THESIS ON NATURAL AND EXACT SCIENCES B58

APPLICATION OF CARBON ISOTOPES TO THE STUDY OF THE ORDOVICIAN AND SILURIAN OF THE BALTIC

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The thesis was accepted for the commencement of the degree of Doctor of Philosophy in Natural Sciences on August 30, 2006.

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Commencement: December 20, 2006 at Tallinn University of Technology, Ehitajate tee 5, Tallinn, Estonia

Declaration: Hereby I declare that this doctoral thesis, my original investigation and achievement, submitted for the doctoral degree at Tallinn University of Technology has not been submitted for any degree or examination.

Tõnu Martma

ISSN 1406-4723
ISBN 9985-59-666-8

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LIST OF PUBLICATIONS

This thesis is based on the following papers, referred to in the text with Roman numerals as listed below:

I Kaljo, D., Kiipli, T., Martma, T. 1997. Carbon isotope event markers through the Wenlock–Pridoli Sequence at Ohesaare (Estonia) and Priekule (Latvia). Palaeogeography, Palaeoclimatology, Palaeoecology, 132(1–4), 211–223.

II Ainsaar, L., Meidla, T., Martma, T. 1999. Evidence for a widespread carbon isotopic event associated with late Middle Ordovician sedimentological and faunal changes in Estonia. Geological Magazine, 136(1), 49–62.

III Kaljo, D., Hints, L., Martma, T., Nõlvak, J. 2001. Carbon isotope stratigraphy in the latest Ordovician of Estonia. Chemical Geology, 175, 49–59.

IV Brenchley, P.J., Carden, G.A., Hints, L., Kaljo, D., Marshall, J.D., 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(1), 89–104.

V Kaljo, D., Martma, T., Männik, P., Viira, V. 2003. Implications of Gondwana glaciations in the Baltic late Ordovician and Silurian and a carbon isotopic test of environmental cyclicity. Bulletin de la Societe Geologique de France, 174(1), 59–66.

VI Kaljo, D., Hints, L., Martma, T., Nõlvak, J., Oraspõld, A. 2004. Late Ordovician carbon isotope trend in Estonia, its significance in stratigraphy and environmental analysis. Palaeogeography, Palaeoclimatology, Palaeoecology, 210, 165–185.

VII Martma, T., Brazauskas, A., Kaljo, D., Kaminskas, D., Musteikis, P. 2005. The Wenlock–Ludlow carbon isotope trend in the Vidukle core, Lithuania, and its relations with oceanic events. Geological Quarterly, 49(2), 223–234.

The co-authorship of the papers reflects that they are part of a collaborative research project. The author was responsible for all analytical whole-rock isotope work and participated in all interpretations, palaeoclimatological ones in particular, concerning the carbon and oxygen isotope data. Geological aspects were more the topic of other members of the team.

1. INTRODUCTION

Isotopic methods have gained an eminent position in palaeoclimatology, palaeoceanography and stratigraphy also in the early Palaeozoic. Despite good progress achieved in isotope palaeoclimatology and palaeoceanology, different environmental interpretations are still under debate or uncertain.

Cyclicity seems to be one of the most common patterns of the changing environment. Quite different features (biotic, climatic, magmatic, oceanic, sedimentological, tectonic, etc.) can be cyclic. In some cases, a cosmic influence has been suggested (e.g., Milankovich cycles; see Jeppsson, 1990), among other forcing mechanisms.

Carbon cycling is one feature of environmental cyclicity. The essence of the cycling in the ocean is photosynthetic reduction of bicarbonate carbon to organic carbon. Organic carbon will mainly be oxidized and returned to the photic zone through the so-called "biological pump" (Kump, 1991; Holser et al., 1995), but will be partly buried in sediments. Under specific conditions (anoxic bottom waters, rapid sedimentation, high biological productivity), this process may result in enhanced removal of light organic carbon from surface waters, and will consequently cause higher $\delta^{13}C$ values in surface waters (recorded in fossils and in sedimentary rocks). A full accounting of carbon cycling also involves carbon influx from land (rivers) and interaction with the atmosphere.

My main aim was to establish the most essential shifts in the carbon isotope ratio of Silurian and Ordovician sedimentary rocks and to discover possible relationships of these shifts with different environmental processes and events.

Success in carbon isotope stratigraphy depends mainly on how complete and detailed is a standard trend used as a basis for comparisons. Of course, correct correlation of sections and biostratigraphic dating of samples are crucial for obtaining reliable results. Despite different complications I believe that the general pattern of carbon isotope changes can well serve as a stratigraphic, and with some caution, also as a palaeoclimatologic tool for Ordovician and Silurian time.

Considering the results of the last few years, a nearly complete and detailed $\delta^{13}C$ trend was composed for the Silurian, based on the data from Baltica and with supplementary information from elsewhere. For the Ordovician the same was done based on the data from Baltica and Laurentia. The latter was supported by a recent paper of Saltzman and Young (2005), providing a nearly complete composite $\delta^{13}C$ curve of the Middle and Upper Ordovician of Nevada. The Baltic and Laurentian curves allow comparison of carbon isotope trends in different continents, reveal global aspects of the trend and in this way contribute to the compilation of a standard carbon isotope curve. Such a curve could serve as a basis for interpretation of world carbon cycling and act as a template for chemostratigraphical correlation. This contribution is the main goal of the present thesis.

2. A REVIEW OF STABLE ISOTOPE RESEARCH

2.1. Carbon and oxygen stable isotopes

Stable isotopes are those isotopes of an element which are stable and that do not decay through radioactive processes over time. Most elements consist of more than one stable isotope. The element carbon (C) exists as two stable isotopes, ^{12}C (98.89%) and ^{13}C (1.11%), while the element oxygen (O) exists as three stable isotopes, ^{16}O (99.759%), ^{17}O (0.037%) and ^{18}O (0.204%).

Variations in stable isotope ratios in nature are mostly small. They are, however, important tracers that can reveal a wealth of information about processes that are happening or have happened in the past.

The abundance of stable isotopes is typically presented in delta notation (δ), in which the stable isotope abundance is expressed relative to a standard:

$$\delta = (R_{sample} / R_{standard} - 1) \times 1000‰,$$

where R is the molar ratio of the heavy to light isotopes (R = $^{13}C/^{12}C$ or $^{18}O/^{16}O$).

Carbon occurs primarily in three reservoirs on the Earth: sedimentary organic matter, the biosphere and sedimentary carbonates. These reservoirs differ in isotopic composition because of different isotope fractionation mechanisms. Kinetic isotope fractionation associated with photosynthesis preferentially enriches plant material in ^{12}C. This enrichment gives rise to organic sediments, coal, and crude oil with $\delta^{13}C$ values near -25‰ and sedimentary carbonates near 0‰. Total dissolved inorganic carbon (DIC) in the oceans consists of dissolved bicarbonate, carbonate, and carbon dioxide in aqueous solution. In the Earth's oceans bicarbonate ion predominates. The primary sources of DIC are atmospheric CO_2, dissolution of carbonate and decay of organic matter. The variation in $\delta^{13}C$ of DIC "modern" ocean water is small, -0.8‰ to +2.2‰ (Kroopnick, 1985).

2.2. Mass spectrometer hardware for analysing stable isotope ratios

A mass spectrometer meant for stable isotope ratio measurements consists of an inlet system, an ion source, an analyser for ion separation, and a detector for ion registration. The inlet system is designed to handle pure gases, principally CO_2, N_2, H_2 and SO_2 but also others. Neutral molecules from the inlet system are introduced into the ion source, where they are ionized via electron impact and accelerated to several kilovolts, and then separated by a magnetic field and detected by Faraday cups positioned along the image plane of the mass spectrometer. The principles guiding the design and operation of each of these individual sections of the mass spectrometer are described and discussed in Brand (2004).

Because of instrumental requirements, carbon and oxygen must be converted to CO_2 for stable isotope ratio measurements. Most of error associated with isotopic measurements results from sample preparation. Carbonate carbon and oxygen are converted to CO_2 by reaction under vacuum with concentrated phosphoric acid. If the reaction temperature remains known and constant and water-free 100% phosphoric acid is used for acidification, this procedure can be used to measure both the $\delta^{13}C$ and $\delta^{18}O$ of the carbonate sample.

If organic matter is present in the carbonate sample, some authors recommend removing the organic by roasting the sample under vacuum at approximately 380º C or by soaking it overnight in 5% hypochloride solution. Still some others do not use pretreatment claiming that it affects the isotope data adversely (Grottoli, 2005).

2.3. Reference materials and reporting of isotope ratios

2.3.1. Carbon

Beginning in the 1950s, isotope-abundance measurements of carbon isotopes were expressed relative to Peedee belemnite (PDB), which was the carbonate skeleton of a belemnite from the Cretaceous Peedee Formation in South Carolina. Because the supply of PDB is exhausted, it was recommended in 1993 that carbon isotope abundances should be reported relative to VPDB (Vienna PDB, the new primary reference for carbon isotope ratios having a $\delta^{13}C$ value of 0‰) by assigning an exact $\delta^{13}C$ value of +1.95‰ on the VPDB scale to the IAEA reference material NBS 19 calcium carbonate. Carbon isotope ratios are determined on gaseous CO_2 and commonly are measured with a standard deviation of ±0.1‰. Secondary reference materials are distributed by the IAEA and NIST and include various carbonates, natural gases, sugars and an oil (Coplen, 2002).

The following laboratory standards for carbonate are used in the Laboratory of Isotope-Palaeoclimatology, Institute of Geology at Tallinn University of Technology, calibrated against the VPDB scale:

TLN-C1 (Marble)

$\delta^{13}C$= +2.1‰, $\delta^{18}O$= -9.3‰

TLN-C2 (Limestone, collected by H. Bauert from Syria)

$\delta^{13}C$= +0.8‰, $\delta^{18}O$= -2.2‰.

2.3.2. Oxygen

Since 1993, the IAEA has recommended that oxygen isotope ratios be reported relative to VSMOW water on a scale normalized such that the exact $\delta^{18}O$ of SLAP water is -55.5‰ or relative to VPDB (defined by adopting an exact $\delta^{18}O$ value of -2.2‰ for NBS 19 $CaC0_3$). Using the data in Coplen et al. (1983) and given a value of -2.2‰ for the $\delta^{18}O$ value of NBS 19 relative to VPDB, the VPDB scale can be related to the VSMOW scale by

$\delta^{18}O_{x\text{-}VPDB} = 0.97001\ \delta^{18}O_{x\text{-}VSMOW} - 29.99$

The $^{18}0/^{16}0$ isotope ratios are determined on gaseous CO_2 and commonly are measured with a 1-∗ standard deviation of +/-0.1‰ (Coplen, 2002).

