### A multiproxy study of the Puhmu core section (Estonia, Upper Ordovician): consequences for stratigraphy and environmental interpretation

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Abstract. A multiproxy study of the Katian and Hirnantian in the Puhmu core in NE Estonia resulted in new data on chitinozoan and brachiopod biostratigraphy. Some mass occurrences of dasycladacean algae are tied to small early Katian 'reefs'. Carbon isotope chemostratigraphy showed four earlier known excursions beginning with the early and middle Katian Rakvere and Saunja events, the late Katian Moe excursion and the most prominent Hirnantian excursion. These new data, combined with the distribution of ostracodes and lithostratigraphy, enabled us to apply five regional stages of the traditional Baltic chronostratigraphic framework. Discontinuity surfaces are numerous and diverse in the Puhmu section, especially at two levels, coinciding with the  $\delta^{13}$ C lows before the two most prominent isotope excursions. A special surface with extra deep cavities at the upper boundary of the Saunja Formation is interpreted as a karstification event likely analogous to the one reported from Sweden. The isotope data from the whole-rock and bioclast material were compared, providing very similar results. This may be connected with a very high content of calcite (more than 90%) in most of the Puhmu rocks and a weak impact diagenetic imprint as evidenced by a low colour alteration index of conodonts. The variability of  $\delta^{18}$ O values is larger than considered good, but the observed trends, even if not understood satisfactorily, suggest that these data might have some use in environmental interpretation.

Key words: Baltica, biostratigraphy, brachiopods, carbon and oxygen isotopes, chitinozoans, Estonia, Hirnantian, Katian.

#### INTRODUCTION

Modern studies in geology of wide as well of narrow topics are based on the simultaneous application of different methods. Bio- and chemostratigraphy serve as main tools in the elaboration of the most reliable stratigraphical framework, where every single well-studied section has a meaning of mainstay in this frame. The multiproxy study of the Katian and Hirnantian in the Puhmu drill core, involving and revising data of previous studies (distribution of ostracodes, Meidla 1996; lithological description by Põlma 1985), enables us to evaluate and compare the importance of different chatracteristics for the stratification of the section and interpretation of the depositional development. The Puhmu-567 drilling is located on the offshore part of the Estonian Shelf in NE Estonia. The relationships of chemo-, bio- and lithostratigraphy are less known in that region than in stratigraphically more complete sections (e.g. Jurmala, Ruhnu, Ainsaar et al. 2010), located in the deeper part of the Baltic Basin of the Livonian Basin and transitional zone (Harris et al. 2004). The reef-like bodies and

*Vermiporella*-limestone, established for the first time in the area in the lowermost part of the study interval in the Puhmu core revealed differences from the wellknown reefs in NW Estonia (Kröger et al. 2016).

The present multiproxy study, based on different lithologies and lithostratigraphical background (see Annexes 1 and 2 online; details at the end of the paper), provides biostratigraphical analysis of the distribution of brachiopods, chitinozoans and ostracodes and comparison of the environmental changes with carbon isotope excursions (see Annex 3 online, for tables with analyses data).

The first task of this multiproxy study is to provide a traditional description of the lithology (not published earlier) and lithostratigraphy of the Puhmu core section to get a detailed background for different correlations and environmental interpretations. Secondly, we identify the content of fossil biota and its changes in the context of basin development. The biostratigraphic dating of rocks and various geological–geochemical events is an important but also complicated task when dates received from different fossil groups are not in good harmony.

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Such a discrepancy had been solved using together data from several fossil groups and chemostratigraphy for control. The third aspect of our study is extending the possible application of carbon and oxygen isotopes to solving different tasks of geology.

Chemostratigraphy, especially when based on carbon isotopes, has become a powerful and popular tool in geology for correlating the study material. Plenty of excellent examples can be found in literature, e.g. papers by Ainsaar et al. (2010), Bergström et al. (2015) and Lehnert et al. (2014) on the Ordovician, and a wider summarizing one by Munnecke et al. (2010), testifying to a considerable progress in understanding the possibilities of the method,  $\delta^{13}C_{carb}$  studies in particular.

We investigated the Upper Ordovician with several  $\delta^{13}C_{carb}$  excursions, beginning with those above the Guttenberg excursion (GICE) in the early Katian up to the Hirnantian excursion (HICE) at the very end (Ainsaar et al. 2010). We use these two abbreviations as traditional acronyms not giving much attention to their causal interpretation by certain authors. A prerequisite was that the study section should represent a rather stable succession of carbonate rocks (without thick terrigenous intercalations) even if a relatively shallow-water facies itself is rather changeable within the carbonate platform realm (Kaljo et al. 1991).

#### **GEOLOGICAL SETTING**

A general facies structure of the Ordovician Baltic Basin was established by Männil (1966) based on drill core sections known by that time. Later Põlma (1967) introduced a transition area between the northern (shallower nearshore) and deeper axial facies belts and revealed two epochs in the sedimentary evolution of the basin with different regimes of development. The turning point was at the beginning of the Katian, close to the transition between the Keila and Oandu regional stages (RSs) (Põlma 1982). Jaanusson (1976) named the main units of facies zonation the confacies belts, but nowadays the terminology and interpretation by Harris et al. (2004) are more commonly used (for a general idea see in Fig. 1). By the early Katian time continental drift brought Baltica closer to the equator (Cocks & Torsvik 2005), which agreed with the Dronov & Rozhnov (2007) classification of the carbonate rocks of the Estonian shelf as tropical ones.

The Puhmu section is located in the distal part of the Estonian Shelf (Fig. 1). It represents mostly typical rocks of this facies belt by Harris et al. (2004), but shares a few lithostratigraphical units of the transitional zone by L. Põlma (Figs 1 and 2). For example, a strong deepening episode of the Baltic Basin during the Vormsi Age (Harris et al. 2004) caused a tongue of deeper-water



Fig. 1. (A) General facies zonation of the eastern part of the Baltoscandian Basin (Männil 1966, Harris et al. 2004, modified). Horizontal lines mark the transitional belt. The dotted line denotes the erosional northern limit of the area of the Ordovician rocks. Location of the Puhmu core and localities mentioned in the text: 1, Vasalemma; 2, Orjaku; 3, Kirikuküla; 4, Lelle-D102; 5, Viki; 6, Võhma; 7, Viljandi-91; 8, Laeva-18; 9, Tartu-453; 10, Valga-10. (B) Outcrop areas in NE Estonia (Puura 1986): I - of the Vendian to Cambrian rocks, II - Ordovician Pakerort to Uhaku RSs, III - Kukruse to Rakvere RSs, IV - Nabala to Porkuni RSs and V - of the Silurian rocks. Legend: 1, town; 2, borehole; 3, outcrop; 4, occurrences of reefs. Several boreholes have also an identification number shown here and in Fig. 1B. These numbers are not used in the text, except for Assamalla where two boreholes are under the same name.

sedimentary rocks (Tudulinna Formation (Fm.)) to reach the area of the Puhmu and nearby Kamariku core sections (Nõlvak 1987). Such a transgression episode seems to occur also at the bottom of the Nabala Regional Stage (RS) (Mõntu Fm.), suggesting that the facies position at the boundary of the belts has been slightly variable but in general rather stable. To facilitate the understanding of the depicted facies relationships and respective stratigraphical units, Fig. 2 presents a summary of stratigraphical terminology used in the paper.



