoclimate. When we compare our data to 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. Although some studies emphasize the lack of evidence of glaciation before the Hirnantian and suggest stable, generally warm climatic conditions for the Katian, they do not rule out a possible cooler episode, or glaciation, in the earlier Sandbian. Our data suggests that the late Darriwilian to earliest Sandbian was not particularly cold. On the contrary, it was a comparatively warm period compared to the Late Ordovician that followed. However, there was a sharp cooling in the early Sandbian. These observations are in agreement with data from the same area.
6. Our study shows that $\delta^{18}O$ values from the brachiopod Ordovician-Silurian carbonates of Baltoscandian Palaeobasin generally agree with other data and thus may be considered a reliable proxy of palaeoenvironmental changes.

REFERENCES

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

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. https://doi.org/10.1016/j.palaeo.2010.01.003

Ainsaar, L., Truumees, J. & Meidla, T. 2015. The position of the Ordovician–Silurian boundary in Estonia tested by high-resolution $\delta^{13}C$ chemostratigraphic correlation. In *Chemostratigraphy*, 395–412 Elsevier. https://doi.org/10.1016/B978-0-12-419968-2.00015-7

Ainsaar, L., Tinn, O., Dronov, A., Kiipli, E., Radzevičius, S. & Meidla, T. 2020. Stratigraphy and facies differences of the Middle Darriwilian isotopic carbon excursion (MDICE) in Baltoscandia. *Estonian Journal of Earth Sciences*, 69: 214–222. https://doi.org/10.3176/earth.2020.16

Azmy, K., Veizer, J., Bassett, M. G. & Copper, P. 1998. Oxygen and carbon isotopic composition of Silurian brachiopods: implications for coeval seawater and glaciations. *Geological Society of America Bulletin*, 110: 1499–1512. https://doi.org/10.1130/0016-7606(1998)110<1499:OACICO>2.3.CO;2

Banner, J. L. & Hanson, G. N. 1990. Calculation of simultaneous isotopic and trace element variations during water-rock interaction with applications to carbonate diagenesis. *Geochimica et Cosmochimica Acta*, 54: 3123–3137. https://doi.org/10.1016/0016-7037(90)90128-8

Bartlett, R., Elrick, M., Wheeley, J. R., Polyak, V., Desrochers, A. & Asmerom, Y. 2018. Abrupt global-ocean anoxia during the Late Ordovician–early Silurian detected using uranium isotopes of marine carbonates. *Proceedings of the National Academy of Sciences*, 115: 5896–5901. https://doi.org/10.1073/pnas.1802438115

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 (4): 195–200. https://doi: 10.3176/earth.2014.18

Bergström, S. M., Schmitz, B., Saltzman, M, R., Huff, W. D., Finney, S. & Berry, W. 2010. The Upper Ordovician Guttenberg $\delta^{13}C$ excursion (GICE) in North America and Baltoscandia: occurrence, chronostratigraphic significance, and paleoenvironmental relationships. *Geological Society of America Special Papers*, 466: 37–67. http://dx.doi.org/10.1130/2010.2466(04)

Bickert, T., Pätzold, J., Samtleben, C. & Munnecke, A. 1997. Paleoenvironmental changes in the Silurian indicated by stable isotopes in brachiopod shells from Gotland, Sweden. *Geochimica et Cosmochimica Acta*, 61(13): 2717–2730. https://doi.org/10.1016/S0016-7037(97)00136-1

Bond, D. P. & Grasby, S. E. 2020. Late Ordovician mass extinction caused by volcanism, warming, and anoxia, not cooling and glaciation. *Geology*, 48: 777–781. https://doi.org/10.1130/G47377.1

Brand, U., Bitner, M. A., Logan, A., Azmy, K., Crippa, G., Angiolini, L., Colin, P., Griesshaber, E., Harper, E. M. & Ruggiero, E. T. 2019. Brachiopod-based oxygen-isotope thermometer: update and review. *Rivista Italiana di Paleontologia e Stratigrafia*, 125(3): 775–778. https://dx.doi.org/10.13130/2039-4942/12226

Brand, U. & Veizer, J. 1980. Chemical diagenesis of a multicomponent carbonate system; 1, Trace elements. *Journal of Sedimentary Research*, 50: 1219–1236. https://doi.org/10.1306/212F7BB7-2B24-11D7-8648000102C1865D

Brenchley, P, J., Marshall, J. D., Carden, G. A. F., Robertson, D. B. R., Long, D. G. F., Meidla, T., Hints, L. & Anderson, T. F. 1994. Bathymetric and isotopic evidence for a short-lived late Ordovician glaciation in a greenhouse period. *Geology*, 22(4): 295–298. https://doi.org/10.1130/0091-7613(1994)022<0295:BAIEFA>2.3.CO;2.