The following laboratory standards are used in the Laboratory of Isotope-Palaeoclimatology, Institute of Geology at Tallinn University of Technology, calibrated against the VSMOW scale:

TLN-A (laboratory tap water)
$\delta^{18}O$= -9.8‰
TLN-B (tap water from the Cambrian-Vendian groundwater layer, town of Keila, Estonia)
$\delta^{18}O$= - 26.2‰
TLN-C (Central-Antarctic Dome B ice)
$\delta^{18}O$= -56‰.

In practice, measurements are made against a working or laboratory reference that has been calibrated carefully against an international reference material. Thus, the measured delta values need to be converted to another scale before reporting:

$$\delta_{Sa/St} = \delta_{Sa/WS} + \delta_{WS/St} + 10^{-3}(\delta_{Sa/WS} \times \delta_{WS/St}),$$

where WS is the working standard, St denotes the international standard material and Sa the measured sample.

2.4. Brief summary of carbon and isotope studies in the Ordovician and Silurian with special attention to Baltoscandia

Isotope studies embracing the southwestern sector of the Palaeozoic Baltica continent, including the present East Baltic (Estonia, Latvia and Lithuania), Gotland, Scania and the Oslo region, but also the Anglo-Welsh area, i.e. a part of Avalonia which joined Baltica in the late Ordovician, commenced roughly 20 years ago. In the Ordovician pioneering work was done by the Liverpool team (Marshall and Middleton, 1990; Middleton et al., 1991; Marshall, 1992; Brenchley et al., 1994). Using bioclast analyses, they identified for the first time the major positive carbon and oxygen isotope excursions in the Hirnantian of the Siljan area and in Estonia and connected these to the corresponding glaciation and mass extinction events. According to their explanation the changes in oxygen isotope values reflect a decrease in temperature and these in carbon suggest enhanced deposition of organic carbon. These processes correlated also with changes in ice cap volume, sea level, and oceanic circulation. A more extensive overview and generalization of the topic was published together with Estonian colleagues ten years later (paper IV).

Among Silurian stable isotope studies an early work by Corfield et al. (1992) on Wenlock isotopes of Shropshire should be mentioned. However, different German teams carried out a much more extensive research based on the Gotland sections. Jux and Steuber (1992) first noted the early Wenlock and Ludfordian positive C and O isotope shifts respectively in the Högklint Beds and Burgsvik, Hamra and Sundre beds of Gotland (Fig. 1), with a $\delta^{13}C_{carb}$ peak of 5.7‰ in the Hamra Beds and $\delta^{13}C_{org}$ peak in the Burgsvik Beds. Based on analyses of brachiopod shells, Wenzel and Joachimski (1996) produced a more complete curve of the same $\delta^{13}C_{carb}$ excursion, beginning in the Lower Eke Beds (mean value 6.9‰), reaching peak values (8.1‰) in the Upper Eke Beds, and continuing through the Burgsvik (6.8‰) and Hamra (3.7‰) beds. The authors of the last two papers highlighted a correlation between the global sea level curve and changes in the distribution of carbon isotopes: the high $\delta^{13}C$ values, generally confined to sea level low-stand episodes, were regarded as indications of enhanced primary productivity and possibly increased burial of C_{org} in Silurian seas. In the same year Samtleben et al. (1996) provided a summary about the Gotland C and O isotope curves with three major excursions, but in their reasoning more stress was put on changes in oceanic circulation, making use of Jeppsson's (1990) ideas about cyclic events in the oceanic environment. Next year Bickert et al. (1997) published a more advanced model.

Very high $\delta^{13}C$ levels were documented in the Ludfordian also by Wigforss-Lange (1999) in Scania (11.2‰) and in paper VII in Lithuania (8.2‰). However, the highest C isotope values (12 to 13‰) were reported by Andrew et al. (1994) from the upper Ludlow Jack Limestone in Australia. The shift is located just above the Pentamerid Event and 40 m above the only known occurrence of *Polygnathoides siluricus*. This dating coincides with Baltic data. Andrew et al. (1994) emphasized causal ties between biotic and isotope events.

The data presently available from the East Baltic (papers I–VII, a.o.) allow us to discuss a more or less continuous curve of $\delta^{13}C$ values beginning with the post-Hunnebergian Ordovician until the Silurian–Devonian boundary beds (~60 m.y.).

3. MATERIAL AND METHODS

A reliable isotope stratigraphy that can be used for palaeoenvironmental work should be based on: a) a sampling strategy fitted for the purpose (samples taken as close as needed, so that events and trends can be identifed) and b) as good as possible biostratigraphic dating of samples.

The isotopic composition of the samples should reflect the composition of the marine DIC from which the carbonate is formed. Well-preserved bioclastic material from calcareous fossils that form in isotopic equilibrium with sea water provide ideal material for isotope analysis (Marshall, 1992). But well preserved shell material is commonly rare and difficult to prepare.

Due to the scarcity of brachiopods in deeper-water sediments of the Baltic Ordovician–Silurian, a whole-rock method for isotopic analysis was chosen. That allows sampling an entire section at more or less regular intervals not depending on the occurrence of bioclasts. By selecting the sampling interval the stratigraphic context (lithology, unit thickness and boundaries) was considered. The bio- and lithostratigraphy was applied in detailed stratigraphical dating of samples. Much of work of our team has been done using drill cores belonging to the Geological Survey of Estonia, Institute of Geology at Tallinn University of Technology, Geological Survey of Lithuania. Therefore microfossils such as conodonts and chitinozoans were the most important tools for dating (Männik, 2001; Männik and Viira, 2005; Nõlvak, 2001, 2005). Graptolites are rare in Estonia, but useful at some levels (e.g. *Nemagraptus gracilis* in the bottom of the Upper Ordovician and several monograptids in the Lower Silurian). The whole-rock samples (about 2500 analyses) used for this work came from 30 boreholes and 2 outcrops (Table 1 and Figs 1, 2) located in the different facies belts of the Palaeobaltic Sea (Estonia, Latvia and Lithuania). The samples were powdered to a grain size of < 10 µm and reacted with 100% phosphoric acid at 100º C for 15 min (Karhu, 1993) and analysed with a Finnigan MAT "Delta E" mass spectrometer. The results are presented in the usual δ-notation, as per mil deviation from the VPDB standard. The reproducibility of the results is better than ±0.1‰.

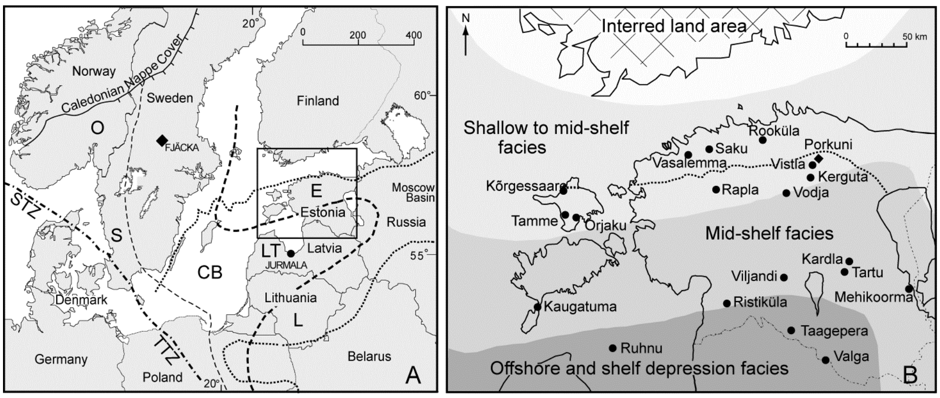

Figure 1. A. General facies zonation of the late Ordovician Baltoscandian basin. General facies belts by Männil (1966): E – North Estonian, L – Lithuanian, CB – Central Baltoscandian with the Livonian Tongue (LT) included, S – Scanian; O – Oslo. Tornquist–Teisseyre (TTZ) and Sorgenfrei–Tornquist (STZ) zones by Tuuling (1998). Dotted line – outer limit of the area with continuous distribution of the Ordovician rocks.
B. Location of the studied core sections (black dots) and outcrops (black rhombs) modified from paper VI. Palaeogeography and facies of Vormsi age (early Ashgill). The belt without signature next to the land denotes uncertain transition between land and sea. Facies distribution north of the dotted line extrapolated from rocks occurring south of the line.

Table 1. List of borehole and outcrop sections considered

No.	Name	Stratigraphy	Interval, m		L, m	No.	Data published by
	Boreholes						
1	Kerguta	Billingen - Nabala	107	192	85	83	Martma, 2006 F; Kaljo, Martma, Saadre, 2006
2	Mehikoorma	Volkhov - Pirgu	247	371	125	112	Martma, 2005 F; Kaljo, Martma, Saadre, 2006
3	Valga - 10	Lasnamägi - Porkuni	309	424	115	137	Ainsaar et al., 2004 F; Kaljo, Martma, Saadre, 2006
4	Ristiküla - 174	Haljala - Vormsi	395	429	33	67	Ainsaar et al., 1999,a F; II; Ainsaar et al., 2000 F
5	Saku - 1098A	Keila - Oandu	1	25	24	25	VI
6	Vasalemma	Keila - Oandu	4	15	11	11	VI
7	Tartu-453	Keila - Rakvere	286	314	27	46	Ainsaar et al., 1999,a F; II; Ainsaar et al., 2000 F
8	Pärnu-6	Keila - Rakvere	325	329	4	9	II
9	Rooküla	Keila - Rakvere			5	20	VI F
10	Kõrgessaare	Keila - Nabala	10	71	61	48	VI
11	Orjaku	Keila - Porkuni+S	36	140	103	87	VI
12	Rapla	Keila - Porkuni	32	144	112	83	Kaljo et al., 1999 F; VI
13	Viljandi	Keila - Porkuni+S	275	350	75	95	VI
14	Jurmala - R1	Keila - Porkuni					unpublished
15	Kardla	Pirgu - Porkuni	160	186	26	43	III; IV F; VI
16	Kaugatuma	Pirgu - Porkuni	330	385	56	37	Kaljo et al., 1999 F; III; IV F; VI
17	Ruhnu	Porkuni - Jamaja	378	624	246	161	Kaljo et al., 1998 F; Kaljo and Martma, 2000 F; III; V F; Martma, 2003
18	Tamme	Pirgu - Porkuni	34	41	7	12	III; IV F
19	Vistla II	Pirgu - Porkuni	11	19	9	14	III
20	Vodja	Pirgu - Porkuni	51	58	7	12	III
21	Ikla	Porkuni - Jaani	260	535	274	107	Kaljo and Martma, 2000 F
22	Kirikuküla	Porkuni - Jaani	1	140	138	102	Kaljo and Martma, 2000 F
23	Taagepera	Porkuni - ?	274	429	155	106	Kiipli et al., 1998 F; IV F; unpublished
24	Ohesaare	Jaani - Kaugatuma	4	364	360	210	I F; V F; Kaljo, Martma, 2006 F
25	Aizpute	Porkuni	983	1002	19	27	Männik et al., 2002 F
26	Ventspils	Dobele - Targale	266	871	605	268	Kaljo et al., 1998 F; Kaljo, Martma, 2006 F
27	Viki	Raikküla - Jaagarahu	14	197	183	134	V F
28	Vidukle	Riga - Minija	1080	1404	324	115	Martma et al., 2005; Kaljo, Martma 2006 F
29	Priekule		919	1338	420	127	I F
30	Pavilosta						unpublished
	Outcrops						
1	Fjäcka	Dalby - Slandrom			21	25	Ainsaar et al., 2000 F; 2001 F
2	Porkuni	Porkuni	1	6	6	10	Kaljo et al., 2001

The names are arranged according to the oldest interval studied. F denotes a figure only (without published values).

