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Modelling Seawater Chemistry of the East Baltic Basin in the Late Ordovocian – Early Silurian

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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 before for any degree or examination at any other university

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CONTENTS

List of original publications (in order of citation in the text**)**
with estimation of the contribution of the author of 'Thesis'

Paper I. **Kiipli, E.** 2004. Redox changes in the deep shelf of East Baltic Basin in Aeronian and early Telychian (Early Silurian). *Proceedings of the Estonian Academy of Sciences Geology 53*, 94-124.
Contribution 100%

Paper II. **Kiipli, E.** 1997. Geochemistry of Llandovery black shales in the Aizpute-41 core, West Latvia. *Proceedings of the Estonian Academy of Sciences Geology 46*, *3*, 127-145.
Contribution 100%

Paper III. **Kiipli, E**., Kallaste, T. & Kiipli, T. 2000. Hematite and goethite in Telychian marine red beds of the East Baltic. *GFF 122*, 281-286.
Contribution 60%

Paper IV. **Kiipli, E.** & Kiipli, T. Calcite-dolomite distribution in the East Baltic deep shelf in late Ordovician - early Silurian implying carbonate system (*submitted).*
Contribution 70%

Paper V. **Kiipli, E.,** Kiipli, T. & Kallaste, T. 2002. Correlation between deep and shallow shelf on the basis of O-bentonite, East Baltic. In *The Fifth Baltic Stratigraphical Conference "Basin Stratigraphy—Modern Methods and Problems", September 22-27, 2002, Vilnius, Lithuania: Extended Abstracts* -- Vilnius, 77-80.
Contribution 40%

Paper VI. Kiipli, T., **Kiipli, E.** & Kallaste, T. 1997. Metabentonite composition related to sedimentary facies in the lower Silurian of Estonia. *Proceedings of the Estonian Academy of Sciences Geology 46*, *2*, 93-104.
Contribution 30%

Paper VII. Kiipli, T., Männik, P., Batchelor, R. A., **Kiipli, E.,** Kallaste, T. & Perens, H. 2001. Correlation of Telychian (Silurian) altered volcanic ash beds in Estonia, Sweden and Norway. *Norwegian Journal of Geology (Norsk Geologisk Tidsskrift) 81,* 179-194.
Contribution 20%

Paper VIII. **Kiipli, E.**, Kiipli, T. & Kallaste, T. 2004. Bioproductivity rise in the East Baltic epicontinental sea in the Aeronian (Early Silurian). *Palaeogeography, Palaeoclimatology, Palaeoecology 205*, 255-272.
Contribution 70%

1. INTRODUCTION

Working out global models for reconstructing the geological past has been a long-term challenge for geologists. Attempts are made to link into causal chain the deep Earth, oceanic, atmospheric, biologic, terrestrial and astronomic processes. The ocean chemistry, though uniform in general through Phanerozoic, reveals evolutionary trends driven by the biologic and inorganic world. Against this background several periodic variations occur, e.g. alteration of 'aragonite' and 'calcite' seas, thermal- and salinity-stratification, isotopic composition of rock, etc.

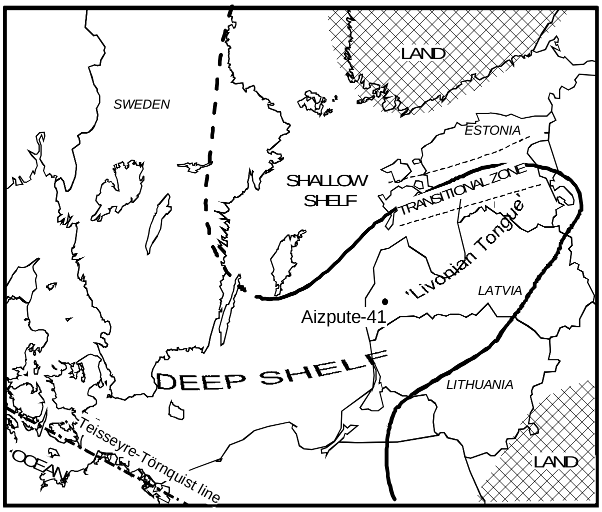

Fig. 1. Scetch-map showing the shelf setting of Palaeo-Baltic Basin in Ordovician and Silurian, modified after Männil (1966), and location of the Aizpute-41, the main reference core of the deep-shelf.

The present work deals with two aspects of seawater chemistry, 1) the oxygenation of deep shelf waters, yielding the Eh-model, and 2) carbonate system responsible for calcite-dolomite formation-dissolution, giving the pH-model, and processes that regulate the conditions. The time under consideration is the late Ordovician -- early Silurian, corresponding to a 20-million-year period. The area of investigation comprises the Palaeozoic East Baltic epicontinental sea, mainly its deep shelf part (Fig.1). The goal of the thesis is to describe the rock chemistry and link it with the basin geochemistry elucidating global and regional processes. The processes under investigation have an influence on a wide area, pointing at the importance of correlations between the shallow and deep shelf. On the one hand, the existing correlations based on faunas and metabentonites enable to work out reliable models, on the other hand, these models allow to predict new correlations, so far unclear.