Brenchley, P. J., Carden, G., Hints, L., Kaljo, D., Marshall, J., Martma, T., Meidla, T. & Nõlvak, J. 2003. High-resolution stable isotope stratigraphy of Upper Ordovician sequences: Constraints on the timing of bioevents and environmental changes associated with mass extinction and glaciation. *Geological Society of America Bulletin*, 115: 89–104. https://doi.org/10.1130/0016-7606(2003)115<0089:HRSISO>2.0.CO;2

Brenchley, P. J. 2004. End Ordovician Glaciation. In Webby, W. D., Paris, F., Droser, M. L. & Parcival, I. G. (eds), *The great Ordovician biodiversification event,* 81–3. New York: Columbia University Press. https://doi.org/10.7312/webb12678-010

Buggisch, W., Joachimski, M. M., Lehnert, O., Bergström, S. M., Repetski, J. E. & Webers, G. F. 2010. Did intense volcanism trigger the first Late Ordovician icehouse? *Geology*, 38: 327–330. https://doi.org/10.1130/G30577.1

Chen, X., Rong, J., Fan, J., Zhan, R., Mitchell, C. E., Harper, D. A., Melchin, M. J., Peng, A., Finney, S. C. & Wang, X. 2006. The Global Boundary Stratotype Section and Point (GSSP) for the base of the Hirnantian Stage (the uppermost of the Ordovician System). *Episodes Journal of International Geoscience*, 29(3): 183–196. https://doi.org/10.18814/epiiugs/2006/v29i3/004

Cocks, L. R. M. & Torsvik, T.H. 2005. Baltica from the late Precambrian to mid-Paleozoic times: the gain and loss of a terrane's identity. *Earth–Science Reviews*, 72: 39–66. https://doi.org/10.1016/j.earscirev.2005.04.001

Clarke, A. 2014. The thermal limits to life on Earth. *International Journal of Astrobiology*, 13(2): 141–154. https://doi.org/10.1017/S1473550413000438

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

Epstein, S., Buchsbaum, R., Lowenstam, H. & Urey, H. C. 1951. Carbonate-water isotopic temperature scale. *Geological Society of America Bulletin*, 62: 417–426. https://doi.org/10.1130/0016-7606(1951)62[417:CITS]2.0.CO;2

Edwards, C. T. & Saltzman, M. R. 2016. Paired carbon isotopic analysis of Ordovician bulk carbonate ($\delta^{13}C_{carb}$) and organic matter ($\delta^{13}C_{org}$) spanning the Great Ordovician Biodiversification Event. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 458: 102–117. https://doi.org/10.1016/j.palaeo.2015.08.005

Edward, O., Korte, C., Ullmann, C. V., Colmenar, J., Thibault, N., Bagnoli, G., Stouge, S. & Rasmussen, C. M. 2022. A Baltic perspective on the Early to Early Late Ordovician $\delta^{13}C$ and $\delta^{18}O$ records and its paleoenvironmental significance. *Paleoceanography and Paleoclimatology*, 37(3): 1–26, e2021PA004309. https://doi.org/10.1029/2021PA004309

Finnegan, S., Bergmann, K., Eiler, J. M., Jones, D. S., Fike, D. A., Eisenman, I., Hughes, N. C., Tripati, A. K. & Fischer, W. W. 2011. The magnitude and duration of Late Ordovician–Early Silurian glaciation. *Science*, 331: 903–906. https://doi.org/10.1126/science.1200803

Goldberg, S. L., Present, T. M., Finnegan, S. & Bergmann, K. D. 2021. A high-resolution record of early Paleozoic climate: *Proceedings of the National Academy of Sciences*, 118(6), e2013083118. https://doi.org/10.1073/pnas.2013083118

Goldman, D., Sadler, P. M., Leslie, S. A., 2020. Chapter 20. The Ordovician Period. In Gradstein, F. M., Ogg, J. G., Schmitz, M. D. & Ogg, G. M. (eds), *Geologic Time Scale 2020 (2),* 631–694. Elsevier. https://doi.org/10.1016/B978-0-12-824360-2.00020-6

Gorjan, P., Kaiho, K., Fike, D. A. & Xu, C. 2012. Carbon-and sulfur-isotope geochemistry of the Hirnantian (Late Ordovician) Wangjiawan (Riverside) section, South China: Global correlation and environmental event interpretation. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 337: 14–22. https://doi:10.1016/j.palaeo.2012.03.021

Grossman, E. L. 2012. Applying oxygen isotope palaeothermometry in deep time. *The Paleontological Society Papers*, 18: 39–68. https://doi.org/10.1017/S1089332600002540

Grossman, E. & Joachimski, M. 2020. Oxygen isotope stratigraphy. In Gradstein, F. M., Ogg, J. G., Schmitz, M. D. & Ogg, G. M. (eds), *Geologic Time Scale 2020 (1)*, 279–307. Elsevier. https://doi.org/10.1016/B978-0-12-824360-2.00010-3