**Fig. 2.** Stratigraphical classification of the studied rock succession. Modified based on Meidla et al. (2014), Nõlvak et al. (2007) (chitinozoan zonation), Vandenbroucke et al. (2013), Kröger et al. (2016). Abbreviations: Global units: Ser. – series; St. – stage; LLA. – Llandovery; RH. – Rhuddanian; HIR. – Hirnantian; SAN. – Sandbian. The unit names in the areas of the shelf are formations with a few members (Mb.). Full taxonomic names are shown in the text, as well as a remark about the Koigi Mb.

This scheme is traditional in essence, but slightly modified as noted at Fig. 2. The lithostratigraphical units like formations and members (in unit names Fm. and Mb.) are combined with chronostratigraphical units which are called in English 'stage' (in Estonian 'lade'), but as a rule are much more detailed than stages in global Ordovician stratigraphy. For example, the Katian Stage comprises our Keila, Oandu, Rakvere, Nabala, Vormsi and Pirgu 'stages' (Meidla et al. 2014). To avoid misunderstandings, we use in this paper the term 'regional stage' (abbreviated RS) for the Estonian unit 'lade'.

Several authors (Bauert et al. 2014; Hints et al. 2014; Ainsaar et al. 2015) reported recently about important observations in some core sections (e.g. Tartu, Viki) that the extent of the HICE in terms of local stratigraphy is much bigger than commonly accepted. For example, Bauert et al. (2014) reported that the HICE terminates in the Tartu core in the lower part of the Silurian Varbola Fm. or Õhne Fm. ca 10 m higher than usually observed. It is also a bit strange that the HICE begins in this core at a considerably higher level than it usually does. The HICE is a very prominent and important marker in Ordovician chemostratigraphy, but not at all a simple one due to its rather variable shape (Kaljo & Martma 2011). The main problem in shelf areas like Estonia lacking graptolite fossils is the correlation with the GSSP level, where the beginning of the Silurian is fixed in Dobs Linn at the FAD of Akidograptus ascensus (Rong et al.

2008). However, there is no need to shift the Ordovician– Silurian boundary anywhere, but to find out the true corresponding level in the section under study. The question is what defines the end of the HICE and how to interpret the gaps at the Ordovician–Silurian boundary. Chemostratigraphy might play here an important role when the goal is approached properly (Ainsaar et al. 2015), but before the above aspects are clarified, we prefer to leave the Koigi Mb. in the bottom of the Juuru RS, with a question-mark within the Silurian.

The Ordovician sea level curve has been repeatedly under discussion during last decades. Recently Dronov et al. (2011) interpreted both the above-mentioned deepening episodes and a third one in the Moe Fm. as separate events within a longer sea level rise through the Oandu lowstand up to the mid-Pirgu highstand (red beds in the Jonstorp Fm.). Still, the Fjäcka black shales (and their correlatives within the Vormsi RS) are a second important rising event that prepared the final highstand.

The Puhmu section exhibits for the first time the Katian biohermal rocks in NE Estonia. These algal-rich rocks differ essentially from the older patch reefs of the Keila RS in NW Estonia (Kröger et al. 2014). Higher parts of the Puhmu section are lithologically well comparable with those in the Kerguta core located about 30 km NW (Põldvere 2006). The differences are mainly in thicknesses of the Rakvere to Vormsi RSs. Several type sections occur in the surrounding areas (Fig. 1B; Põlma et al. 1988).

#### MATERIAL AND METHODS

This study is based on the Puhmu-567 drill core from NE Estonia, about 16 km south of Tamsalu (Fig. 1); latitude 59.00647°N, longitude 26.08413°E. The core penetrates 213 m of strata Floian to Aeronian in age. The borehole was drilled and described in 1982 (see Põlma 1985, Annexes 1 and 2 online).

The interval 20.0–138.0 m studied here comprises most of the Ordovician Oandu to Porkuni RSs and the lowermost part of the traditional Silurian Juuru RS. Shelly fossils (400 samples, mainly brachiopods) were collected by L. Hints during bed-by-bed prime investigation of the core. Most of the other macrofossils (gastropods, trilobites, rugose corals, cephalopods, sponges, algae) collected were taxonomically not identified. A few tabulate corals were identified by Einar Klaamann and some gastropods by Isakar & Peel (1997). The sampling was uneven due to the presence of more or less barren intervals.

A separate collection of L. Põlma consists of 65 rock samples with the surfaces polished for lithological studies. This collection serves also for chemical, isotope and micropalaeontological analyses. A total of 45 samples weighing 100–500 g were processed with acetic acid and residues sieved. Chitinozoan remains were handpicked with a fine glass pipette and stored in plastic boxes in glycerine. Ten samples from biohermal limestones (depth intervals 125.6–132.1 m and 132.85–138.0 m) were barren of organic-walled microfossils. Meidla (1996) published data on the distribution of ostracodes in the Puhmu core. For the purposes of this study we consider also the chitinozoan and brachiopod distribution pattern in the neighbouring core sections.

The general rock composition, i.e. the content of calcite, dolomite and insoluble residue is based on carbonate analyses (see Table 1 in Annex 3 online) of 62 samples made in the 1980s in the chemical laboratory of the Institute of Geology, Estonian Academy of Sciences. The lowermost ca 20 m of the core was analysed by 1 m intervals, the remaining part by roughly 2.5 m intervals. Corresponding analytical methods in carbonate chemistry as well as isotope analyses are explained in more detail by Kaljo et al. (1997).

Carbon and oxygen isotopes were measured in whole-rock and brachiopod and rugosan bioclast samples collected from the entire study interval of the Puhmu core. The rock powder for analyses was taken by means of a dental drill from samples collected by L. Põlma and L. Hints. Altogether 126 samples from 96 depth levels were analysed (Table 2 in Annex 3 online). Unlike the Devonian ones, rugosan skeletons have rarely been used for isotope studies in the Ordovician (Jakubowicz et al. 2015). Their results helped us to refrain from some risks at analyses, e.g. we used only thick (compact) proximal parts of the skeleton.

The isotope analyses were performed in the Laboratory of Mass Spectrometry with the GasBench II preparation line connected to the Thermo Fisher Scientific Delta V Advantage mass spectrometer. The results are given in the usual  $\delta$ -notation, as per mil deviation from the VPDB standard. The reproducibility of duplicate analyses was generally better than  $\pm 0.1\%$ .

The collections of fossils and rock samples used in this study are deposited at the Department of Geology, Tallinn University of Technology (institutional abbreviation GIT) under collections Nos 156 (rocks and chitinozoans), 406 (rugose corals), 574 and 739 (both brachiopods) (see http://geokogud.info/).

#### RESULTS

#### Fossil content of the Puhmu section

Distribution of macrofossils

The distribution of macrofossils is irregular, but the most diverse assemblages of shelly fauna are linked to three more argillaceous intervals (Fig. 3): the Oandu–lower Rakvere interval, the Vormsi RS and the uppermost Pirgu and Porkuni RSs. Due to insufficient preservation, part of brachiopods are identified here under the open nomenclature.