The quality of the carbon isotope data based on whole-rock analyses has been discussed in several papers (e.g. paper I; Marshall et al., 1997). Paper IV investigated in detail the reliability of isotope signals in the Late Ordovician rocks of Estonia and noted that major changes in carbon isotope values reflect primary composition. The comparison of the Baltic latest Ordovician and Silurian whole-rock (Kaljo et al., 1998; paper III) and brachiopod shell isotope data (Marshall et al., 1997; Heath et al., 1998; paper IV) shows only slight difference in $\delta^{13}C$ values but great similarity of the corresponding curves. For example, Heath et al. (1998) reported peak values of 5.9 to 7.1‰ for the Hirnantian brachiopod shells collected from the Ruhnu core at a depth of 610–615 m. Paper III reported from the same interval whole-rock values of 5.0 to 6.9‰. Good harmony of the results obtained by both methods is confirmed also by Silurian data from Gotland (Samtleben et al., 1996). This allows of the conclusion that diagenesis tends to reduce the magnitude of isotope shifts but the general pattern of the carbon cycle is well preserved in Baltic whole-rock samples.

The oxygen isotope ratios are more sensitive to diagenesis (Marshall, 1992; Saltzman, 2002). Whilst marine oxygen isotope values may be preserved in petrographically unaltered brachiopods, whole-rock values are most often altered. This can be due to the incorporation of variable amounts of dolomite, but also because fine-grained carbonates have evidently recrystallized. Oxygen is more susceptible to changes during diagenesis because effective water–rock ratios are greater for O and oxygen isotopic fractionation is strongly temperature dependent. In the studied drill cores the measured $\delta^{18}O$ values vary from -2 to -9‰, which is close to the oxygen isotopic values in the Ordovician brachiopods and marine carbonates (Veizer et al., 1997) and these values evidence that corresponding rocks were not very seriously affected by diagenesis (paper I). The Baltic carbonate rocks are mostly highly variable mixtures of calcite and dolomite, which have different oxygen isotope fractionation factors. Therefore the oxygen isotope data from this whole-rock analysis cannot be interpreted unambiguously and these are not used here in geological or environmental discussions.

4. GEOLOGICAL SETTING AND STRATIGRAPHICAL FRAMEWORK

Sedimentary rocks of the Palaeobaltic Basin (Figs 1, 2) were the main study objects for this thesis. The lithological composition of samples reflects differences in environmental conditions in the sea and a general climatic situation in a wider area. These data as well as stratigraphical dating of samples are important for the palaeoceanological and palaeoclimatological interpretation of the isotope data.

The latest Ordovician Baltic Basin stretched from eastern Norway to western Russia (Fig. 1). In Estonia and Latvia, a ramp sloped southward into the

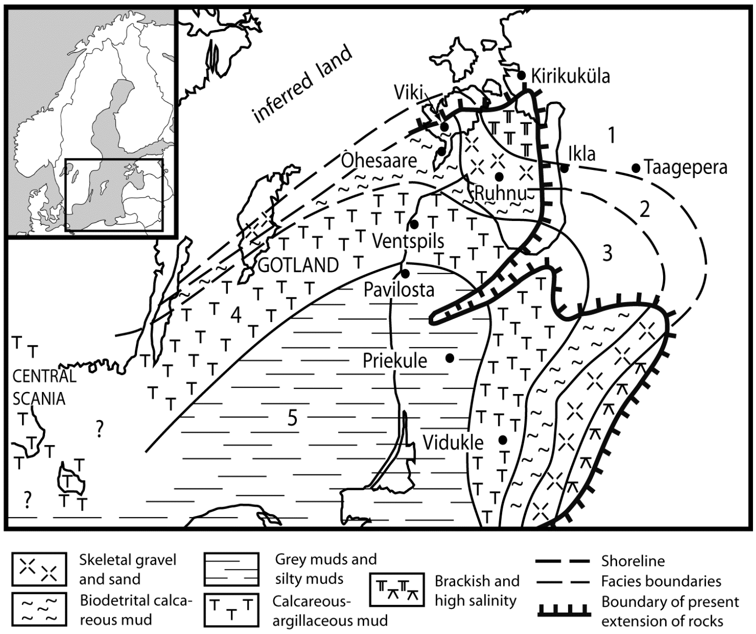

Figure 2. Location of the studied core sections, and general facies zonation of the Baltic Gulf during early Ludlow time. Modified from paper VII. Facies belts: 1 – tidal flat/lagoon, 2 – shoal, 3 – open shelf, 4 – transition from open to deep shelf, 5 – shelf depression.

Jelgava depression. Numerous borehole successions, including the 14 studied here (Fig. 1B, Table 1), record the shallow-marine carbonate sequences of the North Estonian facies belt and the lateral transition into a deeper, more argillaceous facies that comprises the Livonian Tongue in southern Estonia and Latvia. In terms of palaeogeography, Ordovician and Silurian rocks in the northern part of the East Baltic area (Estonia, Latvia and Lithuania) were formed in a wide gulf-like sea on the west margin of the Baltica palaeocontinent (Männil, 1966; Bassett et al., 1989).

Regular associations of sedimentary rocks with specific fossil communities occur as belts subparallel to the shoreline (Fig. 2). Nearshore facies is represented by lagoonal dolomites and/or dolomitic marls. In the high-energy shoal belt predominantly grainstones occur, with organic buildups at several levels in the Late Ordovician and Silurian. In the shallow shelf or mid-shelf area different limestones (wackestones with grain- and packstone intercalations) are present, which are locally nodular or micritic and interbedded with marlstones. Seawards, on the deeper outer shelf, there occur mainly marlstones and mudstones, sometimes also micritic limestones, forming a transition from shelf to the shelf depression and basin, where dark or even black shales and claystones with graptolites dominate. Basinal (and shelf depression) rocks are rich in pyrite and organic carbon, indicating relatively deep-water, oxygen-deficient depositional conditions.

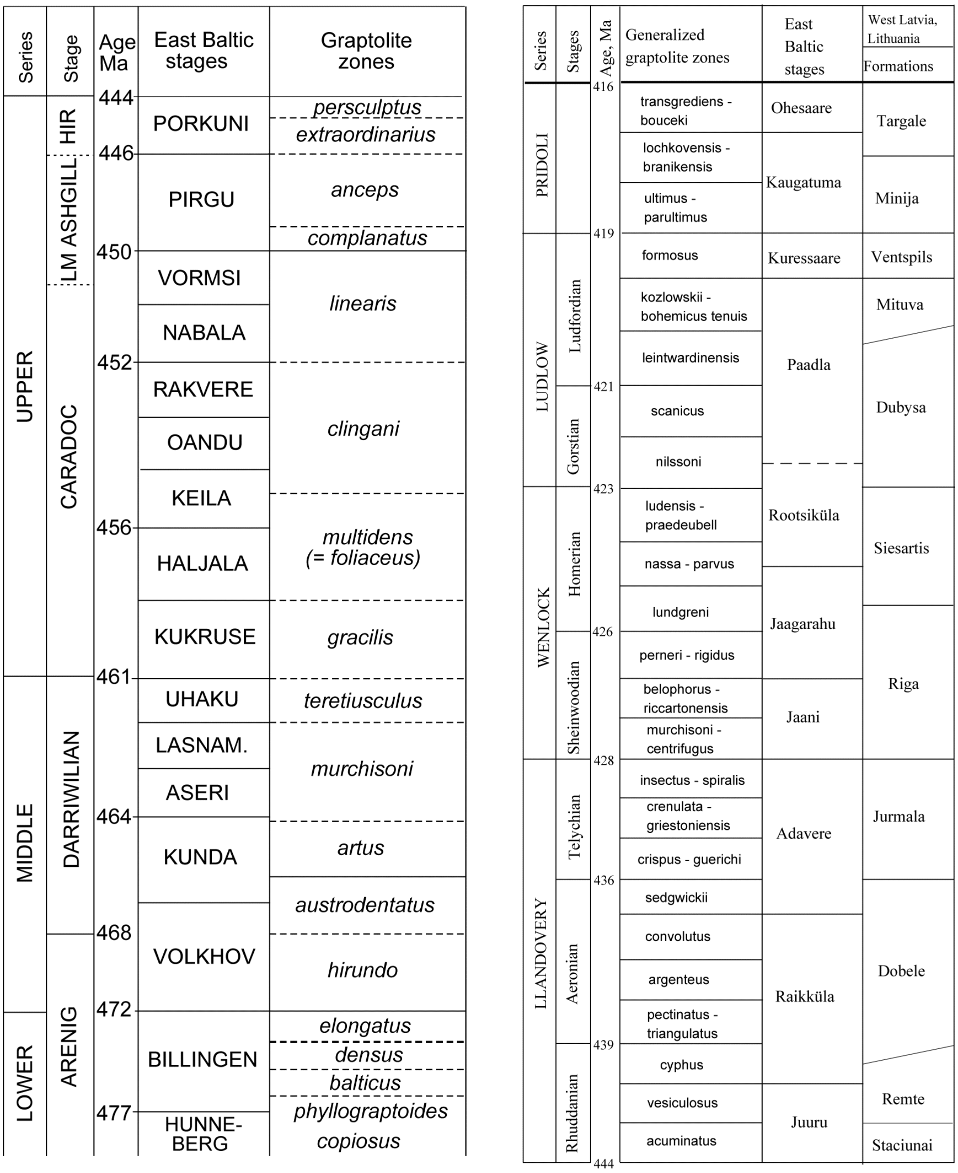

Figure 3. Stratigraphical classifications used in Estonia correlated with British series (principally according to Nõlvak, 1997).

