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$\delta^{13}C$ chemostratigraphy of the Middle and Upper Ordovician succession in the Tartu-453 drillcore, southern Estonia, and the significance of the HICE

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Abstract. The $\delta^{13}C$ isotope data from the Tartu-453 core section in southern Estonia enabled creation of a continuous Ordovician carbon isotope record, ranging from the Floian to the end of the Hirnantian. Five positive $\delta^{13}C$ excursions and one negative $\delta^{13}C$ excursion were recognized. Most of the positive excursions correspond to those defined on the Baltoscandian carbon isotope chemostratigraphic scheme, except for the Paroveja and Rakvere ICEs which are not well expressed in the Tartu-453 curve. Besides the positive $\delta^{13}C$ excursions, a distinctive negative $\delta^{13}C$ excursion, the Lower Sandbian NICE, was recorded in the Tartu-453 succession. The well-expressed HICE extends about 10 m higher than the traditional Ordovician–Silurian boundary (between the Porkuni and Juuru regional stages) into the Juuru Regional Stage, suggesting that the Ordovician–Silurian boundary is positioned significantly higher than traditionally suggested for the East Baltic area.

Key words: Tartu-453 drillcore, $\delta^{13}C$ chemostratigraphy, HICE, Ordovician–Silurian boundary.

INTRODUCTION AND GEOLOGICAL BACKGROUND

The Baltoscandian region is a well-known key area for global Ordovician biostratigraphic and chemostratigraphic research. Extensive stable carbon isotope chemostratigraphic studies of the Baltoscandian Ordovician–Silurian carbonate succession conducted in the last decade have revealed a series of positive $\delta^{13}C$ isotope excursions (ICE) that have shown a great potential for both intrabasinal (in the Palaeobaltic basin) and global stratigraphic correlations.

The log/description of the Tartu-453 drillcore with biostratigraphic data of some microfossil groups on certain stratigraphic units (chitinozoans: Lasnamägi to Porkuni regional stages (RSs); conodonts: Volkhov to Kunda and Lasnamägi to Keila RSs; ostracods: Volkhov to Kunda and Keila to Pirgu RSs) was published by the Geological Survey of Estonia (Põldvere 1998). The purpose of this paper is to describe the Ordovician $\delta^{13}C$ chemostratigraphy in that core and to assess the relationships with coeval successions in Baltoscandia and elsewhere. Particular attention is drawn to the significance of the Hirnantian $\delta^{13}C$ excursion (HICE) in establishing the Ordovician–Silurian boundary in the East Baltic area.

The 431 m deep Tartu-453 borehole that records Devonian–Cambrian strata was drilled in 1992 as a groundwater well in the southern suburb of the town of Tartu, southern Estonia. The published 151 m thick Ordovician succession (depth range 230.4–381.0 m) is mostly represented by variably argillaceous limestones of the Volkhov RS (Dapingian) to the Porkuni RS (Hirnantian). The Ordovician carbonate succession in Tartu was deposited on the area separating the wide, inner ramp or shelf (North Estonian Confacies Belt) from the deep outer ramp or basin known as the Livonian Tongue (Nestor & Einasto 1997, fig. 1). The depositional environment in the entire Baltic area evolved from temperate carbonate ramp in Dapingian–Sandbian time to the tropical carbonate shelf in Katian–Hirnantian time (Nestor & Einasto 1997).

MATERIALS AND METHODS

The $\delta^{13}C$ isotopic data were obtained from 289 samples of the Billingen to Juuru RSs, using a Thermo Delta V Advance mass spectrometer at the Department of Geology of the University of Tartu. The $\delta^{13}C$ values are reported in per mil relative to Vienna Pee Dee belemnite standard and the reproducibility was better than ±0.1‰

(1 δ). Additionally, 33 analyses from an earlier study by Ainsaar et al. (1999; interval 292–307.3 m) were included here. The Tartu-453 drillcore is housed at the Department of Geology, University of Tartu.