A rich association of brachiopods (Fig. 3) occurs in the Puhmu core in the lowermost 6 m (interval 132.4– 138 m), especially below a depth of 135.7 m. Such species as *Howellites wesenbergensis* (Alichova), *Oanduporella reticulata* (Hints), *Parastrophina dura* (Oraspõld) and *Platystrophia* cf. *evari* (Oraspõld) reported indicate the Oandu age. A unique feature of this association is the occurrences of a small gastropod *Mimospira puhmuensis* Isakar & Peel (1997) in clayey cavities and pockets. The entire Oandu–Rakvere interval up to the base of the Nabala RS (122.0 m) is rich in the debris of the alga *Vermiporella*.

The occurrence of *Triplesia insularis* (Eichwald) and *Plaesiomys saxbyana* (Oraspõld) in the upper half of the Saunja Fm. is consistent with the known first appearance of these brachiopods in the Nabala RS in northern Estonia (Oraspõld 1959).

The Vormsi RS stands out by the occurrence of tabulate and rugose corals, and dendroids (*Dictyonema*?) in numerous samples. The brachiopods *Pseudolingula quadrata* (Eichwald), *Plaesiomys saxbyana* (Oraspõld), *Eoplectodonta rhombica* (M'Coy) (*Eoplectodonta schmidti* (Lindström) in Hints 1990) and *Oxoplecia*? sp. (Fig. 3) belong to the faunal association, which is common in the Vormsi RS in northern Estonia (Männil 1990).



**Fig. 3.** Lithologies and lithostratigraphy of the Puhmu section with the distribution of fossils and biostratigraphy. Key to lithologies: 1, micritic limestone; 2, wackestone; 3, argillaceous wackestone; 4, nodular wackestone, partly with marl intercalations; 5, nodular wackestone, argillaceous; 6, biohermal limestone; 7, dolostone: 8, palaeokarst surface; 9, discontinuity surface; 10a, sandy dolostone; 10b, glauconite admixture. Black rectangle – full identification, open rectangle – cf. Ostracodes: black circles – common occurrences, open circles – rare occurrences. Ostracode data from Meidla (1996).

The occurrence of the brachiopod *Dicoelosia* sp. at the 78.8 m level supposedly indicates the lowermost Pirgu RS (Fig. 3). This relatively rare brachiopod is observed in northern Estonia in the Pirgu RS in the Moe and Kerslet outcrops and the Orjaku drill core but in Saxby it was identified as Dicoelosia anticipata Wright (see http://geokogud.info/). However, its first appearance is known from rare occurrences in the deeper-water lithologies of the Vormsi RS (from the Tudulinna Fm.). Still, the beds with Dicoelosia transversa Wright in the Võhma core (central Estonia), occurring exactly below the Võhma mud-mound complex (Kröger et al. 2016), belong more likely to the Pirgu RS than to the Vormsi RS as dated by Wright (1968). In general the Moe Fm., which represents the most part of the Pirgu RS, contains few brachiopods. Atrypinids Eospirigerina sulevi (Alichova) and several related subspecies, identified by Valdar Jaanusson, among specimens of the collection GIT 574, are worth mentioning as characteristic brachiopods of the Pirgu RS. The tabulate coral *Catenipora tapaensis* (Sokolov) appears in the Puhmu core somewhat above the Vormsi-Pirgu boundary. In northern Estonia this species is most common in the Pirgu RS, however, as in case of some brachiopods (Dicoelosia), its first appearance is known from the Vormsi RS.

The interval dated in the Puhmu core as the Porkuni RS is well comparable with that in the stratotype section in the Porkuni quarry, located only about 20 km northwards (Fig. 1B). The brachiopods Elsaella bekkeri (Rosenstein) are found together with *Xenocrinus*-type stem ossicles in the lowermost Röa Mb. in both localities. Brachiopods Streptis undifera (Schmidt), Leptaena (L.) acuteplicata (Schmidt) and Eochonetes (=Thaerodonta in Rõõmusoks 1981) occur together with tabulate and rugose corals in different lithologies of the reef complex of the Porkuni RS. The Kamariku Mb., comprising the topmost beds of the Porkuni RS in North Estonia including the Puhmu core, is poor in any kind of fossils, still the stromatoporoid *Clathrodictyon gregale* (Nestor) could be mentioned besides rare fragments of brachiopods and bryozoans. The occurrences of that stromatoporoid in the Porkuni quarry (Nestor 1964) allow us to suppose that it appears already in the reef complex below the Kamariku Mb. and continues higher.

Only few brachiopods are found above the Porkuni RS, in the Koigi Mb. of the lowermost Silurian Juuru RS. The species *Alispira gracilis* Nikiforova is probably one of the earliest Silurian brachiopods appearing in the lower part of the Juuru RS. In the Orjaku (Kaljo et al. 2004) and Kirikuküla (both in western Estonia, Nõlvak 1984) sections *A. gracilis* appears, respectively, 2.3 and 0.2 m above the Ordovician–Silurian boundary (Rubel 1970). Another Silurian brachiopod *Zygospirella* occurs together with *A. gracilis* in the lowermost bed of the

Juuru RS. Gastropods, rugose corals, bryozoans and stromatoporoids are present, besides the mentioned few brachiopods, in the lowermost part of the Juuru RS.

#### Diversity and distribution of chitinozoans

Details of the distribution of 32 species and a couple of gen. sp. identified are presented in Fig. 3. The picture shows very clearly that the lower part of the section, the Oandu, Rakvere and lower Nabala RSs, contains the most diverse assemblage. In overlying strata, chitinozoan diversity starts to decrease stepwise – six species have survived in the upper Moe Fm., four in the Adila Fm. and none in the Ärina Fm. It seems that during Porkuni time besides sampling density also some local reasons (like shallow sandy sedimentation environment and secondary dolomitization) affect the diversity. However, the picture is in good harmony with a global trend (Paris et al. 2004; Kaljo et al. 2011). It is somewhat intriguing that biohermal rocks produced barren samples, but did not cause any changes in chitinozoan assemblages below and above the reefs. This indicates that the reef-forming event was short-lived and very local.

Thus the chitinozoans from the rare samples available did not contribute sufficiently to establishing exact positions of boundaries of some zones, especially in the upper Vormsi and Pirgu RSs. However, it was possible to identify some time levels (Fig. 3) using additional data from nearby core sections of the same region, e.g. Kerguta (Nõlvak & Bauert 2006) and Assamalla-256 (Calner et al. 2010).

#### Carbon and oxygen isotopes

The results of carbon and oxygen isotope analyses are presented in Table 2 (in Annex 3 online) and Fig. 4. The whole-rock ( $\delta^{13}C_{carb}$ ) curve is rather reliable, without any big gaps in sampling and it documents most of the carbon isotope excursions established in this interval of the Baltic region (for summary see Ainsaar et al. 2010). The Hirnantian and Saunja excursions are most prominent, and the Moe excursion is clearly recognizable (Fig. 4). The Rakvere excursion is less obvious and the Paroveja excursion is missing. The  $\delta^{13}C_{carb}$  data from the pre-Saunja part of the curve as well as the  $\delta^{13}$ O data need especially mindful attention.