Hammarlund, E. U., Dahl, T. W., Harper, D. A., Bond, D. P., Nielsen, A. T., Bjerrum, C. J., Schovsbo, N. H., Schönlaub, H. P., Zalasiewicz, J. A. & Canfield, D. E. 2012. A sulfidic driver for the end-Ordovician mass extinction. *Earth and Planetary Science Letters*, 331: 128–139. https://doi.org/10.1016/j.epsl.2012.02.024

Harris, M. T., Sheehan, M., Ainsaar, L., Hints, L., Männik, P., Nõlvak, J. & Rubel, M. 2004. Upper Ordovician sequences of western Estonia. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 210: 135–148. https://doi.org/10.1016/j.palaeo.2004.02.045

Heath, R. J., Brenchley, J. & Marshall, J. D. 1998. Early Silurian carbon and oxygen stable-isotope stratigraphy of Estonia: implications for climate change. *Silurian cycles – Linkages of dynamic stratigraphy with atmospheric, oceanic and tectonic changes. New York State Museum Bulletin*, 491: 313–327.

Hints, L., Hints, O., Kaljo, D., Kiipli, T., Männik, P., Nõlvak, J. & Pärnaste, H. 2010. Hirnantian (latest Ordovician) bio-and chemostratigraphy of the Stirnas-18 core, western Latvia. *Estonian Journal of Earth Sciences*, 59: 1–24. https://doi.org/10.3176/earth.2010.1.01

Hints, O., Ainsaar, L., Lepland, A., Liiv, M., Männik, P., Meidla, T., Nõlvak, J. & Radzevičius, S. 2023. Paired carbon isotope chemostratigraphy across the Ordovician–Silurian boundary in central East Baltic: regional and global signatures. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 624: 111640. https://doi.org/10.1016/j.palaeo.2023.111640

Hood, A. V. S., Planavsky, N. J., Wallace, M. W. & Wang, X. 2018. The effects of diagenesis on geochemical palaeoredox proxies in sedimentary carbonates. *Geochimica et Cosmochimica Acta*, 232: 265–287. https://doi.org/10.1016/j.gca.2018.04.022

Huff, W. D., Bergström, S. M. & Kolata, D. R. 1992. Gigantic Ordovician volcanic ash fall in North America and Europe: biological, tectonomagmatic, and event-stratigraphic significance. *Geology*, 20(10): 875–878. https://doi.org/10.1130/0091-7613(1992)020<0875:GOVAFI>2.3.CO;2

Immenhauser, A., Kenter, J. A., Ganssen, G., Bahamonde, J. R., Van Vliet, A. & Saher, M. H. 2002: Origin and significance of isotope shifts in Pennsylvanian carbonates (Asturias, NW Spain). *Journal of Sedimentary Research*, 72: 82–94. https://doi.org/10.1306/051701720082

Jochum, K. P., Wilson, S. A., Abouchami, W., Amini, M., Chmeleff, J., Eisenhauer, A., Hegner, E., Iaccheri, L. M., Kieffer, B., Krause, J., Mcdonough, W. F., Mertz-Kraus, R., Raczek, I., Rudnick, R. L., Scholz, D., Steinhoefel, G., Stoll, B., Stracke, A., Tonarini, S., Weis, D., Weis, U. & Woodhead, J. D. 2011. GSD-1G and MPI-DING reference glasses for in situ and bulk isotopic determination. *Geostandards and Geoanalytical Research*, 35(2): 193–226. https://doi.org/10.1111/j.1751-908X.2010.00114.x

Jacobsen, S. B., Kaufman, A. J., 1999. The Sr, C and O isotopic evolution of Neoproterozoic seawater. *Chemical Geology*, 161: 37–57. https://doi.org/10.1016/S0009-2541(99)00080-7

Kaljo, D., Hints, L., Martma, T. & Nõlvak, J. 2001. Carbon isotope stratigraphy in the latest Ordovician of Estonia. *Chemical Geology*, 175: 49–59. https://doi.org/10.1016/S0009-2541(00)00363-6

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(1–2): 138–155.

Kaljo, D., Hints, L., Martma, T. & Nõlvak, J. 2017. A multiproxy study of the Puhmu core section (Estonia, Upper Ordovician): consequences for stratigraphy and environmental interpretation. *Estonian Journal of Earth Sciences*, 66: 77–92. https://doi.org/10.3176/earth.2017.08

Lehnert, O., Meinhold, G., Wu, R., 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(4): 277–286. https://doi.org/10.3176/earth.2014.31

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(2): 204–219. https://doi.org/10.1111/let.12307

Ling, H. F., Feng, H. Z., Pan, J. Y., Jiang, S. Y., Chen, Y. Q. & Chen, X. 2007. Carbon isotope variation through the Neoproterozoic Doushantuo and Dengying Formations, South China: implications for chemostratigraphy and paleoenvironmental change. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 254: 158–174. https://doi.org/10.1016/j.palaeo.2007.03.023