$\delta^{13}C$ CHEMOSTRATIGRAPHY OF THE TARTU-453 DRILLCORE

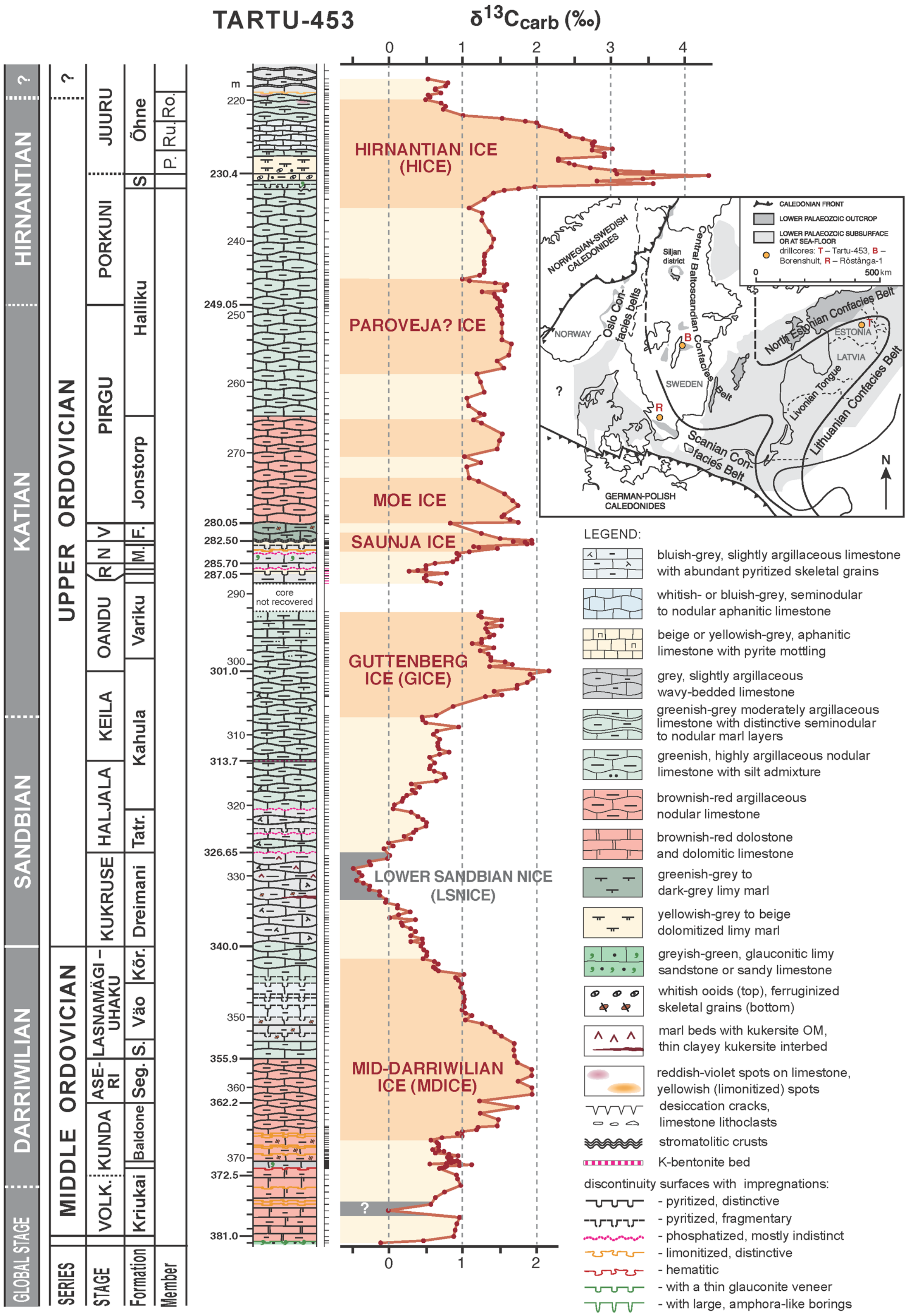
Based on the $\delta^{13}C$ isotope data, a continuous Ordovician carbon isotope record was created, ranging from the Floian to the end of the Hirnantian of southern Estonia. Five positive $\delta^{13}C$ excursions were recognized with certainty in the Ordovician of the Tartu-453 drillcore succession (Fig. 1). Most of these positive $\delta^{13}C$ excursions clearly correspond to excursions established by Ainsaar et al. (2010) on the Baltoscandian composite $\delta^{13}C$ curve, except for the Paroveja and Rakvere ICEs which are not so obvious in the Tartu-453 section. Besides the positive $\delta^{13}C$ excursions, a conspicuous negative excursion, the Lower Sandbian NICE (LSNICE), was recorded in the Ordovician succession.