The  $\delta^{13}C_{carb}$  curve (Fig. 4) serves in this study as a basic framework that might help improve the correlation. The curve begins within the Oandu–Rakvere unidentified lithostratigraphic unit. The three lowermost samples show a short plateau of values ca 0.53–0.75‰, followed by a small but clear peak of 1.82‰ at 134.75 m that is the bottom of the first reef body. Several smaller peaks occur higher in the section, among them the second

highest peak of 1.52% at 129.4 m in the middle of the second biohermal rock bed. All these belong to the lower part of the Rakvere RS and, despite relatively lower values than usual, could be named as Rakvere excursion. Above this peak the curve displays variable values (1.2-0.5%), showing a clear decreasing trend that ends with a value of -0.28% at the bottom of the Paekna Fm. This might be considered as a turning point on the curve where a rising limb of values begins, forming the Saunja excursion (a peak value of 3.5% measured at 106.65 m) higher in the Nabala RS. While changes in the curve through the Nabala RS are well dated lithostratigraphically, a detailed discussion of the biostratigraphical data is needed for the earlier (Oandu–Rakvere) interval (see below).

The  $\delta^{13}C_{carb}$  curve through the Vormsi RS in the Puhmu core (Fig. 4) is a rather typical plateau, a bit more variable at the bottom, but mainly the values vary between 0.2‰ and 0.7‰. A little jump of values up to 1.21‰ occurs just on the junction of the Vormsi and Pirgu RSs, marking the beginning of the Moe excursion and reaching a rather low peak value (1.3‰) a bit higher at 71.45 m. The excursion seems relatively wide here, with three low-level peaks (at 77.85, 71.45 and 68.1 m), whereas the last one marks also the end of the Moe excursion. The upper part of the Moe Fm. shows a plateau of negative values between -0.5% and -0.7%. It is followed by a small rise up to -0.12% (at 52.25 m), which cannot be classified for any known excursion but is a variation of values. It is interesting that this low peak is seconded by a much stronger rise of values in the  $\delta^{13}$ O curve. The next two samples at the very end of the Moe Fm. show a negative value of -1.28% that makes the small peak more visible and marks a turning point of the trend - throughout the Adila Fm. the isotope curve demonstrates a slightly variable but rising limb of the excursion. A clear jump of values from 0.03‰ to 1.73‰ occurs at the very beginning of the Porkuni RS. We consider this change as a true beginning of the HICE and the uppermost Adila rising limb is a preparatory process within the late Katian climate change (Kaljo et al. 2008, 2011).



**Fig. 4.** Comparison of the  $\delta^{13}$ C and  $\delta^{18}$ O data from the wholerock samples and bioclasts. For data for curves see Table 2 (Annex 3 online). Legend: 1a, whole-rock  $\delta^{13}$ C; 1b, whole-rock  $\delta^{18}$ O; 2, rugose bioclast analyses,  $\delta^{13}$ C and  $\delta^{18}$ O; 3, brachiopod bioclast, the same; 4, yellow line –  $\delta^{13}$ C<sub>carb</sub> and  $\delta^{18}$ O<sub>carb</sub> running three-point means; 5, levels with discontinuity surfaces. For lithologies see Fig. 3. Colours are illustrative: light green shows different wackestones, darker green more argillaceous rock, yellow micrite; other colours are unit-specific.

The bioclast analyses for carbon isotopes are very much the same as  $\delta^{13}C_{carb}$  data with a few exceptions. Oxygen isotope ( $\delta^{18}O_{carb}$ ) data are more variable (mostly between -3% and -6%), and a similarity with the carbon pattern is difficult to ascertain, except that the HICE is seconded by a double-peaked  $\delta^{18}O$  excursion, the highest point of the Saunja excursion and of an anonymous one at 52.3 m with a similar positive excursion (see Fig. 4). All bioclast data vary in the same interval as the whole-rock analyses, but  $\delta^{18}O_{bra}$  data vary mostly in the higher and  $\delta^{18}O_{rug}$  data more in the middle part of the variation interval.

#### DISCUSSION

#### Puhmu section: some regional comparisons

The Puhmu core, within the studied interval, represents 100.6 m of Katian and 7.5 m of Hirnantian shallow shelf successions. Relatively pure carbonate rocks with the insoluble residue mostly less than 10% dominate up to the Vormsi RS. From the Saunja Fm. upwards there appear interbeds with a high content of dolomite (20–30%), reaching 80% in the lowermost Porkuni RS. The components analysed vary most in the Pirgu RS, and the higher part of the Porkuni RS is more similar to the pre-Saunja rocks (see Annex 1 online).

Climate changes, caused by plate tectonic movements as mentioned above, resulted in the development of the rimmed-type basin with tropical carbonates (Dronov & Rozhnov 2007) and essential changes in the facies pattern and thickness variation in northern Estonia (Ainsaar & Meidla 2001). As detailed lithofacies maps for this time interval are lacking, the position of the reef-like mounds described from the early Katian in North Estonia (in the Vasalemma area by Dronov & Rozhnov 2007 and Kröger et al. 2014, Võhma by Kröger et al. 2016 and Puhmu here) relative to facies zones is not certain. Having in mind the long distance of these mounds to the outer border of the shelf and general views about reef evolution expressed by the last authors, we prefer to call them as nearshore shallow-water organic build-ups.

The relatively continuous distribution of late Sandbianearly Katian Keila RS in a thickness of 12–14 m in NE Estonia is replaced by the more variable deposits of the Oandu RS, whose thickness increases northwards from a few centimetres to about 5 m. The Puhmu borehole is located at the southern limit of the distribution area of the Hirmuse Fm., which forms the main part of the Oandu RS and is capped by the Tõrremägi Mb. (Põlma & Haas 1987). The latter forms the only part of the Oandu RS in the southernmost sections. The biostratigraphical data on ostracodes (Meidla 1996) and chitinozoans in several sections support the practical goal to draw the lower boundary of the Rakvere RS below the Rägavere Fm. including the Tõrremäe Mb. The main faunal renovation among biostratigraphically important microfossils occurs on the lower boundary of this member (e.g. the chitinozoan *Spinachitina cervicornis* (Eisenack) disappears and *Fungochitina spinifera* (Eisenack) appears). This boundary is less obvious in Puhmu than elsewhere.

The more changeable thickness of the Rakvere and Nabala RSs in northeastern Estonia shows a sea bottom with considerable relief at a relatively short distance. However, other explanations are also possible. Calner et al. (2010) suggested that the variable thickness of the Nabala RS is caused by subaerial exposure and erosion of the strata. The palaeokarst that developed in South and Central Estonia and in Sweden reaches down to the Oandu RS (Calner et al. 2010). In the Puhmu section (at 91.0 m, Fig. 3 and Annex 1 online) cavities of the karstified surface (discontinuity) reach into the rock as a maximum of 2.5 m at the top of the Saunja Fm. The large cavities with pyrite impregnation in micritic limestone with calcite cracks (GIT 156-889; depth 92.85-93.05 m) are filled with argillaceous sediments. We agree that these structures most likely indicate the palaeokarst in shallow shelf, but the erosional loss of earlier sediments seems moderate in Puhmu. Some other cores show much greater changes. For example, the thickness of the Saunja Fm. in the nearby Kerguta (Põldvere 2006) and Puhmu sections is, respectively, 11.4 and 24.1 m; in the Assamalla-256 section the same thickness reaches 20.6 m, but in the Assamalla-251 section only 7 m (Calner et al. 2010).