Männik, P., Loydell, D. K., Nestor, V. & Nõlvak, J. 2015. Integrated Upper Ordovician–lower Silurian biostratigraphy of the Grötlingbo–1 core section, Sweden. *GFF*, 137(3): 226–244. https://doi.org/10.1080/11035897.2015.1042032

Männik, P., Lehnert, O., Nõlvak, J. & Joachimski, M. M. 2021. Climate changes in the pre-Hirnantian Late Ordovician based on $\delta^{18}O_{phos}$ studies from Estonia. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 569: 110347. https://doi.org/10.1016/j.palaeo.2021.110347

Männik, P., Paiste, T. & Meidla, T. 2022. Sandbian (Late Ordovician) conodonts in Estonia: distribution and biostratigraphy. *GFF*, 144(1): 9–23. https://doi.org/10.1016/j.palaeo.2021.110347

Meidla, T., Ainsaar, L. & Tinn, O. 2004. Middle and Upper Ordovician stable isotope stratigraphy across the facies belts in the East Baltic. In Hints, O. & Ainsaar, L (eds), *WOGOGOB 2004, 8th Meeting of the Working Group on Ordovician Geology of Baltoscandia, Conference Materials, Abstracts and Field Guidebook,* 11–12. Tartu University Press Tartu.

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

Meidla, T., Truuver, K., Tinn, O. & Ainsaar, L. 2020. Ostracods of the Ordovician–Silurian boundary beds: Jūrmala core (Latvia) and its implications for Baltic stratigraphy. *Estonian Journal of Earth Sciences*, 69: 233–247. https://doi.org/10.3176/earth.2020.20

Meidla, T., Ainsaar, L., Hints, O. & Radzevičius, S. 2023. Ordovician of the Eastern Baltic palaeobasin and the Tornquist Sea margin of Baltica. *Geological Society Special Publications*, 532: 317–343. https://doi.org/10.1144/SP532–2022–14

Muehlenbachs, K. 1998. The oxygen isotopic composition of the oceans, sediments and the seafloor: *Chemical Geology*, 145: 263–273. https://doi.org/10.1016/S0009-2541(97)00147-2

Munnecke, A., Calner, M., Harper, D. A. & Servais, T. 2010. Ordovician and Silurian sea–water chemistry, sea level, and climate: a synopsis. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 296: 389–413. https://doi.org/10.1016/j.palaeo.2010.08.001

Nielsen, A. T. 2004. Ordovician sea level changes: a Baltoscandian perspective. In Webby, W. D., Paris, F., Droser, M. L. & Parcival, I. G. (eds), *The great Ordovician biodiversification event,* 84–94. Columbia University Press. https://doi.org/10.7312/webb12678–011

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

Paton, C., Hellstrom, J., Paul, B., Woodhead, J. & Hergt, J. 2011. Iolite: Freeware for the visualisation and processing of mass spectrometric data. *Journal of Analytical Atomic Spectrometry*, 26(12): 2508–2518. https://doi:10.1039/c1ja10172b

Pörtner, H. O. 2001. Climate change and temperature-dependent biogeography: Oxygen limitation of thermal tolerance in animals. *Naturwissenschaften*, 88: 137–46. https://doi.org/10.1007/S001140100216

Quinton, P. C., Law, S., MacLeod, K. G., Herrmann, A. D., Haynes, J. T. & Leslie, S. A. 2018. Testing the early Late Ordovician cool-water hypothesis with oxygen isotopes from conodont apatite. *Geological Magazine*, 155: 1727–1741. https://doi.org/10.1017/S0016756817000589

Rasmussen, C. M. O., 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: 1–9. https://doi.org/10.1038/srep18884

Rosenau, N. A., Herrmann, A. D. & Leslie, S. A. 2012. Conodont apatite $\delta^{18}O$ values from a platform margin setting, Oklahoma, USA: implications for initiation of Late Ordovician icehouse conditions. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 315: 172–180. https://doi.org/10.1016/j.palaeo.2011.12.003