The **Middle Darriwilian excursion (MDICE)** is a well-known $\delta^{13}C$ excursion which has by now been reported from various palaeocontinents (see a review in Calner et al. 2014). It was initially recognized in the core sections of the East Baltic area by Ainsaar et al. (2004). In the Tartu-453 drillcore, the MDICE is characterized by a broad positive shift with a considerable temporal extent – spanning from the Kunda to Lasnamägi ages. The protracted $\delta^{13}C$ excursion starts around 0.5‰ values in a highly condensed succession of red-coloured limestones with numerous hardgrounds, peaking around 1.9‰ values in red-coloured limestones of Aseri age and then declining in greyish to greenish limestones of Lasnamägi age. The exact termination of the MDICE is not obvious as there is a continuous declining trend of $\delta^{13}C$ values through the Lasnamägi, Uhaku and Kukruse RSs. Here we have chosen the $\delta^{13}C$ value 0.5‰ as a baseline value for the MDICE, which marks the end of the MDICE about 1 m underneath the Uhaku–Kukruse RSs boundary. The MDICE is well represented in several drillcore sections of the East Baltic (e.g. Kerguta-565, Mehikoorma-421, Männamaa F-367, Ruhnu-500, Jurmala R-1, Viki; for reviews of the MDICE see Kaljo et al. 2007; Ainsaar et al. 2010; Hints et al. 2014) as well as in Swedish sections on Öland (Tingskullen drillcore: Calner et al. 2014) and in Dalarna (Kårgärde section: Ainsaar et al. 2010). However, there are also densely-sampled sections in Estonia where the MDICE does not show up (e.g. Uuga cliff section at Cape Pakri, NW Estonia: fig. 2 in Tammekänd et al. 2010).

The **Lower Sandbian NICE (LSNICE)** exhibits the most negative $\delta^{13}C$ values for the whole Ordovician succession of the Tartu-453 drillcore, reaching –0.49‰ in the topmost beds of the Kukruse RS. The exact temporal extent of the LSNICE is hard to determine and needs further investigations. We have tentatively set the baseline values for the LSNICE at 0‰ in the Tartu-453 drillcore, resulting in the late Kukruse age for it. The LSNICE is designated as the 'upper Kukruse low' by Kaljo et al. (2007) in the Valga-10, Mehikoorma-421 and Kerguta-565 drillcore sections, although its exact temporal extent has not been shown. A strikingly similar $\delta^{13}C$ curve for the MDICE and LSNICE, with the lowest $\delta^{13}C$ values for the whole Ordovician succession recorded in the LSNICE, was also reported from the Ruhnu-500 drillcore (Ainsaar et al. 2004, fig. 1). In Sweden, the LSNICE most probably occurs within the Dalby Limestone in the Gullhögen quarry section, Västergötland (Meidla et al. 2004, fig. 1) and this NICE is only barely observable (max. negative shift about –0.5‰ from background values) in the Borenshult drillcore section, Östergötland (Bergström et al. 2012, fig. 5). A remarkable decrease in $\delta^{13}C$ values to almost –4‰, succeeding the MDICE peak around +1‰, was recorded by Leslie et al. (2011, fig. 3) in the Clear Spring, Maryland section along Interstate-70. This conspicuous negative $\delta^{13}C$ excursion in the Clear Spring section could be regarded as LSNICE, however, the conodont data from the Appalachian section imply a somewhat older age (the top of the *Cahabagnathus friendsvillensis* Zone) compared to conodont data from the Tartu-453 core (the lowest $\delta^{13}C$ values were recorded in the topmost Kukruse beds, immediately below the base of the *Baltoniodus gerdae* Subzone; S. Stouge unpublished data).