The sequence of rocks, described above, marks a transition from shallow to deep sea and shows a clear pattern where the terrigenous siliciclastic component (clay and fine silt) in rocks increases and the carbonate content decreases. The calcite content exceeds 90% in grainstones and biohermal limestones and is close to 90% in some micritic limestones, but falls below 75% in skeletal wackestones and is only 10–20% in deep shelf mudstones.

During the time studied these main facies belts were shifted in response to sea level changes, some of which might be of eustatic origin or caused by tectonic movements or changes in the sedimentation regime. Some idea about that can be obtained in Figure 2. The early Ludlow reconstruction of Figure 2 is for a period of sea level high-stand, but after a considerable regression in the late Wenlock. The relatively deep-water outer-shelf facies belt (number 4 in Fig. 2) occurs in the Ventspils area, but in the early Wenlock occupies the northern belt including Kirikuküla, Viki and Taagepera areas. Earlier in the Rhuddanian and Aeronian, this region belonged to the nearshore and shallow shelf facies belts. Due to a general shoaling of the Baltic Basin beginning in the middle Wenlock, the shallow shelf belt moved south in a stepwise manner. As a result, the Ohesaare area in the late Wenlock and the Ventspils area in the Pridoli were covered by a shallow sea. Deep-water Ludlow sediments with graptolites are present in the Pavilosta and Priekule regions. General lithology of the sections is shown below in logs of the Mehikoorma, Vidukle and Ventspils cores.

Due to minor differences in local geological history, the sections might be more or less complete and the whole set of sections has been correlated biostratigraphically. Most of the cores studied represent relatively deeper water facies with a decreased carbonate content, but they were chosen in order to avoid the gaps in the sequence which occur rather often in the sections of the shallow shelf area. Nevertheless, as seen from the Ruhnu core, for various geological reasons hiatuses must also be considered in the deep shelf area. The stratigraphical terminology employed in the thesis is summarized in Figure 3. For better orientation also generalized graptolite zones (Koren et al., 1996) and absolute ages (modified after Tucker and McKerrow, 1995, see Kaljo et al., 1998) are included. Information on lithologies of the units identified in cores is shown in Figure 2.

Local climate was influenced by the drifting of Baltica from high latitudes of the Southern Hemisphere in the early Ordovician to an equatorial position by the mid-Silurian (Cocks and Torsvik, 2002), as well as by global changes in the climate and oceanic circulation (Jeppsson, 1990; Bickert et al., 1997). This means that the local climate became tropically warm in the Wenlock, and towards the Devonian some signs of increasing aridity and evaporation have been observed. However, these changes include also alternating humid and arid conditions, sea level changes and a major glacial event in the Hirnantian, and several minor glacial episodes in the Early Silurian (Caputo, 1998; Munnecke et al., 2003; papers IV, V, VI; in more detail see below).

5. RESULTS AND DISCUSSION

The most important result of my isotopic studies is an analytical database of more than 2500 whole-rock samples. For economy of space the analyses are not presented here but only listed by number and localities in Table 1. Below I discuss the data set according to certain stratigraphical intervals: the post-Hunnebergian Ordovician embraces in terms of Baltic stratigraphy (Fig. 3) the sequence from the Billingen Stage up to the Pirgu Stage. The topmost Ordovician stage – the Hirnantian (= Porkuni Stage) – is discussed separately, because of its importance in the study history. The Silurian part of the discussion begins with the Llandovery Series and ends with the summary of the Wenlock, Ludlow and Pridoli series.

The study interval embraces ~60 m.y. of geological time. Background values of $\delta^{13}C$ vary, but are mainly close to 0–1‰ with a few negative shifts and more importantly a number of positive excursions (positions shown in Figs 4, 6).

One of the key findings of this work is that the occurrence of a series of carbon isotope shifts, mostly of global importance, has been proved. Six medium-seized positive excursions occur in the Ordovician: one in the Darriwilian (at 463 Ma), three in the Caradoc (at 454, 453 and 451 Ma), two in the Ashgill (at 449 and 447 Ma). The Ordovician was finished by a major excursion at 445 Ma. The Silurian began with two medium-seized shifts in the Llandovery (at 438 and 434 Ma), two medium to major excursions in the Wenlock (428 and 424 Ma) and a very high shift in the late Ludlow (at 420 Ma). Considering their distribution along the geological time scale and the environmental background of the corresponding age the carbon cycling during the study interval and the reasons driving the processes can be established, as discussed below.

5.1. General pattern of the carbon isotope trend in the Ordovician and Silurian

The magnitude and frequency of carbon isotope shifts divide the post-Hunnebergian Ordovician into two parts:

(1) The earlier low-variability interval embraces the middle part of the Ordovician from the bottom of the Billingen Stage up to the beginning of the mid-Caradoc excursion in the upper part of the Keila Stage (Fig. 3A). During ca 23 m.y. the $\delta^{13}C$ values were varying mainly between 0 and 1‰ (partly also below 0‰), with one relatively low positive shift and one very broad negative excursion. These two “anomalies” could not seriously change the generally quiet pattern of the carbon isotope trend, which seems to be typical of the middle to early late Ordovician. Still, this conclusion might be modified later, when the oldest part of the succession, the Billingen Stage (represented by three analyses only) in particular, will be studied in more detail.

(2) The increasingly variable interval (10 m.y.) embraces the upper part of the Ordovician beginning with the mid-Caradoc excursion at 454.5 Ma. During the first 9 m.y. the medium-sized $\delta^{13}C$ shifts show a regular increase in values from about 2‰ to 2.5‰ and result in the major Hirnantian excursion at 445 Ma with values reaching 6‰ to 7‰.

This change in the carbon fractionation pattern should be considered fundamental. It must reflect global changes in climatic and oceanic conditions, but some regional processes connected with the evolution of the sedimentary basin, drift of Baltica, etc. may have had certain influence (Kaljo et al., 1999; paper VI). Taking the global aspect, I note that Shields et al. (2003) suggest a major reorganisation of ocean chemistry and the surface environment around the Middle–Late Ordovician transition. This change, marked mainly by rapid fall of the $^{87}Sr/^{86}Sr$ ratio in seawater, occurred about 5 m.y. earlier than noted above for carbon isotopes. The reported changes in $\delta^{18}O$ and $\delta^{13}C$ are much smoother and show slow increase in values (the oxygen values are interpreted as decreasing temperature) through the late Ordovician, except the very end with rapid changes (Shields et al., 2003). Considering these differences in trends of Sr, O and C, it seems important to note that chemistry of the world ocean began to change around 461 Ma, but not at once in all aspects and some local overprinting is also possible.

The Baltica palaeocontinent drifted from mid-latitudes to a subequatorial position during the Ordovician (Cocks and Torsvik, 2002). That means certain warming in regional climatic conditions, as well as global influence on the climate resulting in glacial conditions in the Southern Hemisphere in the Hirnantian (paper IV) or earlier (Hamoumi, 1999). Shields et al. (2003) also noted decreasing temperature, but some other authors advocated for a short-lived pre-Hirnantian global warming, based on the Boda mud-mound data (Fortey and Cocks, 2005). The mid-Caradoc shift marks the beginning of intense $\delta^{13}C$ variations and the differentiation stage of basin development in the late Caradoc (Nestor and Einasto, 1997). The first coral-stromatoporoid reefs and abundance of algal particles in the mid-Caradoc and younger limestones of Estonia have been interpreted as proxies of warmer climate (Põlma, 1972) and oceanic conditions (Kaljo et al., 1999) that are consistent with drift of Baltica. The sedimentary record and carbon isotope excursions in the light of the oceanic models by Jeppsson (1990) and Bickert et al. (1997) show repeated alternations of arid and humid climate in the late Ordovician, which partly might be accompanied by several pre-Hirnantian cooling episodes (paper VI).

Summarizing the above data, we can say that the Late Ordovician, especially its younger part beginning with the mid-Caradoc, was environmentally a more variable time than most of the Middle Ordovician. This is clearly reflected in the character of the two main subdivisions of the Ordovician general carbon isotope trend.

A similar general pattern is observed in the Silurian: infrequent middle-sized shifts in the Llandovery (16 m.y.), two major sifts in the Wenlock and an extremely high $\delta^{13}C$ peak in the late Silurian. However, the frequency of carbon isotope shifts is much smaller in the Wenlock–Ludlow (every 4 m.y.), than in the late Ordovician, but the $\delta^{13}C$ values are nearly twice higher. The fundamental reason for such an arrangement seems to be global changes in carbon cycling, but some regional correction of values is also obvious (see below).

To sum up, it seems possible to distinguish the Ordovician and Silurian as major cycles in the general trend of carbon isotope changes. During these cycles the amplitude of values was increasing step by step as demonstrated below.

5.2. Post-Hunnebergian Ordovician

The following positive carbon isotope events were observed (Ainsaar et al., 2004,a,b; papers II, VI; Martma, 2005, 2006) and placed into the Baltic stratigraphical framework in order to understand local environmental implications:

(1) the mid-Darriwilian excursion (peak $\delta^{13}C$ value 1.9‰, found in the Jurmala drill core) in the Aseri Stage;
(2) the mid-Caradoc excursion (2.2‰, Tartu core) in the uppermost part of the Keila Stage;
(3) the first late Caradoc excursion (2.3‰, Valga core) in the lower part of the Rakvere Stage;
(4) the second late Caradoc excursion (2.4‰, Kõrgessaare core) in the upper part of the Nabala Stage;
(5) the early Ashgill excursion (2.5‰, Kaugatuma core) in the lowermost part of the Pirgu Stage;
(6) the mid-Ashgill excursion (2.0‰, Jurmala core) in the upper part of the Pirgu Stage;
(7) the widely known large Hirnantian excursion (in Estonia the peak value reaches 6.7‰, Kardla core) in the Porkuni Stage (see comments in chapter 5.3).