#### Vermiporella and reef

The lowermost part of the Puhmu section, the Oanduearly Rakvere interval (depth 125.6–138.0 m), is unique for NE Estonia due to the occurrence of reef-like bodies and dasycladacean algal Vermiporella limestones. The similarities with the lateral facies of reefs as described in Norway (Kröger et al. 2016), where the marginal facies of massive reefs of the Mjøsa Limestone are rich in Vermiporella, might indicate that the Puhmu section depicts more or less the same situation. According to the composition of the brachiopod assemblage, we can suggest two levels for the Rakvere–Oandu boundary at depths of 132.4 or 135.7 m within relatively argillaceous beds of the section (Põlma et al. 1988; Hints 1998). However, Vermiporella occurs in Puhmu below these levels (Fig. 3), which is uncommon for the Hirmuse Fm. elsewhere. For example, in the Rooküla and Sibila Sections (Fig. 1) west of the study area, the Vermiporella bioclasts form about 80% of the bioclast material (up to ca 30% in the composition of rock) in the 10-20 cm thick

bed delimited by the pyritized discontinuity surfaces in the Tõrremägi Mb. of the Rägavere Fm. (Põlma et al. 1988; Hints 1998).

In the Aavere section (Haas & Saadre 1984) the Vermiporella-limestone and micritic reef limestone with light-green marly films in a thickness of 7.2 m overlie the 0.3 m thick Tõrremägi Mb. These beds are described as the lowermost part of the Rakvere RS. It is not clear if the mentioned beds in the Aavere are analogues to the reef and algal limestone in the Puhmu core, but it seems probable. The brachiopod data from the latter section indicate Oandu age up to 135.7 m or even up to 132.4 m. The chitinozoan species Belonechitina villosa, which in the Piilse and Rapla cores appears in the Hirmuse Fm., occurs in the same interval. In some other sections its first appearance is identified in the Tõrremägi Mb. (Orjaku, Viki), and in southern Estonian sections (Viljandi, Valga) possibly in the Rakvere RS. If this correlation is correct, the main part of reef limestone in the Puhmu core (interval 125.6–132.1 m) belongs to the Rakvere RS as shown in the Aavere core.

The temporal relationship of the Vermiporella-rich limestone intervals in the Oandu, Rakvere and Nabala RSs in northern Estonia needs future investigation. Despite a general understanding that green algae indicate very shallow waters, their distribution is more common in micritic limestone, which is characteristic of algal communities favouring the environments with little influx of terrigenous material (Johnson & Sheehan 1985). The Vermiporella-rich 'reefs' in the Puhmu core differ from all four types of reefs of the Vasalemma Fm. in NW Estonia (Kröger et al. 2014), where dominant faunas are represented by bryozoans or echinoderms, or receptaculitids together with bryozoans or tabulates. The distribution of different algae (Vermiporella, Palaeoporella, Cyclocrinites) increases markedly in the Oandu to Pirgu RSs (Kaljo et al. 1999). The abundance of Palaeoporella in some intervals of the Moe Fm. (Kõrts et al. 1990) refers to their possible frame-builder role in the deeper shelf area (Jonstorp Fm., Kröger et al. 2016). Partly such a diversity of favoured environments might be caused by a rather variable facies pattern in the study area (Ainsaar & Meidla 2001).

#### Ostracode biostratigraphy in the Puhmu section

Ostracodes are a rather diverse and rich group of fossils in the Baltic area (Meidla 1996). Their taxonomic diversity increased constantly through most of the Katian, as demonstrated by the rise in the number of species (from 20 to 120) identified in the Oandu to the uppermost Pirgu RSs. The Hirnantian Porkuni assemblage shows a conspicuous drop in diversity to 73 species (Meidla 1996) and a link to the well-known End-Ordovician mass extinction seems obvious. However, the Late Ordovician ostracode assemblage is a uniform, relatively independent phase in the evolution characterized by a wide distribution of long-ranging podocopes (Hints et al. 1989; Meidla 1996).

Out of nine associations known in North Estonia, Meidla (1996) established five in the Puhmu core. The lowest association of *Sigmoopsis granulata* Sarv is mainly confined to the Hirmuse Fm. of the Oandu RS, and only a few occurrences are noted in the uppermost Keila RS and overlying Rakvere RS. However, this association has not been established in the Puhmu core section either due to lack of the Hirmuse Fm. or because the lowermost studied beds of the section do not reach the needed level. The first assumption seems more justified, but both are possible.

The two overlying associations, *Steusloffia neglecta* Sarv and *Daleiella admiranda* Meidla, embrace, respectively, the lower and upper parts of the Rakvere RS. It should be noted (based on fig. 23 in Meidla 1996) that both associations are the richest in the section and very well defined by eponymous species (a limit between them is at 125.5 m, tentatively due to sampling density) and the LAD of *Daleiella admiranda* is just below the Nabala RS at 122.0 m (Fig. 3). This boundary is well marked also by the first appearance of the longranging ostracodes *Steusloffina cuneata* (Steusloff) and *Medianella blidenensis* (Gailīte), the index fossils of the third association (Fig. 3). At the same level there appeared the short-ranging chitinozoan *Armoricochitina reticulifera*, making it a trustworthy biostratigraphic level.

The middle to upper Katian interval (Nabala, Vormsi and Pirgu RSs) comprises a rather diverse ostracode assemblage (Fig. 3). Long-ranging *Olbianella fabacea* (Pranskevičius) became abundant in the middle of the Moe Fm. and its LAD is in the uppermost Adila Fm., indicating the fourth association. Still, in general the ostracodes do not give many useful hints for correlation in the upper Katian. A few samples from the middle Porkuni RS comprise the *Medianella aequa* (Stumbur) association.

### Chitinozoan biostratigraphy and hints for correlation

One of the main tasks in the study of chitinozoans (Fig. 3) was to determine the age of the limestone layers below the reefs from the interval 135.4–138.0 m and higher between two bodies of reef in the interval 132.1–132.85 m.

In the nearby Kerguta core (see Nõlvak & Bauert 2006, app. 9), as well as in other sections in North Estonia, the argillaceous limestones of the uppermost Keila RS contain an assemblage with abundant *Desmochitina* 

nodosa Eisenack, Conochitina elegans Eisenack, an unusually curved form of Belonechitina cf. comma Eisenack, Pistillachitina sp. 1, abundant prasinophycean Leiosphaeridia baltica Eisenack, etc. All these are not identified below the reefs in Puhmu. Thus, the Keila Age for these limestone beds seems to be not justified.

The assemblage typical of the Keila RS disappears below the Hirmuse Fm. A morphologically peculiar chitinozoan Sphaerochitina? sp. is found in the topmost Hirmuse Fm. of several sections, but missing in Puhmu. This is another indication of the specific character of the chitinozoan assemblage in the Puhmu core. This species has been identified in two samples from 0.6 m thick Oandu beds of the Kerguta core (Nõlvak & Bauert 2006, app. 6) and in some other condensed sections nearby (see Põlma & Haas 1987, fig. 3.4.31). Slightly argillaceous limestones in Puhmu (interval 135.4-138.0 m) are lithologically different from those of the Tõrremägi Mb. The lowermost three samples from this interval contain a chitinozoan assemblage (Fig. 3) which is very similar to that from the Saku Mb. However, it lacks zonal Spinachitina cervicornis, which is present in the Saku stratotypical outcrop (unpublished data by J. Nõlvak) in the Hirmuse Fm. and below.