The second largest $\delta^{13}C$ isotope excursion known in the Ordovician, the **Guttenberg ICE (GICE)**, is recorded in the Tartu-453 drillcore as a distinct asymmetric peak in the highly argillaceous to silty

Fig. 1. Stratigraphy, carbon isotope chemostratigraphy and a core log of the Tartu-453 drillcore, southern Estonia. Stratigraphy is after Põldvere (1998). Abbreviations: N, Nabala RS; R, Rakvere RS; V, Vormsi RS; VOLK., Volkhov RS; F., Fjäcka Fm.; Kõr., Kõrgekallas Fm.; M., Mõntu Fm.; S, Saldus Fm.; Seg., Segerstad Fm.; S., Stirnas Fm.; Tatr., Tatruse Fm.; P., Puikule Member (Mb.); Ro., Rozeni Mb.; Ru., Ruja Mb. The inset is a sketch map of southern Baltoscandia (modified from fig. 1 in Bergström et al. 2014) with locations of the Tartu-453, Röstånga R-1 and Borenshult drill sites.



TARTU-453
δ13Ccarb (‰)
GLOBAL STAGE
SERIES
STAGE
Formation
Member
HIRNANTIAN
KATIAN
SANDBIAN
DARRIWILIAN
UPPER ORDOVICIAN
MIDDLE ORDOVICIAN
JUURU
PORKUNI
PIRGU
OANDU
KEILA
HALJALA
KUKRUSE
LASNAMÄGI–UHAKU
ASE-RI
KUNDA
VOLK.
Õhne
Halliku
Jonstorp
Variku
Kahula
Tatr.
Dreimani
Kõr.
Väo
S.
Seg.
Baldone
Kriukai
P.
Ru.
Ro.
core not recovered
HIRNANTIAN ICE (HICE)
PAROVEJA? ICE
MOE ICE
SAUNJA ICE
GUTTENBERG ICE (GICE)
LOWER SANDBIAN NICE (LSNICE)
MID-DARRIWILIAN ICE (MDICE)
CALEDONIAN FRONT
LOWER PALAEOZOIC OUTCROP
LOWER PALAEOZOIC SUBSURFACE OR AT SEA-FLOOR
drillcores: T – Tartu-453, B – Borenshult, R – Röstånga-1
500 km
NORWEGIAN-SWEDISH CALEDONIDES
Siljan district
Central Baltoscandian Confacies Belt
Oslo Confacies belts
NORWAY
SWEDEN
North Estonian Confacies Belt
ESTONIA
LATVIA
Livonian Tongue
Lithuanian Confacies Belt
Scanian Confacies Belt
GERMAN-POLISH CALEDONIDES
N
LEGEND:
bluish-grey, slightly argillaceous limestone with abundant pyritized skeletal grains
whitish- or bluish-grey, seminodular to nodular aphanitic limestone
beige or yellowish-grey, aphanitic limestone with pyrite mottling
grey, slightly argillaceous wavy-bedded limestone
greenish-grey moderately argillaceous limestone with distinctive seminodular to nodular marl layers
greenish, highly argillaceous nodular limestone with silt admixture
brownish-red argillaceous nodular limestone
brownish-red dolostone and dolomitic limestone
greenish-grey to dark-grey limy marl
yellowish-grey to beige dolomitized limy marl
greyish-green, glauconitic limy sandstone or sandy limestone
whitish ooids (top), ferruginized skeletal grains (bottom)
marl beds with kukersite OM, thin clayey kukersite interbed
reddish-violet spots on limestone, yellowish (limonitized) spots
desiccation cracks, limestone lithoclasts
stromatolitic crusts
K-bentonite bed
discontinuity surfaces with impregnations:
- pyritized, distinctive
- pyritized, fragmentary
- phosphatized, mostly indistinct
- limonitized, distinctive
- hematitic
- with a thin glauconite veneer
- with large, amphora-like borings