In addition, some more facts should be considered when interpreting the data. A broad negative excursion through the upper Darriwilian/lower Caradoc with a maximum negative $\delta^{13}C$ value of -1.6‰ (Kerguta core) occurs in the upper part of the Kukruse Stage (Martma, 2005, 2006). This negative excursion coincides with the early part of the Caradoc transgression and large-scale accumulation of kerogenous organic matter (forming the Estonian oil shale, kukersite) and is well dated by occurrences of *Nemagraptus gracilis,* an index species for the beginning of the Upper Ordovician.

Low $\delta^{13}C$ values in the pre- and lower Darriwilian occur in relatively cool-water carbonate rocks enriched in part by glauconite and/or iron oxides. Storm-generated sedimentary rocks with hardgrounds and karstified surfaces are found at many levels (Dronov, 1998). The early Ashgill excursion in Estonia is well observable in the Kaugatuma core (2.5‰, paper VI), but less expressed in some other sections. The mid-Ashgill excursion is relatively weak in Estonia. In three localities $\delta^{13}C$ values reach 1.7‰ to 2.0‰, but the excursion is not well traceable in the Valga core.

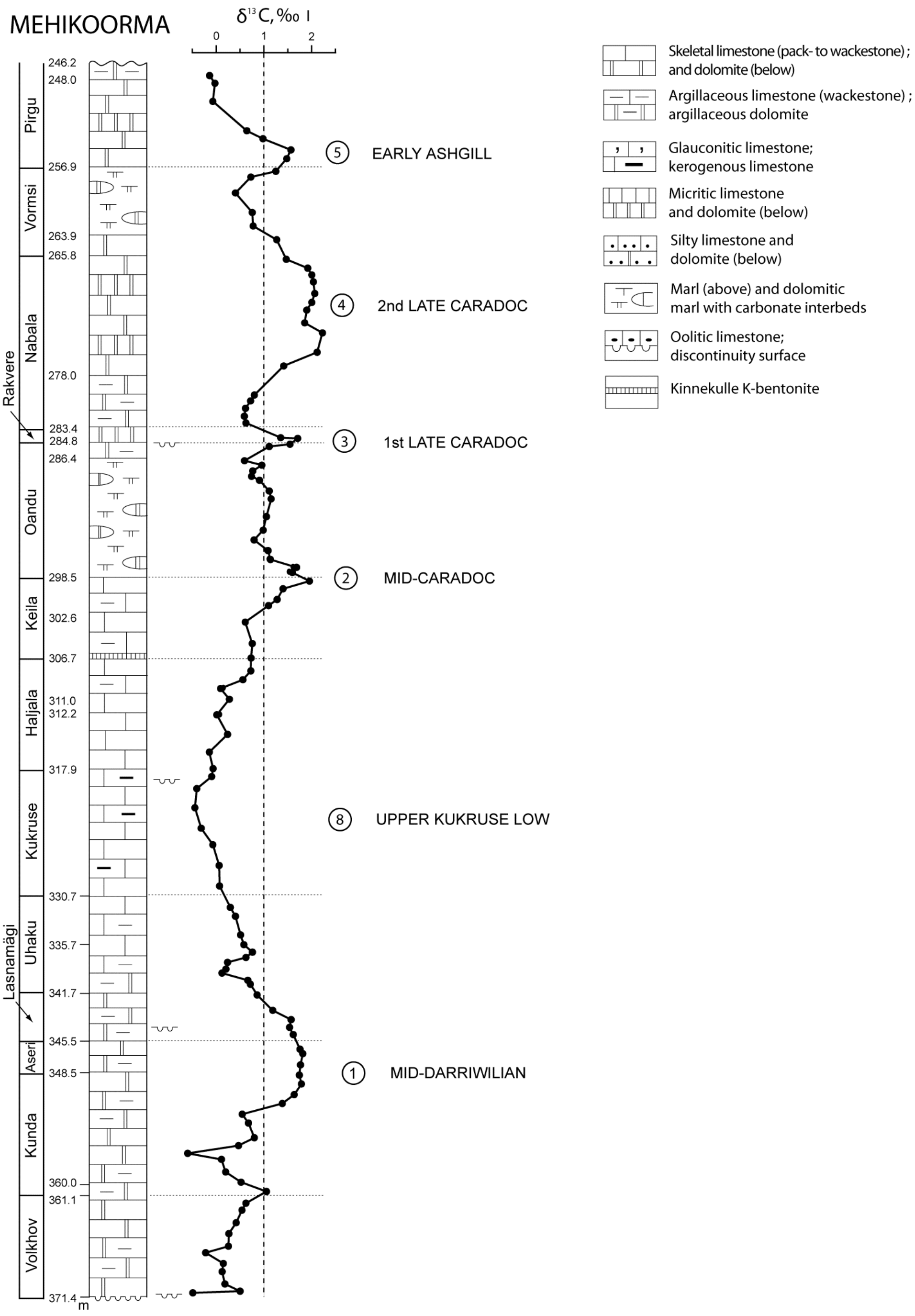

Figure 4. Lithology and carbon isotope data of the Mehikoorma core section (see Fig. 1B). Log and stratigraphy of the core according to Põldvere (2005).

5.3. Hirnantian (end of the Ordovician cycle)

The end-Ordovician within the limits of the Hirnantian, the final stage of the Ashgill, or a bit more, was a time of dramatic biotic and environmental changes (Brenchley et al., 1994; Finney et al., 1999; Webby et al., 2004). The corresponding mass extinction is one of the five major bioevents in the Phanerozoic, and, as estimated by Jablonski (1991), it eliminated 86% of species. The extinction has been linked with environmental changes accompanying the glaciation on Gondwanaland (paper V). At times of rapid environmental changes, chemostratigraphy enables correlation of specific rocks at a much higher resolution than biostratigraphy. Papers III, IV and V illustrate the use of chemostratigraphic correlation for identifying patterns of global change at the end of the Ordovician.

Stable isotope studies have demonstrated that the environmental and biotic changes are interrelated with a major positive excursion in the $\delta^{13}C$ and $\delta^{18}O$ values of marine carbonates and the $\delta^{13}C$ of organic matter. At the same time, the mechanisms and reasons for the processes are still understood differently (Brenchley et al., 1994; Finney et al., 1999; Kump et al., 1999; Marshall et al., 1997; Underwood et al., 1997; papers III, IV, V). The oxygen isotope excursion (Marshall and Middleton, 1990; Brenchley et al., 1994; Heath et al., 1998) has been interpreted in terms of changes in ice volume and temperature. Carbon isotope shifts of up to +6‰ indicate a significant change in the global carbon cycle. Brenchley et al. (1994) suggested that these shifts were related to enhanced carbon burial or sequestration of light organic carbon in deep ocean water, whereas Kump et al. (1999) linked the carbon isotope excursion to a change in the weathering regime associated with the exposure of carbonate platforms.

In the Baltic area the stratigraphic pattern of $\delta^{13}C$ values in whole-rock and bioclast samples consistently indicates a single large positive isotopic excursion. The Porkuni (Hirnantian) Stage has bioclasts with $\delta^{13}C$ values predominantly between +2‰ and +8‰, as opposed to values of < 2‰ in the underlying Pirgu and overlying Juuru stages. However, as shown by Samtleben et al. (1996), Wenzel and Joachimski (1996) and the author (paper VI), differences in the initial marine $\delta^{13}C$, associated with the depth of water in which the sediments were deposited, cannot be excluded. The sequences in the North Estonia, which terminatewith the post-Ärina unconformity (Fig. 5), have profiles that show a similar rise in $\delta^{13}C$ values to a peak, but then have a sharp downward step at the top of the preserved Porkuni Stage. The configuration of the C isotope curve helps to identify gaps in some sections, especially with using biostratigraphy.

The carbon isotope profiles show a consistent relationship to the chitinozoan zonal boundaries (Fig. 5). The base of the *gamachiana* Zone corresponds closely to the start of the excursion. The base of the *taugourdeaui* Zone corresponds to the lower part of the rise; the base of the "*scabra*" Zone occurs higher on the rise, and the base of the lowermost Silurian *fragilis* Zone lies in the middle part of the rapidly declining $\delta^{13}C$ values. The Hirnantian brachiopod fauna consistently appears midway up the rise.

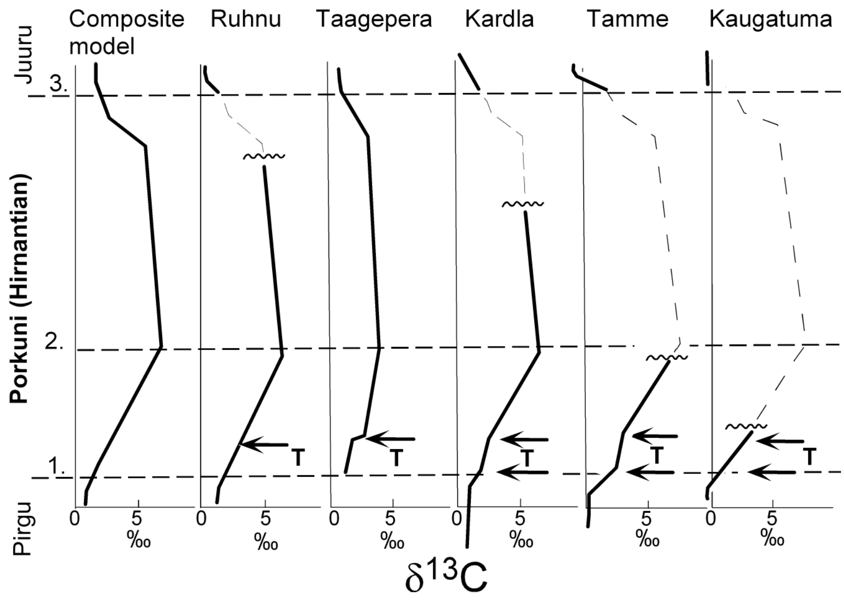

Figure 5. Interpretation of the carbon isotope profiles from five stratigraphic sections of Estonia (see Fig. 1 for locations). Estimates of the position and likely magnitude of stratigraphic gaps in carbon isotope profiles are based on the carbon isotope value and the size of the jump in values at any substantial step in the profile. 1 – Base of the Porkuni Stage as indicated by a sharp facies change and the base of the *taugourdeaui* chitinozoan Zone. 2 – Peak of the carbon isotope excursion. 3 – Base of the Juuru Stage as indicated by a sharp facies change, commonly coinciding with a disconformity and the base of the *fragilis* Zone. Relative sedimentation rates are assumed to be similar. The dotted lines show the estimated extent of the missing sections. Arrows mark the top and the base, where identified, of the *taugourdeaui* Zone (T). Note the relatively consistent position of the top of the zone in each core (from paper IV).