The occurrence of zonal *Fungochitina spinifera* in two samples just below the reefs but above the first three samples is remarkable. Elsewhere, as identified up to now, this zonal marker appears in the rocks of the Tõrremägi Mb. However, further studies are needed where the topmost layers of the Saku Mb. are covered with younger beds than those cropping out in the stratotypical Saku outcrop, which are poorly known in detail. Nevertheless, although the exact age is still under question, the assemblage of chitinozoans from the three lowermost samples could be compared with those in the Oandu age beds in general.

In a new stratigraphical chart of the Oandu RS Kröger et al. (2014) suggested a rather high and long-ranging position for the Saku Mb. from the uppermost Keila (above the GICE) up to the lower Rakvere RS (Fig. 2). However, the correlation of the traditional boundaries of the lithological units of the Oandu RS, such as the Saku Mb., Hirmuse Fm. and Tõrremägi Mb., remains not proved in North Estonia.

In the limestone layer within the reef there appears *Cyathochitina patagiata* Jenkins whose FAD is in the Hirmuse Fm. in the nearby Virunurme core (for lithology see Põlma et al. 1988, fig. 34), serving as a stratotype of this formation. Other characteristic species of the Hirmuse Fm. have not been found in small samples available for the present study.

Reefs are most probably covered by beds of the upper part of the Rakvere RS. This is lithologically also proved by the distribution of micritic limestones of the Tudu Mb., and by the absence of burrows and mottles of pyrite if compared to beds of the Piilse Mb. in the nearby Kerguta section (Põldvere 2006, p. 40). The composition of the chitinozoan assemblage is similar to those known from the other Rakvere Age rocks. Still, subzonal *Cyathochitina angusta* Nõlvak & Grahn (see Nõlvak et al. 2007, text-fig. 1) was not encountered in Puhmu, but it is common in the uppermost Tudu beds in the other North Estonian sections (e.g. Paekna quarry, Nõlvak & Meidla 1990). This age designation is supported by occurrences of the ostracode *Daleiella admiranda* in the uppermost beds of the Rakvere RS (Fig. 3; Meidla 1996, fig. 23).

Higher in the Puhmu section the lower boundary of the Nabala RS is well defined by the appearance of *Armoricochitina reticulifera* (Grahn) in the glauconitebearing limestones of the Mõntu Fm. This biostratigraphical level can be followed precisely in entire Baltoscandia in collections available so far. The chitinozoan assemblage in the Nabala RS is similar to that in other sections of that area, e.g. in the Kerguta (Nõlvak & Bauert 2006, app. 9) and both Assamalla (Calner et al. 2010, fig. 4) cores.

Samples from the Vormsi RS show the appearance of *Spinachitina coronata* (Eisenack) and zonal *Tanuchitina bergstroemi* Laufeld (in the Lelle core, Hints et al. 2007, fig. 2). However, the well-known and biostratigraphically important *Acanthochitina barbata* Eisenack was not revealed, perhaps due to insufficient sampling resolution.

As identified up to now, *Ancyrochitina ancyrea* Eisenack appears always in the lowermost part of the Pirgu RS (Moe or Halliku formations) in the East Baltic sections, however, being usually rare. Higher up a specific form of *Belonechitina micracantha* (sp. nov.?) occurs, which is elsewhere found (unpublished data by J. Nõlvak) only together with *Conochitina rugata* Nõlvak, indicating that the corresponding beds are probable coeval within the late Pirgu Age.

Chitinozoans are particularly rare in the Porkuni RS (Fig. 3) and there are no productive samples from the micritic limestone of the Koigi Mb. which traditionally has been described as a base of the Silurian in Estonia. The Puhmu section is not an exception but all sections in the area are barren (e.g. Kamariku, Padaküla and Kerguta sections) in northern Estonia. This situation leaves the level of the Ordovician and Silurian boundary based on chitinozoans biostratigraphically open.

### The integrated stratigraphy of the Puhmu core section

The lithostratigraphy of the Puhmu section was compiled after Põlma (1985) based on different lithologies observed in the section and by applying a common unit terminology (Raukas & Teedumäe 1997). The scheme has been rather stable throughout time, that means the succession of lithological units and their boundaries used in the log in Fig. 3 are reliable. The local chronostratigraphy (regional stages) still needs more attention due to progress in palaeontology, especially in the study of microfossils like chitinozoans and conodonts. The results of carbon isotope analyses as a third component in this multiproxy study also are considered.

As discussed above, the bottom of the section is most complicated, evidently due to the presence of reeflike structures. Põlma (1985) expressed this situation by labelling the interval 125.6-138.0 m as the Lower Rakvere-Oandu RSs (a not subdivided and formally not identified lithological complex). Ostracode distribution (Meidla 1996, summary above) allows of the following subdivision and boundaries (from the bottom): the Sigmoopsis granulata association ranges from the top of the Keila RS and occurs abundantly in the Hirmuse Fm., forming the upper part of the Oandu RS (Kröger et al. 2014; Meidla et al. 2014). The Hirmuse Fm. together with Sigmoopsis granulata is in a gap in the Puhmu section. The range of the second association of Steusloffia neglecta begins at the bottom of the Puhmu section (at 138.0 m, Fig. 3) and its rich occurrence continues nearly up to the top of the reef beds. The FAD of Steusloffia neglecta has been documented in the Tõrremägi Mb., a lower part of the Rägavere Fm. The latter is the main body of the Rakvere RS, but according to stratigraphic charts, the Tõrremägi Mb. belongs to the Oandu RS (Fig. 2). The Tõrremägi Mb. has not been identified in the Puhmu section, but Põlma (1985) suggested that it might be there at the bottom of the first reef – like a body with Vermiporella. Anyway, the first occurrences of Steusloffia neglecta are reported from the very beginning of the studied interval, i.e. together with Vermiporella, but below the first reef. The higher part of the Rägavere Fm. (Tudu Mb.) is dominated by the Daleiella admiranda association, a very rich and stable community distributed not only in northern Estonia.

The brachiopod information about the age of the very bottom of the study interval (Fig. 3) is rather similar. The brachiopods *Howellites wesenbergensis*, *Oanduporella reticulifera*, *Parastrophina dura* and others, occurring below a depth of 135.7 m, indicate the Oandu RS, i.e. this indication is at least partly in harmony with ostracode data.