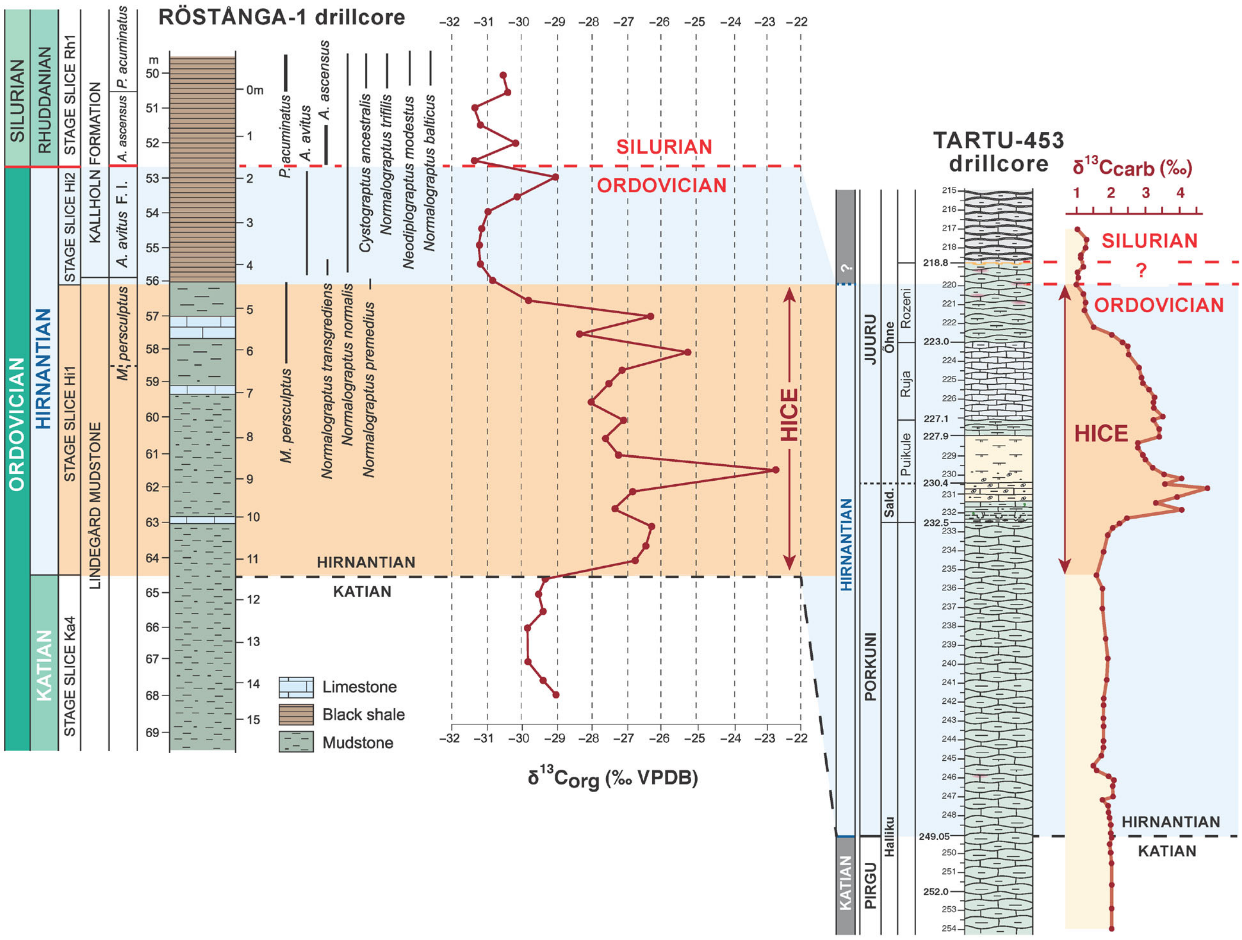


Fig. 2. Comparison of the HICE and the Hirnantian Stage in the Tartu-453 drillcore with coeval strata in the Röstånga R-1 drillcore (modified from Bergström et al. 2014), which shows ranges of stratigraphically important graptolites. Figures along the left side of the drillcore log indicate drillcore depth and along the right side – a stratigraphical thickness.