The long carbon isotope profiles from thick Baltic sequences (the Ruhnu and Taagepera cores, Fig. 5) and the Monitor Range, Nevada (Finney et al., 1999), indicate that a complete Late Ordovician $\delta^{13}C$ profile has a relatively short and steep rise, a plateau with constant or slightly falling values and a steep terminal fall. The range in the amount of truncation of the $\delta^{13}C$ profiles in the Baltic cores is a reflection of the amount of erosion at the unconformity within the Hirnantian. Cores from a down-ramp situation have a complete carbon isotope profile (Fig. 5) or exhibit a small terminal downward step in $\delta^{13}C$ values (+2‰, Fig. 5). Cores higher on the ramp show a larger terminal downward step in $\delta^{13}C$ values (+4‰, Fig. 5). The most extreme truncation appears to be in the Kaugatuma core, where the section has been truncated part-way through the rise.

5.4. Llandovery (beginning of the Silurian cycle)

The following positive carbon isotope excursions have been established in the East Baltic Silurian (dating in terms of local stratigraphy and graptolite zonation according to Kaljo et al., 1998; Kaljo and Martma, 2000, 2006; papers I, V, VI):

(1) The early Aeronian excursion (the peak $\delta^{13}C$ values reach +3.7‰ in the Ikla core, South Estonia) in the Raikküla Stage at a level corresponding to the *Demirastrites triangulatus* Biozone.

(2) The early Telychian excursion (+2.7‰ in the Ohesaare core) in the lower part of the Adavere Stage and *Spirograptus guerichi-Streptograptus crispus* Biozone.

(3) The early Sheinwoodian excursion (maximum $\delta^{13}C$ values up to +5.2‰ measured in the Viki core), a wide excursion in the lower part of the Jaani Stage with a peak in the *Monograptus riccartonensis* Biozone or slightly above it.

(4) The middle to late Homerian double-peaked excursion in the Rootsiküla Stage corresponding to the *Gothograptus nassa* and *Monograptus ludensis* biozones. The maximum value (+4.6‰) was determined in the Ohesaare core.

(5) The late Gorstian excursion (+1.1‰) in the Hemse Beds of Gotland, correlated with a level within the *Pristiograptus tumescens* graptolite and *Ancoradella ploeckensis* conodont biozones and tied to the Linde Event (and to the level just above it), defined by conodonts (Samtleben et al., 2000). This excursion is very weak and not traced in Estonia so far.

(6) The middle Ludfordian shift (maximum values in the East Baltic reach +8.2‰), the most prominent shift in the Phanerozoic. This excursion has been correlated with the *Neocucullograptus kozlowskii* Biozone, but conodonts provide an exact dating – the last occurrences of *Polygnathoides siluricus.*

The Silurian is a relatively short period (28 m.y., from 444 to 416 Ma) in the middle of the Palaeozoic Era, where, however, several important events have been recorded (Kaljo et al., 1995). The Llandovery embraces a considerable part of it i.e. 16 m.y. (444–428 Ma) of this time-span, but stable isotopes have been less studied than in the rest of the Silurian. This period deserves more serious attention due to important processes observed in the early Silurian environment.

First of all, the Llandovery could be considered as a time of recovery from the latest Ordovician glaciation, accompanied by sea level low-stand, mass extinction and diversity low of biota. Climatically, the early Silurian belongs to a long greenhouse period (Fischer, 1984), interrupted by three glaciation episodes as reported from South America (Caputo, 1998). These interruptions were probably analogous to the well-studied Hirnantian short-term glaciation (Brenchley et al., 1994), but of lower rank, as might be deduced from their smaller environmental (*sensu lato*) after-effects. According to modern reconstructions of early Palaeozoic plate positions, Baltica moved from the near-equatorial position at the end of the Ordovician to the equatorial position by the Wenlock (Cocks and Torsvik, 2002). Climatic consequences of the movement are obvious for Baltica, but not so clear globally. According to Wilde et al. (1991), the Llandovery was cooler than the late Ordovician (fall from about 140% to 130% compared to modern temperature values, the latter global average is about 15 ºC). At the same time, the temperature curve compiled by Frakes (1979, cited in Morrow et al., 1995) shows steady warming beginning from the end of the Hirnantian glaciation episode, while the level of modern values was reached only in the middle of the Silurian. The oxygen isotope data published by Heath et al. (1998) shows a very gradual change towards more negative $\delta^{18}O$ values throughout the Llandovery (from -4.2‰ at the bottom to -5.3‰ at the top, indicating a slow rise in temperature).

All three Gondwana glacial episodes, identified in the Llandovery and the lowermost Wenlock of South America by tillites, microconglomeratic clays, etc. and dated biostratigraphically (Caputo, 1998), are recognized in the Baltic area through clear positive carbon isotope excursions at the same levels. It has been shown that in general lines the glaciation-induced isotopic model by Brenchley et al. (1994) is applicable also to the early Silurian (paper V; Kaljo and Martma, 2000). At the same time, the oceanic model by Jeppsson (1990) reveals too many contradictions between model predictions and measured values (paper V). The revised model by Bickert et al. (1997) gives a better result, but still not good enough. This means that the current environmental background of isotopic events and relationships with oceanic events should be revised. For delimitation of the climatic and oceanic episodes a more general marker identifying the environmental change based on a basinal approach seems useful. For this purpose, besides conodont a.o. biodiversity data, also lithological, geochemical or palaeontological criteria should be used (paper V).

5.5. Wenlock–Ludlow–Pridoli

Llandovery carbon isotope excursions are hardly known outside the Baltic area, but three positive carbon isotope excursions recognized in the Wenlock and Ludlow are well studied in the sequences of the world. The first excursion, with the $\delta^{13}C$ values reaching 4 to 5‰, occurs in the lowermost Wenlock and is the best-known Silurian shift (for a summary see Munnecke et al., 2003). The second excursion, observed in the top of the Wenlock, is double-peaked and depending on sedimentary facies, showing different $\delta^{13}C$ values. In deep shelf rocks the values remain below 2‰ (paper I; Kaljo et al., 1998; Porębska et al., 2004), but reach 3 to 4‰ in slightly shallower sediments in Britain and on Gotland (Corfield et al., 1992; Azmy et al., 1998; Samtleben et al., 2000). A record high value of 4.6‰ is known from the Ohesaare core, Estonia (paper I). The youngest among the three excursions is the most prominent one, even in terms of the entire Phanerozoic. It is recognized by $\delta^{13}C$ values of over 10‰ in the upper Ludlow (Ludfordian) of Baltica, Laurentia, Perunica and Australia, giving evidence of the truly global dimension of this stable isotope event. The same evaluation is also acceptable for the first two excursions. These excursions are stratigraphically related to the following consecutive oceanic events: the early Wenlock Ireviken Event, the late Wenlock Mulde Event and the late Ludlow Lau Event, proposed by Jeppsson (1998) and by Jeppsson and Aldridge (2000) on the basis of a variety of environmental signals and conodont biodiversity changes.

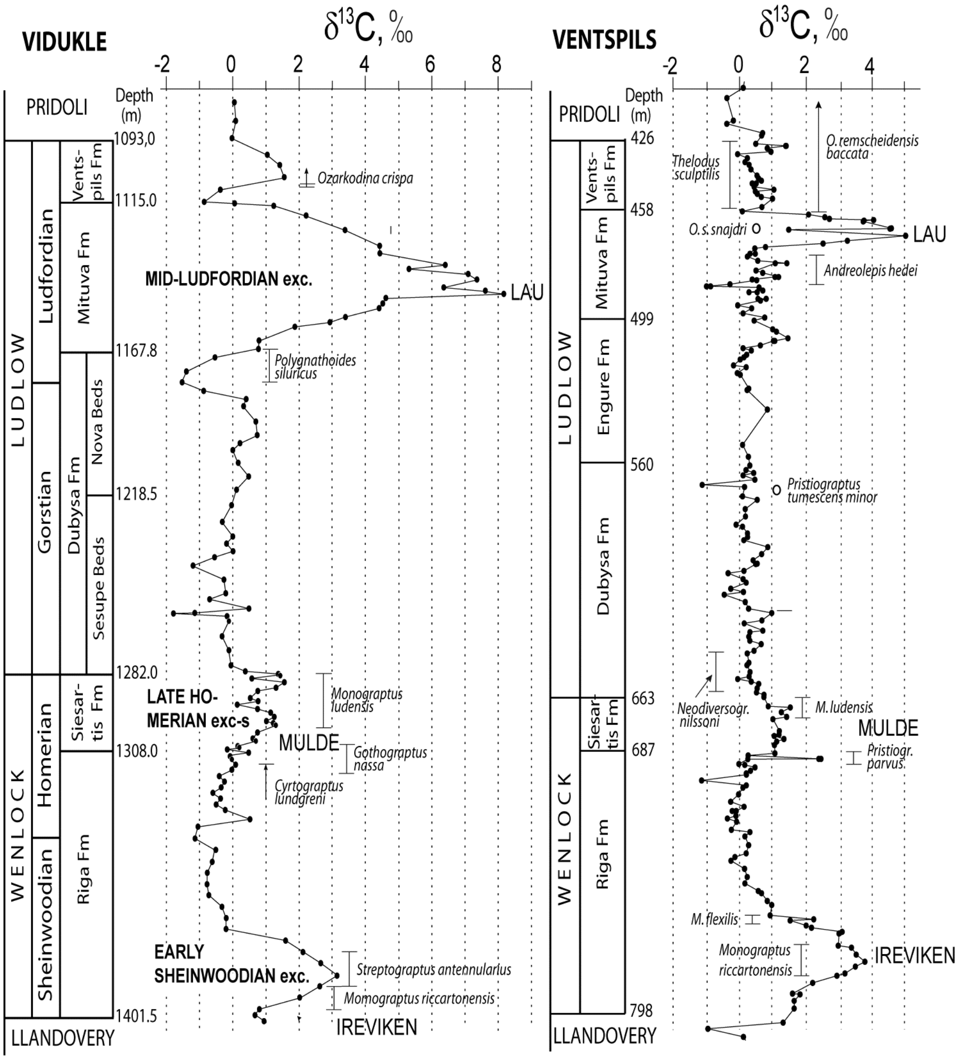

Figure 6. The Vidukle and Ventspils core sections: stratigraphy, carbon isotope trend and biostratigraphical data from Kaljo and Martma, 2006 (modifed)

In the East Baltic the Ludfordian $\delta^{13}C$ excursion has been established in three core sections of Latvia (paper I; Kaljo et al., 1998) and in the Vidukle core of Lithuania (paper VII), (Fig. 6). In the Priekule core the peak values reach 5.9‰ in the Nova Beds of the Dubysa Formation, in the lower part of the Pavilosta core (4.2‰), and in the top of the Mituva Formation in the Ventspils core (5.0‰). In the Ohesaare core the peak level is represented by a gap. The shift correlates with the early and mid-Ludfordian sea level low-stand and the following sea level rise, with two bioevents (serious extinctions in several groups of biota, Kaljo et al., 1995, 1998; paper VII) and with the Lau P-S Event of Jeppsson (1998).