Defining the chitinozoan distribution pattern in the lowermost part in the Puhmu section is clearly hampered by barren samples from reef intervals, nevertheless, they are very helpful for the dating of the beds below the reefs. The chitinozoans from the bottommost three small samples (Fig. 3) just below the FAD of *Fungochitina spinifera* (found elsewhere in the Tõrremägi Mb.) show certain similarity to the chitinozoan association in the Oandu RS, in general containing Rhabdochitina sp. 1 and Belonechitina wesenbergensis brevis (Eisenack) among others. Should this statement prove correct, the chitinozoan-based arguments in line with those from ostracodes and brachiopods could support the late Oandu age of the very bottom of the Puhmu section, while the Rakvere age begins slightly higher together with the FAD of Fungochitina spinifera (at a depth of ca 136.0 m). Such a dating is also supported by carbon isotope data (Fig. 4), showing that the Rakvere excursion begins close to this level (the first peak of the  $\delta^{13}$ C excursion 1.82‰ at a depth of 134.75 m) and ends before the lower boundary of the Tudu Mb. of the upper part of the Rakvere RS. A rather similar location of the Rakvere excursion is observed in some other core sections, e.g. Rapla (Kaljo et al. 1999). Summarizing the above data, we can see that the lowermost 2 m are most probably of Oandu age (below the Tõrremägi Mb.) despite the occurrences Vermiporella and Steusloffia neglecta, but the FAD of Fungochitina spinifera at ca 136 m highlights the beginning of the early Rakvere age. If this dating is correct, it means that in Puhmu a bed occurs between the Hirmuse Fm. (missing here) and the Rägavere Fm. (Tõrremägi Mb.) which has not been observed earlier.

Macrofossils are rare higher in the mid-Katian (Nabala RS). Ostracodes are represented by several longranging species, e.g. *Steusloffina cuneata* and *Medianella blidenensis*, both of which appeared in the lowest part of the Nabala RS. The same is true of chitinozoans, where *Armoricochitina reticulifera* forms a good subzonal marker. The  $\delta^{13}$ C curve demonstrates the prominent Saunja excursion within that regional stage, with a peak of values (3.5‰) at 106.65 m. All these data are in good harmony with each other and support the definition of chronostratigraphical units (regional stages).

The content and diversity of macrofossils, especially of brachiopods and different corals, increased in the Vormsi and Pirgu RSs. Some index fossils appeared, which help to classify and correlate the rock units, e.g. Pseudolingula quadrata and Plaesiomys saxbyana in the Vormsi RS and Dicoelosia sp. and Eospirigerina sulevi in the Pirgu RS. Due to extinction events at the very end of the Katian (Adila age) and in the early Hirnantian (Porkuni time), the latter is rather poor in fossils despite the innovation in certain groups (e.g. rugose corals) during this time interval. Rugosans in the Puhmu section have been sampled for isotope analyses but not for taxonomical study. Therefore several common brachiopods like Elsaella bekkeri, Streptis undifera and Leptaena acuteplicata are most reliable index species. Out of the other groups studied here, we could mention a few chitinozoans, not Conochitina rugata itself but members of this association, confirming that the beds equivalent to the *Conochitina rugata* Biozone are likely present in the Adila Fm., and the ostracode *Medianella aequa* in the Porkuni RS. Fortunately, the upper Katian (stage slices K3, K4) and the Hirnantian are rich in carbon isotope events (the Vormsi low, Moe and HICE), allowing of rather detailed and trustworthy stratification.

## Links between different isotope data, discontinuities and their environmental sense

Most papers on chemostratigraphy apply  $\delta^{13}$ C data. We have been advocating (e.g. Kaljo et al. 1997) that whole-rock analyses are the easiest way of getting reliable results from a section because sampling is possible at any resolution. The  $\delta^{18}O_{carb}$  data, in contrast, are as a rule unsatisfactory due to various secondary effects possible.

In order to understand how different are the isotope values based on the whole-rock and bioclast material, we discussed three different sets of data from the Puhmu core. The first includes 86 samples for whole-rock  $\delta^{13}C_{carb}$  and  $\delta^{18}O_{carb}$  analyses, 23 brachiopod shell samples and 12 samples from rugose corals (mainly the proximal part of a conical corallum, all from the same levels where whole-rock analyses are made). All three kinds of material were analysed at a few levels (Table 2 in Annex 3 online). The bioclast material is rather limited, but some patterns are clearly visible (Fig. 4).

The whole-rock  $\delta^{13}C_{carb}$  curve serves as a basic data set for current discussion. The curve shows four subglobal excursions at expected stratigraphical levels. It is composed of a set of samples with rather stable values of analyses. This is well demonstrated by a three-point running mean trendline (Fig. 4) – a great many of the analysed values are placed very close to that line. Variability is rather low, which may indicate a relatively stable sedimentary environment in the framework of global changes in carbon isotope composition and adequate analysis procedure. However, the stability of the environment should be understood here in general lines and it should be considered that discontinuity surfaces occurring in several intervals of the section (Fig. 4) disturb the facies stability locally or wider substantially.

The discontinuities recorded (Fig. 4) are different, partly plain and very weakly phosphatized or pyritized, perhaps without any serious impact on the basin history. Still, the double or triple ones with deep dissolution cavities and strong impregnation (see the 'Description of the Puhmu section' in Annex 1 online) are clearly more serious events in the basin history, even if we cannot say to what degree. The bearing of different discontinuity surfaces is not exactly known, but Bates & Jackson (1987, p. 187) mark their role as 'a minor break in the sedi-

mentary column, chiefly intraformational but including interformational junctions that have not involved largescale erosion'. Putting the positions of the observed discontinuity surfaces (28) against the curve in Fig. 4, it is easy to see that nearly all but two discontinuities in the entire study interval are linked to the lows of the  $\delta^{13}$ C value curves incorporating some parts of falling or rising limbs. This pattern is even more strikingly seen in two series of discontinuities, one located between the Rakvere and Saunja excursions (seven surfaces within the Tudu Mb. and Paekna Fm., Fig. 4) and the other in the Adila Fm. (13 surfaces). The latter series begins at the lowest point of the curve below the HICE and ends at the very top of the formation with the 0.03‰ value. In the section 'Carbon and oxygen isotopes' we referred to this part of the curve as a preparatory process before the true HICE started with a clear jump of values (the first sample shows the value of 1.73%). The same pattern of location is true also for the most prominent discontinuity surface (the karst level, Calner et al. 2010) in the very top of the Saunja Fm.

Such a pattern of the location of discontinuity surfaces and carbon isotope excursions seems to refer to some common environmental agents that are controlling the shape of the value curves. The process is to some extent cyclic, not very regular, but a certain state of the isotope curve accompanies a certain state of the environment that is favourable for the formation of discontinuities (Fig. 4). It seems that most of the discontinuities should have originated in a shallow sea environment with numerous hiatuses, erosion, etc., therefore we tend to see here the influence of changing sea level. Munnecke et al. (2010) discussed different drivers in available models of isotope processes and considered sea level changes as a serious agent, but not always. Plenty of positive excursions are recorded in proximal settings, but an opposite pattern is also possible. Both versions need surely additional reasoning and the above data from the Puhmu core seem to show rather clearly that discontinuity surfaces mark the lows of the isotope curve, but not the lows of the sea level curve. Vice versa, the prominent HICE and Saunja excursions are not accompanied with discontinuities, which makes the pattern more curious.