limestones of late Keila to early Oandu age. The GICE is characterized by a continuous increase in δ^{13}C values (from ca 0.5‰ to a max value of 2.20‰) in late Keila limestones, followed by a sharp decline to 1.36‰ at about the Keila and Oandu RSs boundary. This sharp turnover level marks a major change in chitinozoan faunas (J. Nõlvak pers. comm. 2014) and an increased influx of fine silt-sized siliciclastic material into the sedimentary basin during the Oandu age (Variku Formation: Ainsaar & Meidla 2001). The middle part of the GICE shows slightly fluctuating δ^{13}C values around 1.4‰ and the characteristics of the GICE falling limb are unknown due to missing core between 288.45 and 292.5 m.

Based on the δ^{13}C chemostratigraphy reviews in the Baltic area by Kaljo et al. (2007) and Ainsaar et al. (2010), the GICE displays a well-developed positive peak in the drillcore sections derived from southern Estonia and Latvia (Mehikoorma-421, Valga-10, Ruhnu-500, Viljandi, Jurmala R-1). However, this excursion is not that clear or even might be missing in central and western Estonia (Kerguta-565, Rapla, Männamaa F-367 drillcore sections). It should be noted that the GICE curves both in the Tartu-453 and Mehikoorma-421 sections look remarkably similar to each other.

Elsewhere in Baltoscandia, the pronounced GICE curves have been reported from Norway – in the Frognerkilen Formation, Oslo-Asker area (Bergström et al. 2011, fig. 4) and in the Mjøsa Formation, Lake Mjøsa area (Bergström et al. 2011, fig. 3). In Sweden, the GICE was recently firmly recorded in the Freberga Formation of the Borenshult drillcore, Östergötland (Bergström et al. 2012, fig. 6). A comprehensive overview of the GICE occurrences in North America is given by Bergström (2010a).

The Middle Katian succession, comprising the Rakvere, Nabala and Vormsi RSs, is highly condensed and only 8.4 m thick in the Tartu-453 drillcore section. Thus, the **Rakvere ICE** cannot be reliably identified, however, the **Saunja ICE** (with an almost 1‰ positive shift) clearly stands out on the isotope curve at the boundary interval of the Nabala and Vormsi RSs. The Saunja ICE in the Mehikoorma-421 drillcore in SE Estonia is correlated by Bergström et al. (2010b, fig. 7) with the Waynesville ICE – the latter is observed in several Katian sections of the US Midcontinent. The Saunja ICE peak is usually easily recognizable on $\delta^{13}C$ curves of Estonian drillcores (Kaljo et al. 2007, fig. 3; Ainsaar et al. 2010, figs 3, 4; Hints et al. 2014, fig. 2) as well as in the Jurmala R-1 drillcore, Latvia (Ainsaar et al. 2004, fig. 1), but it seems to be missing due to the gap in sedimentation in the Borenshult drillcore section from Östergötland, Sweden (Bergström et al. 2012, fig. 3).

Two small positive $\delta^{13}C$ shifts, in a range of about 0.5–0.8‰, have been identified in the Jonstorp Formation of the Tartu-453 drillcore. The lower ICE is considered on the grounds of its lithostratigraphic position to correspond to the **Moe ICE**. However, it should be mentioned that we lack any biostratigraphic age evidence for both isotope excursions in the Jonstorp Formation because chitinozoans were destroyed by oxidation in red-coloured limestones. Owing to this uncertainty, we have not assigned a name to the upper ICE in the Jonstorp Formation. There seems to occur an interval with somewhat elevated $\delta^{13}C$ data (shift from background values is <0.5‰) in the boundary beds of the Pirgu and Porkuni RSs. Most probably this small $\delta^{13}C$ shift could represent the **Paroveja ICE** proposed by Ainsaar et al. (2010, fig. 7).