Saltzman, M. R. & Young, S.A. 2005. Long-lived glaciation in the Late Ordovician? Isotopic and sequence-stratigraphic evidence from western Laurentia. *Geology*, 33: 109–112. https://doi.org/10.1130/G21219.1
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. https://doi.org/10.1016/j.epsl.2017.02.011
Servais, T., Harper, D. A., Munnecke, A., Owen, A. W. & Sheehan, P. M. 2009. Understanding the Great Ordovician Biodiversification Event (GOBE): Influences of palaeogeography, palaeoclimate, or palaeoecology. *GSA Today*, 19(4), 4–10. https://doi.org/10.1130/GSATG37A.1
Sheehan, M. 2001. The late Ordovician mass extinction. *Annual Review of Earth and Planetary Sciences*, 29: 331–364. https://doi.org/10.1146/annurev.earth.29.1.331
Shields, G. A., Carden, G. A., Veizer, J., Meidla, T., Rong, J. Y. & Li, R. Y. 2003. Sr, C, and O isotope geochemistry of Ordovician brachiopods: A major isotopic event around the Middle-Late Ordovician transition: *Geochimica et Cosmochimica Acta*, 67: 2005–2025. https://doi.org/10.1016/S0016-7037(02)01116-X
Swart, K. J. S. 2015. The geochemistry of carbonate diagenesis. *The past, present and future, Sedimentology*, 62: 1233–1304. https://doi.org/10.1111/sed.12205
Thiagarajan, N., Lepland, A., Ryb, U., Torsvik, T. H., Ainsaar, L., Hints, O. & Eiler, J. 2024. Reconstruction of Phanerozoic climate using carbonate clumped isotopes and implications for the oxygen isotopic composition of seawater. *Proceedings of the National Academy of Sciences*, 121(36), e2400434121. https://doi.org/10.1073/pnas.2400434121
Torsvik, T. H. & Rehnström, E. F. 2003. The Tornquist Sea and Baltica–Avalonia docking. *Tectonophysics*, 362(1–4), 67–82. https://doi.org/10.1016/S0040-1951(02)00631–5
Torsvik, T. H. & Cocks, L. R. M. 2011. The Palaeozoic palaeogeography of central Gondwana. *Geological Society, London, Special Publications,* 357(1), 137–166. https://doi.org/10.1144/SP357.8
Trotter, J. A., Williams, I. S., Barnes, C. R., Lécuyer, C. & Nicoll, R. S. 2008. Did cooling oceans trigger Ordovician biodiversification? Evidence from conodont thermometry. *Science*, 321: 550–554. https://doi.org/10.1126/science.1155814
Trotter, J. A., Williams, I. S., Barnes, C. R., Männik, P. & Simpson, A. 2016. New conodont $\delta^{18}O$ records of Silurian climate change: implications for environmental and biological events. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 443: 34–48. https://doi.org/10.1016/j.palaeo.2015.11.011
Truuver, K. & Meidla, T. 2015. A Hirnantian deep-water refuge for warm-water ostracods in Baltoscandia. *Geological Quarterly*, 59(4), 738–749. https://doi.org/10.7306/gq.1258
Ullmann, C. V., Frei, R., Korte, C. & Lüter, C. 2017. Element/Ca, C and O isotope ratios in modern brachiopods: Species-specific signals of biomineralization. *Chemical Geology*, 460: 15–24. https://doi.org/10.1016/j.chemgeo.2017.03.034
Urey, H. C. 1947. The thermodynamic properties of isotopic substances. *Journal of the Chemical Society*, 562–581. https://doi.org/10.1039/jr9470000562
Veizer, J., Ala, D., Azmy, K., Bruckschen, P., Buhl, D., Bruhn, F., Carden, G. A., Diener, A., Ebneth, S. & Godderis, Y. 1999. $^{87}Sr/^{86}Sr$, $\delta^{13}C$ and $\delta^{18}O$ evolution of Phanerozoic seawater. *Chemical Geology*, 161: 59–88. https://doi.org/10.1016/S0009–2541(99)00081–9

Woodhead, J., Hellstrom, J., Hergt, J., Greig, A. & Maas, R. 2007. Isotopic and elemental imaging of geological materials by laser ablation Inductively Coupled Plasma mass spectrometry. *Journal of Geostandards and Geoanalytical Research*, 31: 331–343. https://doi.org/10.1111/j.1751-908X.2007.00104.x

Zhang, J., Lyons, T. W., Li, C., Fang, X., Chen, Q., Botting, J. & Zhang, Y. 2022. What triggered the Late Ordovician mass extinction (LOME)? Perspectives from geobiology and biogeochemical modelling. *Global and Planetary Change*, 216: 103917. https://doi.org/10.1016/j.gloplacha.2022.103917

SUMMARY IN ESTONIAN

Paleotemperatuuri rekonstrueerimine Baltoskandia Ordoviitsiumi ja Siluri käsijalgsete kojamaterjali stabiilsete hapnikuisotoopide põhjal

Käesoleva töö üldiseks eesmärgiks on hinnata käsijalgse koja kaltsiidi sobivust paleotemperatuuri informatsiooni allikana, arvestades selle kaltsiidi vastupidavust diageneesile. Uurimistöös käsitletakse ka globaalseid ja piirkondlikke jahenemise trende Ordoviitsiumi ja Siluri ajastul ja olulisi kliimamuutusi, mis kulmineerusid Hilis-Ordoviitsiumis Hirnanti jäätumisena. Eesmärgid hõlmavad ka $\delta^{13}C$ ja $\delta^{18}O$ isotoopekskursioonide korreleerimist varasemate uuringute tulemustega, esialgse kaltsiidi-põhise paleotemperatuuri kõvera koostamist Baltoskandia regiooni kohta ning hinnangu andmist sellele, kas käsijalgsete kaltsiit üldse peegeldab usaldusväärselt mineviku temperatuure. Selle uuringu hüpoteesid keskenduvad erinevate jahenemisfaaside esinemisele Ordoviitsiumi ja Siluri ajastu vältel ning Baltoskandia paleotemperatuuri andmete sarnasusele teiste piirkondade põhjal postuleeritud globaalsete kliimamuutustega.