Another complicating environmental situation should be mentioned in the Puhmu case. All changes discussed in the  $\delta^{13}C_{carb}$  curve and accompanying discontinuity surfaces have formed at a time of slightly variable but steadily rising sea level in the East Baltic (Dronov et al. 2011), with the highest points in the Vormsi and lower Pirgu RSs (the Fjäcka and Jonstorp Fms, respectively; Fig. 2) in the deeper part of the basin. A rather steep drop in the sea level began in the upper Pirgu RS (Adila Fm.), whereas the lowest point was reached in the mid-Porkuni RS. The distribution patterns of both, the

Oxygen isotope ( $\delta^{18}O_{carb}$ ) data from whole-rock analyses are much more variable between -2.9‰ and -6.5‰ (Fig. 4). However, a three-point running mean trendline reveals some similarity (parallelism) in the  $\delta^{13}C_{carb}$  and  $\delta^{18}O_{carb}$  curves at the Rakvere excursion and HICE. At the Saunja and Moe excursions the course of the trend is converse, as well as the Vormsi low between them and positive excursions in O isotope data (Fig. 4). Talking about that parallelism of the C and O isotope curves in the Hirnantian, Brenchley et al. (2003) applied  $\delta^{18}O_{bra}$  data. Surely the quality of their data set was much higher than reported here, but as shown by Munnecke et al. (2010), also there both scenarios are possible. One more observation should be noted about the  $\delta^{18}O_{carb}$  data. As a rule, the oxygen values measured in Puhmu are highly unstable, but there is an interval, just parallel to the Moe carbon isotope excursion, with seven (or more) analyses showing a very steady trend that seems strange on the background of a highly variable data set in general. We also note that during Saunja, Vormsi and Moe times the sea level was highest in the Katian in the Baltic area (Dronov et al. 2011). It seems obvious that the discontinuity topic is rather curious but worth of future studies for better understanding of environmental processes.

Bioclast  $\delta^{13}$ C data from brachiopod shells and rugosan corallums are rather concordant with the  $\delta^{13}C_{carb}$ analyses. Only three brachiopod analyses (13%) deviate significantly from the trendline position (the trendlines shown in Fig. 4 are constructed based on whole-rock samples) and practically all coral analyses data but one are situated at the trendline. The analyses are slightly less variable than those from whole-rock samples, while the rugosan ones are situated closer to the trendline than  $\delta^{18}O_{bra}$ . Most of the latter ones have a mean value of -4.5‰, which is clearly within the upper part of the variation interval of  $\delta^{18}O_{carb}$ . Beginning this comparative study, we expected to get more diverging results, but this was not the case. The  $\delta^{13}C$  data from all three materials (whole-rock, rugose coral skeletons and brachiopod shells) are very similar to each other. We did not see a usual pattern in the Puhmu core that brachiopod values are as a rule 1-1.5‰ (rarely 2‰) higher than wholerock values (Hints et al. 2010). Such an anomaly may be caused by two circumstances: (1) the percentage of calcite in most of the Puhmu rocks analysed is very high (mostly 90–97%) and (2) the impact of diagenesis is mostly weak, as evidenced by a low conodont CAI index (Männik 2003). The variability of  $\delta^{18}$ O values is greater than considered good, but the observed trends, even if not understood satisfactorily, show that these data might have some use in environmental interpretation.

#### CONCLUSIONS

- 1. The multiproxy study of the Puhmu core resulted in a set of new (or first published) data about the lithologies and lithostratigraphy of the section, its biostratigraphical characterization based on brachiopod, ostracode and chitinozoan distribution and some mass occurrences of dasycladacean algae. Carbon isotope chemostratigraphy exhibited four earlier known  $\delta^{13}$ C excursions beginning with the middle Katian Rakvere and Saunja excursions, the late Katian Moe excursion and the most prominent one, the HICE. The integration of these data sets allows us to more firmly apply the traditional Estonian chronostratigraphic framework consisting of five regional stages.
- 2. A faunistically proved gap, embracing at least the Hirmuse Fm., established in the bottom of the studied Puhmu section, was followed by a thin transgressive unit below the Tõrremägi Mb. (both identified mainly faunistically) of the lowermost Rägavere Fm. The FADs of several species in the Tõrremägi Mb. underline the importance of changes at the bottom of the Rägavere Fm., indicating that the lower boundary of the Rakvere RS is better motivated at this level.
- 3. Discontinuity surfaces are numerous and diverse in the Puhmu section, especially at two levels. One series of seven discontinuities occurs at the junction of the Tudu Mb. and Paekna Fm. and another series of 13 discontinuities is present through the Adila Fm. The positions of the both series coincide with a low (embracing also parts of the falling and rising limbs) of the carbon isotope excursion, referring to a low or falling sea level. A special discontinuity surface with heavy burrowing and deep cavities occurs between these series in the top of the Saunja Fm. It was treated by Calner et al. (2010) as a palaeokarst event embracing in southern Estonia nearly the entire Saunja Fm. and extending much more downwards in Sweden. In Puhmu, however, it is limited to a couple of metres without significant loss of thickness.
- 4. Checking the data obtained from the whole-rock and bioclast material in order to detect differences between them, we found that the  $\delta^{13}C$  data from all three materials (whole-rock, rugose coral skeletons and brachiopod shells) were very similar to each other. Such a situation might be caused by two circumstances: (1) most of the Puhmu rocks analysed have a very high percentage of calcite (more than

90%) and (2) the impact of diagenesis is mostly weak, as evidenced by a low CAI index. The variability of  $\delta^{18}$ O values is higher than considered as a good level, but the observed trends, even if not understood satisfactorily, suggest a possible use of these data in environmental interpretation.

5. Bioclast  $\delta^{13}C$  data from brachiopod shells and rugosan corallums are well concordant with the  $\delta^{13}C_{carb}$  analyses. The  $\delta^{18}O_{bio}$  analyses are slightly less variable than those from whole-rock samples, while the rugosan ones are placed closer to the trendline than  $\delta^{18}O_{bra}$ .

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#### Supplementary online data

Supplementary online data associated with this article can be found at http://doi.org/10.15152/GEO.17. There are presented 'Description of the Puhmu section' (Annex 1), a figure of photos of the typical rocks (Annex 2) and two tables (Annex 3): Table 1. Carbonate content (Cal, Dol) and share of insoluble residue (Ter) and Table 2. Data on whole-rock and bioclast C and O isotope analyses from the Puhmu core.

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# Puhmu puursüdamiku (Eesti, Ülem-Ordoviitsium) kompleksne uuring: järelmid stratigraafiale ja keskkonna tõlgendamisele

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Puursüdamiku litoloogiline, litostratigraafiline, brahhiopoodide, ostrakoodide ja kitiinikute uurimine koos süsiniku kemostratigraafiaga võimaldas oluliselt täiendada teadmisi Põhja-Eesti geoloogilise arenguloo kohta. Selgitati läbilõike alumise osa vetiklubjakivi tõenäoline kuulumine Rakvere lademesse ja selle all olevate kihtide omapärane brahhiopoodide ning kitiinikute koosseis, mis viitavad Oandu vanusele. Süsiniku ja hapniku isotoopide koosseisu dünaamika selgitamisel kasutati esmakordselt kompleksselt proove kivimist, käsijalgsete kodadest ning tetrakorallide skeletist. Paleokarsti esinemine Saunja kihistu ülemisel pinnal ja Paekna ning Adila kihistu sagedaste katkestuspindade paiknemine süsiniku isotoopide madalseisu tasemetel viitavad paleokeskkonna keerukustele, mida seni ei ole piisavalt selgitatud.