The **Hirnantian ICE** exhibits the most spectacular positive $\delta^{13}C$ excursion in the Ordovician succession of the Tartu-453 drillcore with the peak value of +4.33‰ (this shift is over 3‰ from the baseline value of ca 1‰). Instead of a commonly observed relatively uniform curve, the Hirnantian ICE displays a rather unusual twin-peaked $\delta^{13}C$ curve in the Tartu-453 section. A similar, well-developed twin-peaked Hirnantian ICE is also recorded in the NACP drillcore section of Anticosti Island, Canada (Desrochers et al. 2010, fig. 4). The overall shape of the $\delta^{13}C$ excursion in the Tartu-453 drillcore is clearly asymmetric, characterized by a fast rise in $\delta^{13}C$ values on the lower limb and by a considerably slower decline in $\delta^{13}C$ values on the upper limb. The onset of the Hirnantian ICE is recorded at a depth of about 235 m in the argillaceous limestones of the Halliku Formation (Late Porkuni age) and it terminates at a depth of about 220 m in the marlstones of the Õhne Formation (Juuru age).

THE ORDOVICIAN–SILURIAN BOUNDARY IN THE TARTU-453 DRILLCORE

The Ordovician–Silurian boundary is marked by the FAD of *Akidograptus ascencus* and *Parakidograptus acuminatus* at the GSSP site for the base of the Silurian System in the Dob's Linn section of Scotland (Williams, 1988). These biostratigraphically diagnostic graptolites, however, are not known in the Baltic area. The base of the Silurian System in Estonia is traditionally drawn at the base of the Juuru RS (Nestor 1997). Based on the $\delta^{13}C$ chemostratigraphic studies of the Ordovician–Silurian boundary beds in central Estonia, Ainsaar et al. (2011) concluded that the lowermost strata of the Juuru RS (Koigi Member) may be Ordovician rather than Silurian in age. Hints et al. (2014, fig. 3) reached the same conclusion on the grounds of carbon and sulphur isotope studies of the Hirnantian ICE in the Viki drillcore, Saaremaa Island.

The uniqueness of the HICE in the Tartu-453 drillcore section, compared to the other sections (Kaljo et al. 2008; Ainsaar et al. 2010; Hints et al. 2014), lies in the fact that the HICE extends substantially upwards (about 10 m) from the Porkuni–Juuru RSs boundary, into the marlstones of the Õhne Formation. In their recent overview on the Hirnantian chemostratigraphy in Sweden and elsewhere Bergström et al. (2014, fig. 2) have shown that the diagnostic graptolites for the Ordovician–Silurian boundary were first found even a few metres above the termination of the HICE. This evidence allows us to tentatively draw the Ordovician–Silurian boundary in the Tartu-453 drillcore section at a depth of 218.8 m, which marks the change in lithologies in the Õhne Formation at the level of a limonitized dicontinuity surface.

CONCLUSIONS

Based on the high-resolution $\delta^{13}C$ chemostratigraphic study of the Ordovician succession in the Tartu-453 drillcore, we firmly identified five positive excursions and one negative excursion, which correlate well with other chemostratigraphically studied sections in Baltoscandia. The well-expressed HICE extends about 10 m from the traditional Ordovician–Silurian boundary (between the Porkuni and Juuru RSs) into the Juuru RS. According to the recent $\delta^{13}C$ chemostratigraphic studies in Sweden, containing diagnostic graptolites for establishing the base of the Silurian System, it seems plausible to raise the Ordovician–Silurian boundary in the Tartu-453 drillcore section 11.6 m upwards into the Juuru RS and to draw it at a level of a limonitized discontinuity surface at a depth of 218.8 m (Fig. 2).

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