Fennoskandia kilbi lõunanõlval asuva Eesti vanaaegkonna läbilõigetes on laialt levinud hästi säilinud fossiilide ja vähese termilise mõjutusega settekivimid. Ala geoloogilist ehitust kujundavad Paleo- ja Mesoproterosoikumi vanusega kristalne aluskord ning seda katvad Neoproterosoikumi ja Paleosoikumi settekivimid, kusjuures Ordoviitsiumi ja Siluri ajastul on domineerinud karbonaatne settimine. Kambriumi ajastul eraldus Baltica paleokontinent Gondwanast ning selle triivimisega paleoekvaatori poole Kesk- ja Hilis-Ordoviitsiumi vältel kaasnes vulkaaniline tegevus. Baltoskandia paleobasseinis on eristatud kolm peamist fatsiaalset vööndit mis kajastasid erinevaid merelisi settekeskkondi. Siluri ajastul iseloomustasid Eesti ala valdavalt madalmerelised tingimused ja meretaseme kõikumisi peegeldavad fatsiaalsed muutused. Põhja-Eesti ja Leedu fatsiaalsed vööndid esindasid Baltoskandia paleobasseini kõige madalamaveelisi piirkondi ja neid iseloomustab eelkõige karbonaatsete kivimite lai levik geoloogilises läbilõikes. Lõuna-Eestit, Lääne-Läti ja Rootsit hõlmav Kesk-Baltoskandia fatsiaalne vöönd vastab sügavamale šelfialale, mille piires kuhjusid laialdaselt varieeruva karbonaatsusega savimudad. Paleobasseini sügavaimat osa, Skandinaavia lõunaosas levivat Skåne fatsiaalset vööndit iseloomustab tänapäeval graptoliite sisaldavate mustade kiltade laialdane levik. Käesoleva töö jaoks Eestist kogutud materjal pärineb paleobasseini rannalähedasematest piirkondadest, kuid kasutatud on ka varem avaldatud materjale teistest piirkondadest.

Paljanditest ja puursüdamikest kogutud käsijalgsete kojad ja nende fragmendid (mõõtmed valdavalt 3–10 mm) pulbristati stabiilsete isotoopide analüüsimiseks massispektromeetrilisel meetodil ning analüüsiti $\delta^{13}C$ ja $\delta^{18}O$ väärtusi VPDB standardi suhtes. Paleotemperatuuride arvutamiseks kasutati $\delta^{18}O_{brac}$ väärtusi valemis $T°C = 17{,}3750–4{,}2535\ (\delta c\text{-}\delta w)\ +0{,}1473\ (\delta c\text{-}\delta w)^2$, lähtudes eeldusest, et karbonaatsed kojad on moodustunud merevees, mille $\delta^{18}O$ algne väärtus oli –1‰. Mikroelementide kontsentratsiooni mõõtmised viidi läbi laserablatsiooniga induktiivselt sidestatud plasma massispektromeetriga (LA-ICP-MS), koos nõutava standardite kalibreerimisega. Fossiilse materjali säilivuse kontrolliks analüüsiti magneesiumi, mangaani, strontsiumi ja uraani sisaldusi kodade kaltsiidis. Nende mikroelementide kontsentratsioonid uuritud materjalis sarnanesid tänapäevaste käsijalgsete kojamaterjali koostisele, mis viitab uuritud kodade heale säilivusele. Diageneetilisi mõjusid isotoopkoostisele hinnati ka käsijalgsete kojamaterjali $\delta^{13}C$ ja $\delta^{18}O$ vahelist sõltuvust kirjeldava ristdiagrammi alusel, mis näitab hilisemat põhjavee mõju karbonaatide koostisele. Käesoleva uuringu diagrammid ei peegelda enamuse leiukohtade puhul selget kovariatsiooni $\delta^{13}C$ ja $\delta^{18}O$ väärtuste vahel, mis viitab samuti materjali suhteliselt heale säilivusele.