In both Wenlock cases the oceanic events directly precede the carbon isotope events. The Ireviken Event precedes the major early Wenlock $\delta^{13}C$ excursion and the Mulde Event the late Homerian less prominent but double shift. The peak values of the mid-Ludfordian $\delta^{13}C$ excursion occur within the limits of the Lau Event as defined by conodonts, but the rising and falling limbs are at least in part located before and after the Event. This indicates that the global processes causing the carbon isotope excursion and the Lau oceanic Event were active to a large extent during the same time span. Extraordinarily high $\delta^{13}C$ values identified in Scania (11.2‰, Wigforss-Lange, 1999) and in Australia (~12‰, Andrew et al., 1994) make the last event really intriguing.

5.6. Environmental implications

In the preceding chapters we repeatedly referred to the environmental conditions that might have caused certain changes in the carbon isotope trend. Without doubt the Hirnantian excursion is best studied and the end-Ordovician glacial event as the main triggering reason for climatic, oceanic, etc. perturbations is widely accepted even if some driving mechanisms are differently understood (Brenchley et al., 1994, 2003; Kump et al., 1999). Recently Saltzman and Young (2005) expanded the glacial model also for explaining the Mohawkian series of the $\delta^{13}C$ excursions and suggested a long-lived glaciation in the late Ordovician greenhouse period. For motivation the authors mention:

(1) enhanced organic carbon burial that lowered atmospheric pCO_2 (Kump et al., 1995; Patzkowsky et al., 1997);
(2) sea level fall within the Eureka Quarzite may have positive feedback for further cooling;
(3) a reduction of poleward heat transport may have influenced in the same way (Herrmann et al., 2004) and
(4) glacigenic rocks in North Africa studied by Hamoumi (1999).

My understanding of driving forces in these processes is very much the same, I would only like to draw attention to some limiting circumstances, e.g. whether the amount of burial of organic carbon is sufficient for having serious impact on carbon cycling. Corresponding studies are rather scarce and unconvincing. Another limitation is that the glacigenic rocks mentioned are insufficiently dated and can be seriously considered with difficulties yet. A sea level drop confined to the Eureka Quarzite according to Figure 4 is correlated with the Baltic late Caradoc, where several lower-level regressions occur. A more serious fall has been observed earlier at the level of Baltic mid-Caradoc excursion. However our experience shows that the sea level low-stands are often tied to isotope shifts (Kaljo et al., 1998) and intent attention to them is surely justified but correct succession of implications is important.

In our Silurian studies we have employed oceanic models by Jeppsson (1990) and Bickert et al. (1997), paying much attention to the changes in oceanic circulation. The same driving force although from a different aspect, was discussed by Herrmann et al. (2004). I do think that these oceanic processes, which are influenced by movements and regroupings of continents through time, are most universal and can direct the formation of the general carbon isotope trend as defined in subsection 5.1. Otherwise it would be very difficult to understand why a fundamental change in the pattern of carbon cycling occurs in the middle of the Caradoc.

CONCLUSIONS

1. This thesis presents the first compilation in isotope stratigraphy for most of the Ordovician and Silurian (477–416 Ma) of Baltica. The sequence of post-Hunnebergian Ordovician and Silurian rocks is stratigraphically nearly complete in Baltoscandia. Complications caused by several local hiatuses, condensed sections and facies changes were mitigated by the study of overlapping sections.

2. The Baltic carbonate rocks studied are well preserved (not metamorphosed, diagenetically weakly altered), allowing successful use of the whole-rock method in analyses and achieving a continuous $\delta^{13}C$ trend from the latest early Ordovician up to the very end of the Silurian. The trend is biostratigraphically very well dated thanks to good cooperation with palaeontologists and stratigraphers of several institutions, in particular of the Institute of Geology at Tallinn University of Technology. A correct and detailed biostratigraphical background makes the $\delta^{13}C$ trend especially valuable for detailed correlation with other palaeocontinents (Saltzman 2001, 2005; papers II, IV, VI, VII).

3. Achievement of trustworthy data about oxygen isotopic composition and the $\delta^{18}O$ trend in the Baltic Ordovician and Silurian based on the whole-rock analyses is impossible due to the following reasons:

(1) The oxygen isotope ratio is more sensitive to diagenesis than that of carbon and diagenetic alterations may easily happen in sediments or later in rocks.

(2) Cathodoluminescence checking is a simple and rather cheap method for determination of diagenetic changes in calcite in brachiopod shells but not in rocks.
(3) The Baltic carbonate rocks are mostly highly variable mixtures of calcite and dolomite, which have different oxygen isotope fractionation factors. Therefore the oxygen isotope data from whole-rock analysis cannot be interpreted unambiguously.

4. The magnitude and frequency of carbon isotope excursions divide the Ordovician Period into two parts with considerably different types of carbon cycling. An interval (~20 m.y.) of minor and infrequent variations lasts through the middle Ordovician up to the middle of the Caradoc. The rest of the late Ordovician (~11 m.y.) shows frequent isotopic shifts of increasing magnitude ending with the major Hirnantian Event (paper VI). The latest Ordovician Hirnantian excursion (Brenchley et al., 1994; paper IV) is considered to be triggered by a major glaciation, even if the carbon cycling mechanisms are not completely understood. The environmental causes suggested for the earlier minor Ordovician shifts range from global climatic and glacial events to very local changes in basin regime and sea level.

5. A similar general pattern is observed in the Silurian: infrequent middle-sized shifts in the Llandovery (16 m.y.), two major sifts in the Wenlock and an extremely high $\delta^{13}C$ peak in the late Silurian accompanied with strong biodiversity and environmental changes. However, the frequency of carbon isotope shifts is much smaller in the Wenlock–Ludlow (every 4 m.y.), than in the late Ordovician. The Wenlock carbon isotope excursions correlate well with earlier data from Baltica and elsewhere in the world. It has been proved that $\delta^{13}C$ values clearly reflect the depth of the sedimentary basin (paper VI; Kaljo et al., 1998).

6. I consider the changes in the $\delta^{13}C$ curve "global". They reflect global changes in climate and ocean, but also more regional processes connected with the evolution of the sedimentary basin and drift of Baltica. The data presented here indicate that most probably changes in climate and ocean circulation were triggered and directed also by movements and regroupings of continents through time. Otherwise it would be very difficult to understand why a fundamental change in the pattern of the Ordovician carbon cycling takes place in the middle of the Caradoc.

7. Carbon isotope excursions serve as reliable tools for different geological correlations. In addition to correlation of sections within the Baltoscandian study area, the resulting general trend allows rather detailed synchronization of geological events in Baltica with those as far as Nevada (in Laurentia) and Australia.

ACKNOWLEDGEMENTS

This work has been carried out with great help and useful advice of many people at different institutions in Estonia and abroad.

First of all, I would like to acknowledge the input of my supervisors Professor Rein Vaikmäe and Professor Dimitri Kaljo on writing this thesis. I also thank the supervisor of my MSc thesis Professor Jaan-Mati Punning for introducing me to the world of isotope geology.

General discussions with my colleagues at the Institute of Geology, Dr. Linda Hints, Dr. Jaak Nõlvak, Dr. Peep Männik, Dr. Olle Hints, Dr. Tarmo Kiipli and others, have greatly contributed to my better understanding of the Ordovician and Silurian geology of the Baltic area.

I express my gratitude to the people from the Institute of Geology at Tallinn University of Technology, Institute of Geology of the University of Tartu, and the Geological Survey of Estonia, involved in producing the final outcomes of this thesis, that is all the publications, both to co-authors and all others who helped me with providing the relevant material. A complete list of all names would take too much space. However, in particular I would like to thank Dr. Linda Hints, Dr. Jaak Nõlvak, Professor Tõnu Meidla, Dr. Leho Ainsaar and Anne Põldvere for productive cooperation.

Suggestions of Dr. Heldur Nestor and Professor Jim Marshall aided in improving the manuscript. Gennadi Baranov and Anne Noor are thanked for technical and linguistic assistance.

I greatly appreciate the friendship and supportive attitude shown by my colleagues at the “Lomonosovfonna” and “Holtedahlfonna” glaciology community. Field trips to Svalbard were like holiday after hard work in the laboratory.

Finally, I thank my parents and family for the understanding and tolerant attitude to my profession and long periods of absence from home due to the work.

The study was supported by the Estonian Target Financed Research Programmes SF0332089s02 and SF0331760s01 and by the Estonian Science Foundation (grants 5042, 6127). This is a contribution to IGCP project 503.

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ABSTRACT

Isotopic methods have gained an eminent position in early Palaeozoic palaeoclimatology, palaeoceanology and stratigraphy. Despite good progress achieved in these fields, different environmental interpretations of isotope data are still under debate or uncertain. Success in carbon isotope stratigraphy is more likely to be achieved, but it depends mainly on how complete and detailed a standard trend used as a basis for comparisons is. Of course, correct correlation of sections and biostratigraphic dating of samples are crucial for obtaining reliable results.

Isotope studies embracing the southwestern sector of the Baltica continent, including the present East Baltic (Estonia, Latvia and Lithuania), Gotland, Scania and the Oslo region, but also the Anglo-Welsh area, i.e. the part of Avalonia which joined Baltica in the late Ordovician, commenced roughly 20 years ago. The data presently available from the East Baltic allow us to discuss a more or less continuous curve of $\delta^{13}C$ values beginning with the post-Hunnebergian Ordovician until the Silurian/Devonian boundary (~60 m.y.).