Baltoskandia Ordoviitsiumi ja Siluri läbilõigete käsijalgsete $\delta^{13}C$ ja $\delta^{18}O$ väärtused kajastavad selgeid trende, mida saab kõrvutada hästi uuritud kogukivimi süsiniku ja hapniku isotoopkoostise trendidega. Nende läbilõigete karbonaatkivimite $\delta^{13}C$ kõveral ilmnevaid ekskursioone tõlgendatakse sageli globaalsete või piirkondlike keskkonnamuutuste kajastajatena. Mitmed Ordoviitsiumi ja Siluri ladestu $\delta^{13}C$ ekskursioonid on dokumenteeritud erinevates paljandites ja puursüdamikes üle kogu Baltoskandia regiooni ning mõned neist on jälgitavad mitmel paleokontinendil, nagu näiteks Hirnanti süsiniku isotoopekskursioon (HICE) ja ka Irevikeni ekskursioon Siluris. Käesolevas töös uuritud käsijalgsete kodade $\delta^{13}C$ väärtused peegeldavad suhteliselt hästi varem teada olevate kogukivimi (*bulk rock*) süsinikukõverate trende ja ekskursioone.

Uuritud Ordoviitsiumi läbilõigetes suurenevad käsijalgsete kodade $\delta^{18}O$ väärtused järkjärgult Flo lademest kuni Hirnanti lademeni. Flo-Darriwili intervallis tõusevad $\delta^{18}O$ väärtused –6 ‰ tasemelt kuni –5 ‰-ni. Sandby ja Katy lademes hajuvad väärtused vahemikus –6 ‰ kuni –3 ‰. Llandovery ladestiku basaalkihtides naaseb isotoopkõver madalate väärtuste juurde. Siluris ladestus on võimalik täheldada $\delta^{18}O$ väärtuste väikest tõusu Rhuddani ülemistes kihtides, sellele järgneb langus kuni Telychi-Sheinwoodi piirini ja tõus Sheinwoodi keskel, enne kui isotoopsuhte väärtused Přidolis uuesti langevad.

Andmed viitavad olulistele kliimamuutustele Ordoviitsiumi ja Siluri ajastul ja peegeldavad jäätumissündmusi, millele järgnesid soojemad perioodid. Käsijalgsete kaltsiidil põhinevad merevee temperatuuriarvutused annavad Flo ja Dapingi eal väärtusi vahemikus 36–43 °C, millele järgneb langus 30–38 °C-ni Darriwili ja Sandby eal. Hirnanti jäätumise algusega seondub temperatuurilangus ligikaudu 27 °C-ni ning jäätumise vältel edasi kuni umbes 22 °C-ni. Jahedale Hirnanti eale järgses temperatuuride kaheastmeline tõus: Rhuddani temperatuurid jäid vahemikku 31–38 °C, sellele järgnes taas jahenemine Sheinwoodi eal ja uus soojenemine Přidoli ajastikul. Temperatuuriarvutuste tulemused sõltuvad aga tugevalt iidse merevee eeldatavast $\delta^{18}O$ väärtusest. Mõnes hiljutises mudelis on pakutud, et $\delta^{18}O_{seawater}$ oli Ordoviitsiumi kasvuhooneperioodi jaoks madalam kui käesolevas töös ja varasemates rekonstruktsioonides kasutatud –1 ‰. Näiteks Goldberg et al. (2021) pakkusid välja väärtuse –1,4‰ ja Thiagarajan et al. (2024) isegi –4‰ kuni –5,7‰. Viimati mainitud väärtuse korral võisid arvutuslikud merepinna paleotemperatuurid olla kuni 10 °C madalamad kui käesolevas töös pakutud väärtused. Siiski on oluline märkida, et temperatuurimuutuste trendid ei sõltu nendest aruteludest, kuna hapniku residentsusaeg jäävabades ookeanides on pikem kui uuritud ajavahemik ja merevee isotoopkoostis pidi olema nendel ajastutel seetõttu üsna stabiilne.

Käsijalgse kojamaterjali analüüsil põhinevad temperatuuritrendid langevad üldjoontes kokku varem kirjeldatud globaalsete muutustega. Käsijalgsete $\delta^{18}O_{brach}$ andmekogum kajastab pidevat jahtumistrendi läbi kogu Kesk-Ordoviitsiumi ning on heas kooskõlas Grossmani ja Joachimski (2020) ning Trotteri jt. (2008) tulemustega. Nii käesoleva uuringu kui varasemate tööde andmed viitavad suhteliselt stabiilsele ja soojale Katy eale (Shields et al., 2003), millele järgnes märkimisväärne ülemaailmne jahenemine Hirnanti eal (nt Trotter et al., 2008; Grossman ja Joachimski, 2020), mis langeb ajaliselt kokku väljasuremissündmustega erinevates regioonides.

Saadud käsijalgsete temperatuuriarvutused on kooskõlas konodondiapatiidi analüüsil põhinevate andmetega, näidates sarnaseid madalaid temperatuuriväärtusi nii Hirnanti eal kui ka Siluri algul (Grossmani ja Joachimski 2020). Käesolevas uuringus täheldatud temperatuur langus 39 °C-lt 32 °C-le Sandby lõpul ja Katy eal on sarnane Männiku jt. (2021) poolt Eesti läbilõigetes konodontide isotoopkoostise kaudu kirjeldatud temperatuurimuutusega. Nii käsijalgsete kui ka konodontide andmed Eesti läbilõigetest toetavad varem teistelt paleokontinentidelt teada olevaid tulemusi Hilis-Ordoviitsiumi jahenemise kohta enne Hirnanti algust ning see kinnitab, et globaalne jahtumistrend sel perioodil elimineeris Baltoskandia mere eeldatava soojenemise, mida on paljudes varasemates töödes oletatud seoses Baltika paleokontinendi teadaoleva liikumisega madalamatele paleolaiuskraadidele.

Kokkuvõtteks võib öelda, et käesoleva uuringu andmed on kooskõlas Ordoviitsiumi üldise jahenemise trendiga, millele järgnes temperatuuri tõus Siluri alguses, uus jahenemine ja hilisem taassoojenemine. Kuigi käesolevas töös esitatud absoluutsed temperatuurid on diskuteeritavad ja võivad sisaldada süstemaatilist ebatäpsust, on kirjeldatud trendid kooskõlas Ordoviitsiumi-Siluri üldtunnustatud kliimamuutuste stsenaariumitega. Ordoviitsiumi ja Siluri Baltoskandia paleobasseini käsijalgsete karbonaatide $\delta^{18}O$ väärtustel põhinevate temperatuurihinnangute üldine kokkulangevus muude paleokliima andmetega kinnitab brahhiopoodide biokaltsiidi usaldusväärsust minevikus aset leidnud keskkonnamuutuste kajastajana.

ACKNOWLEDGEMENTS

First and foremost, I would like to express my deepest gratitude to my supervisors, Professor Tõnu Meidla and Professor Leho Ainsaar, for their continuous support, mentorship and encouragement throughout my PhD research. Additionally, I want to sincerely thank Professor Kalle Kirsimäe for all his help and advice. I am grateful to the entire staff of the Department of Geology for their assistance and for providing the resources necessary for completing this work. Also, a heartfelt thank you goes to my colleagues and friends for their encouragement and suggestions. Finally, I am deeply thankful to my family for their unwavering support and understanding during this journey.

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Gul, B., Ainsaar, L. & Meidla, T. 2023**.** High resolution carbon and oxygen isotopes of the Early Ordovician-late Silurian of the Baltica: Implications for palaeoenvironmental changes and palaeotemperature trends. Geological Society of America Abstracts with Programs. Vol. 55, No. 6, 2023. 15–18 October Pittsburg, Pennsylvania, USA. http://doi: 10.1130/abs/2023AM-389596

Gul, B., Ainsaar, L. & Meidla, T. 2024. Baltoscandian Ordovician and Silurian brachiopod carbon and oxygen stable isotope trends: implications for palaeoenvironmental and palaeotemperature changes. *Geological Quarterly*, 68–13. http://dx.doi.org/10.7306/gq.1742

Gul, B., Ainsaar, L. & Meidla, T. 2024. Palaeotemperature reconstruction based on oxygen stable isotopic trends from the Ordovician-Silurian brachiopods. 9th International brachiopod congress St. Catharines, Ontario, Canada. 24–27 June, 2024

Gul, B., Ainsaar, L. & Meidla, T. 2024. Baltoscandian Middle Ordovician brachiopod oxygen stable isotope trends: implications for palaeotemperature changes. *Baltica*, 37 (2): 87–97. https://doi.org/10.5200/baltica.2024.2.1

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Baltoskandia Ordoviitsiumi ja Siluri brahhiopoodide geokeemia ja paleokeskkonna rekonstrueerimine.

Publikatsioonid:

Gul, B., Ainsaar, L. & Meidla, T. 2021**.** Latest Ordovician-early Silurian palaeoenvironmental changes and palaeotemperature trends indicated by stable carbon and oxygen isotopes from northern Estonia. *Estonian Journal of Earth Sciences*, 70: 196–209. https://doi.org/10.3176/earth.2021.14

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Gul, B., Ainsaar, L. & Meidla, T. 2024. Baltoscandian Ordovician and Silurian brachiopod carbon and oxygen stable isotope trends: implications for palaeoenvironmental and palaeotemperature changes. *Geological Quarterly*, 68–13. http://dx.doi.org/10.7306/gq.1742

Gul, B., Ainsaar, L. & Meidla, T. 2024. Palaeotemperature reconstruction based on oxygen stable isotopic trends from the Ordovician-Silurian brachiopods. 9^{th} International brachiopod congress St. Catharines, Ontario, Canada. 24–27 June, 2024

Gul, B., Ainsaar, L. & Meidla, T. 2024. Baltoscandian Middle Ordovician brachiopod oxygen stable isotope trends: implications for palaeotemperature changes. *Baltica*, 37 (2): 87–97. https://doi.org/10.5200/baltica.2024.2.1

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