Carbon isotopes for the present study were determined at the Isotope Palaeoclimatology Laboratory of the Institute of Geology, Tallinn University of Technology, using the whole-rock method that allows sampling an entire section at more or less regular intervals not depending on the occurrence of bioclasts. The quality of the carbon isotope data based on whole-rock analyses has been discussed in several papers. It has been shown that the isotope signals in the Ordovician and Silurian rocks of Estonia are reliable and these reflect primary composition in the ocean. The comparison of the whole-rock and brachiopod shell isotope data (Heath et al., 1998) shows only slight difference in $\delta^{13}C$ values but great similarity of the corresponding curves.

The studies summarized in this thesis have revealed seven positive carbon isotope excursions in the Baltic Ordovician, including the strong Hirnantian excursion (in Estonia the peak value reaches 6.7‰) in the Porkuni Stage. In the Silurian six positive $\delta^{13}C$ excursions are known, including the mid-Ludfordian shift, the most prominent one in the entire Phanerozoic. Most of isotope shifts occur close to levels of biodiversity changes, as shown by the most widely recognized Oandu crisis in the Caradoc, mass extinction in the Hirnantian, and the Ireviken and Lau events in the Wenlock and Ludlow, respectively.

The magnitude and frequency of carbon isotope excursions divide the Ordovician Period into two parts with considerably different types of carbon cycling. An interval (~22 m.y.) of minor and infrequent variations lasts through the middle Ordovician up to the mid-Caradoc. The rest of the late Ordovician (~10 m.y.) shows frequent isotopic shifts of increasing magnitude ending with the Hirnantian major event. The last excursion was triggered by a major glaciation, even if the carbon cycling mechanisms are not completely understood.

The environmental causes suggested for the Ordovician earlier minor shifts range from global climatic and glacial events to local changes in basin regime and sea level. In the Silurian the general pattern is the same: infrequent middle-sized shifts in the Llandovery (16 m.y.), two major sifts in the Wenlock and an extremely high $\delta^{13}C$ peak in the late Silurian accompanied with strong biodiversity and environmental changes.

KOKKUVÕTE

SÜSINIKU ISOTOOPIDE KASUTAMINE BALTI ORDOVIITSIUMI JA SILURI ARENGULOO UURIMISEL

Isotoopmeetodite rakendamine Paleosoikumi klimatoloogias, okeanoloogias ja stratigraafias on tänapäeval tõusnud silmapaistvale kohale. Hoolimata olulisest edenemisest nendes valdkondades on isotoopandmete tõlgendamine keskkonna tingimuste selgitamisel veel paljus vaieldav või ebakindel. Stratigraafias on edu olnud kõige suurem, sõltudes peamiselt võrdluste ja korrelatsioonide alusena kasutatud standardkõvera täiuslikkusest ja detailsusest. Muidugi on äärmiselt oluline usaldusväärsete tulemuste saavutamisel korralik biostratigraafiline kontroll ja proovide dateerimine.

Hapniku ja süsiniku isotoopide kasutamine Baltika kontinendi lääneosa, kuhu kuuluvad tänapäevased Ida-Baltikum (Eesti, Läti ja Leedu), Gotland, Lõuna Rootsi ja Oslo ümbrus, geoloogilise mineviku uurimisel algas ligikaudu 20 aastat tagasi. Kuna tegemist on üle 400 miljoni aasta vanuste Ordoviitsiumi ja Siluri kivimitega, siis kaheldi, kas algne isotoopide suhe on säilinud nii pika aja jooksul. Esimesed analüüsid tehti käsijalgsete kaantest, kuna nende puhul on võimalik hinnata diageneetiliste muutuste ulatust ja esialgse informatsiooni säilivust. Brahhiopoodide analüüsil ei ole võimalik saada ajaliselt pikki ja ilma lünkadeta kõveraid, kuna nende kivistised kõigil tasemetel ei esine. Võrreldes suure osa muu maailmaga on Ida-Baltikumis tingimused Ordoviitsiumi ja Siluri karbonaatkivimite säilimiseks olnud väga soodsad, seepärast hakkasime TTÜ Geoloogia Instituudi isotoop-paleoklimatoloogia laboris $\delta^{13}C$ analüüsiks kasutama kivimis olevat karbonaati. Praeguseks on olemas Ida-Baltikumi kohta enam-vähem täielik $\delta^{13}C$ väärtuste kõver, alates Kesk-Ordoviitsiumi Billingeni lademest kuni Siluri-Devoni piirini (ligikaudu 60 miljonit aastat).

Ordoviitsiumi kivimitest on leitud järgmised positiivsed $\delta^{13}C$ väärtuste kõvera anomaaliad (sulgudes tippväärtused):

(1) Kesk-Darriwiliani tipp ($\delta^{13}C$ väärtus 1.9‰) Aseri lademes;
(2) Kesk-Caradoci tipp (2.2‰) Keila ja Oandu lademe piirialas;
(3) esimene Hilis-Caradoci tipp (2.3‰) Rakvere lademe alumises osas;
(4) teine Hilis-Caradoci tipp (2.4‰) Nabala lademe ülemises osas;
(5) Vara-Ashgilli tipp (2.5‰) Pirgu lademe alumises osas;
(6) Kesk-Ashgilli tipp (2.0‰) Pirgu lademe ülemises osas;
(7) üldtuntud suur Hirnantiani tipp (Eestis $\delta^{13}C$ väärtus kuni 6.7‰) Porkuni lademes.

Ida-Balti Siluris on leitud järgmised süsiniku isotoopkõvera positiivsed anomaaliad:

(1) Vara-Aeroniani tipp (3.7‰) *D. triangulatus* biotsoonis Raikküla lademes;
(2) Vara-Telychiani tipp (3.7‰)

(3) Vara-Sheinwoodiani tipp (5.2‰) *M. riccartonensis* biotsoonis või natuke kõrgemal, Jaani lademes;

(4) Kesk-Homeriani kahe tipuga (maksimaalne 4.6‰) anomaalia *G. nassa* ja *M. ludensis* biotsoonis Rootsiküla lademes;

(5) Kesk-Ludfordiani tipp (8.2‰) on suurim positiivne hälve Fanerosoikumis, korreleerub *N. kozlowskii* biotsooniga, aga konodontide abil on dateeritud kui aega viimaste *Polygnathoides siluricus*'te ja esimeste *Ozarkodina wimani* ja *O. crispa* esinemise vahel. Lünga tõttu see tipp puudub Ohesaare puursüdamiku Paadla lademes, aga esineb Läti ja Leedu puursüdamikes.

Süsiniku isotoopkoostise hälvete amplituudi ulatus ja muutumise sagedus jagavad Ordoviitsiumi ajastu kahte perioodi, mil süsiniku globaalne ringkäik oli oma laadilt oluliselt erinev. Esimest neist, mis esines alates Kesk-Ordoviitsiumist kuni Caradoci ajajärgu keskosani (ca 22 mln a), oli suhteliselt stabiilne aeg, mil $\delta^{13}C$ kõvera muutused olid väikesed ja harvad. Teist poolt Hilis-Ordoviitsiumist (ca 10 mln a) iseloomustab süsiniku isotoophälvete amplituudi ja sageduse järkjärguline suurenemine ajastu lõpu suunas. Ajastu lõpetabki nn Hirnantia suursündmus, mille tekkepõhjuseks peetakse sel ajal aset leidnud ulatuslikku mandrijäätumist Maa lõunapoolkeral. Samas tuleb tunnistada, et nende tekkeseoste mehhanismides ei ole veel üksmeelt leitud. Ordoviitsiumi varasemate hälvete põhjustena nähakse nii globaalseid kliima ja ookeani veetaseme muutusi ning mandrijäätumisi kui ka üsna lokaalseid settebasseinide tingimuste muutusi. Siluri ajastu süsiniku tsüklilisus järgib praktiliselt sama malli – algul (Llandovery, 16 mln a) harvad keskpärased hälbed, Wenlock'is ja Ludlow's ca 4 mln aastaste vahemikkude järel kaks suuremat ja lõpuks üks väga suur hälve. Nendega kaasnevad ka olulised keskkonna ja elustiku muutused, sh paljude taksonite väljasuremised.

Uurimistöö tulemusi kasutatakse stratigraafias, paleoklimatoloogias ja mineviku merelise keskkonna parameetrite selgitamisel. $\delta^{13}C$ kõverat rakendatakse erinevate läbilõigete korrelatsioonil, kivimite vanuse määramisel ning läbilõigetes esinevate lünkade avastamisel ja nende ulatuse määramisel.

ORIGINAL PUBLICATIONS

I

Kaljo, D., Kiipli, T., Martma, T. 1997. Carbon isotope event markers through the Wenlock–Pridoli Sequence at Ohesaare (Estonia) and Priekule (Latvia). Palaeogeography, Palaeoclimatology, Palaeoecology, 132(1–4), 211–223.

II

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IV

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VI

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ETF5925 — Baseline chemical and isotopic composition and age of Estonian groundwater: geochemical foundation for implementation the EU Water Framework Directive in Estonia (2004-2007, R. Vaikmäe)
ETF6127 — Relationships of climate and biotic evolution during the Ordovician and Silurian in Baltic based on palaeontological and isotope geological data (2005-2008, D. Kaljo)

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Tunnustused: 2001. a. geo- ja bioteaduste alal teadustööde tsükli "Isotoopuuringute tulemusi Eesti paleosoilise arenguloo selgitamisel (ordoviitsiumi ja siluri stratigraafia, klimatoloogia ja okeanoloogia)" eest riikliku teaduspreemia saanud kollektiivi liige

Teadustöö põhisuunad: Stabiilsete isotoopide massispektromeetria ja selle rakendused geoloogias

Projektid:
SF0332089s02 — Hiliskvaternaari ja paleosoikumi kliima- ja keskkonnamuutused ning nende isotoop-geokeemilised salvestused põhjapoolkera kontinentaalsetes ja merelistes setetes, hüdro- ja krüosfääris (2002-2006, R. Vaikmäe)
ETF5925 — Eesti põhjavee looduslik keemiline- ja isotoopkoostis ning vee vanus: geokeemilised alused EL vee raamdirektiivi rakendamiseks Eestis (2004-2007, R. Vaikmäe)
ETF6127 — Kliima ja elustiku arengu seosed Baltika kontinendi Ordoviitsiumis ja Siluris paleontoloogilistel ja isotoopgeoloogilistel andmetel (2005-2008, D. Kaljo)

Teaduspublikatsioonid: üle 50 (sh. 25 CC / SCI indekseeritud ajakirjades)