The Eh, the redox, model (Paper I) describes the changes in seawater oxygenation. Redox reaction between organic matter, as the most important electron donor in the sea, and free or bound oxygen, as the most important electron acceptor, determine the redox state. The changes in redox conditions become obvious mainly below wave-base, in the bottom waters of the deep shelf. The low-Eh conditions associate with sulphides of iron and transitional trace metals, and organic carbon of the sediment (Paper II). Ferric iron in the form of hematite and goethite giving red colouration to the rock points at the oxic environment and relatively high Eh (Paper III). Aeronian black shale and Telychian marine red beds form a visible contrast in the deep shelf rocks. The rocks under investigation have inherited their appearance and composition largely from early diagenesis when the water exchange between seawater and sediment was active. The factors of early diagenesis -- the sedimentation rate, initial content of organic carbon, and free or bound oxygen for organic carbon bacterial reduction -- determine the sediment redox conditions (Berner 1971; Tromp et al. 1995). Seawater features can be derived from these indicators.

The pH-model describes the response of carbonates to changing pH of seawater. This reconstruction follows the calcite and dolomite distribution in the late Ordovician and early Silurian (Paper IV). The absence of calcite in deep shelf suggests its dissolution due to low pH. The pH of seawater is part of global carbonate system involving CO_2 from the atmosphere and from biological processes in seawater. Cycling of carbon between organic and inorganic pools forms the link between Eh and pH, the electron- and proton-related transfer systems.

During the geological history of the East Baltic the sedimentary cover has been insignificantly affected by thermal processes as shown by the low alteration index of conodonts, 1-2 (Männik & Viira 1990). Subaeral weathering of deep shelf sections was excluded due to the permanent deep burial. For the red beds of the Telychian the *in situ* hematite formation in the marine environment was proved by red metabentonite layers, ruling out the possibility that hematite would have been carried into the sedimentary basin in the form of a ready mineral (Paper III). The shallow shelf carbonates and deep shelf claystones have preserved a variety of initial synsedimentary signals, e.g. trace elements, stable isotopes, etc. Nevertheless, diagenetic and epigenetic overprints must be found out and taken into account. The stratigraphy of deep shelf sections is rather complete. Correlations between the deep and shallow shelf are necessary as the processes affecting the deep shelf have an impact on the shallow shelf and *vice versa*. Available correlations of geological sections facilitate the modelling of reliable synsedimentary processes in the east Baltic.

2. STRATIGRAPHY

	Series	Stages	Graptolite biozones	Regional stages	S-Estonian formations	W-Latvian formations
SILURIAN	Llandovery	Telychian	*spiralis* *crenulata* *griestoniensis* *sartorius* *crispus* *turriculatus* *guerichi*	Adavere	Velise Rumba	Jurmala: Irlava Beds Degole Beds
		Aeronian	*halli* *sedgwickii* *convolutus* *leptotheca* *magnus* *triangulatus*	Raikküla	Saarde	Dobele
		Rhudd-anian	*cyphus* *vesiculosus* *acuminatus*	Juuru	Õhne	Remte
ORDO-VICIAN	Ashgill	Hirnan-tian	*persculptus* *extraordinarius*	Porkuni	Salduse Kuldiga	Salduse Kuldiga
		Rawt-heyan	*anceps* *complanatus*	Pirgu	Halliku Jonstorp	Jelgava Jonstorp

Fig. 2. Stratigraphy and correlation of Late Ordovician -- Lower Silurian rocks of the East Baltic. Sources: Nõlvak (1997), Nestor (1997), Nestor et al. (2003) and Loydell et al. (2003).

The stratigraphy of the investigated interval is given in Figure 2. Recent studies of graptolites, chitinozoans and conodonts of the west Latvian Aizpute-41 core (Loydell et al. 2003) and chitinozoans and conodonts from the shallow shelf cores (Nestor et al. 2003) correlated the lower boundary of the Saarde Formation (Fm.) of Estonia with the lower boundary of the Dobele

Fm. of west Latvia. This refinement proved that lithological changes -- the onset of micritic limestones in the shallow shelf and black shales in the deep shelf -- were contemporaneous, giving evidences for initiation by the same cause.

The Osmundsberg metabentonite, identified in the Aizpute-41 and Engure cores of the deep shelf, suggests synchronity of the upper boundaries of the Dobele Fm. and the Saarde Fm. (Fig. 3). This O-bentonite occurrence in Sweden within Telychian *turriculatus* zone (Bergström et al. 1998), in the same graptolite zone in Latvia in the lower Degole Beds (Loydell et al. 2003), and in the upper Rumba Fm. of Estonia, made the correlation of the lower boundary of the Rumba Fm. with the lower boundary of the Degole Beds probable (Paper V). The contemporaneous lithological changes in the deep and shallow shelf at the beginning and end of the Raikküla time allowed to distinguish a characteristic seawater circulation, the upwelling, for that time.

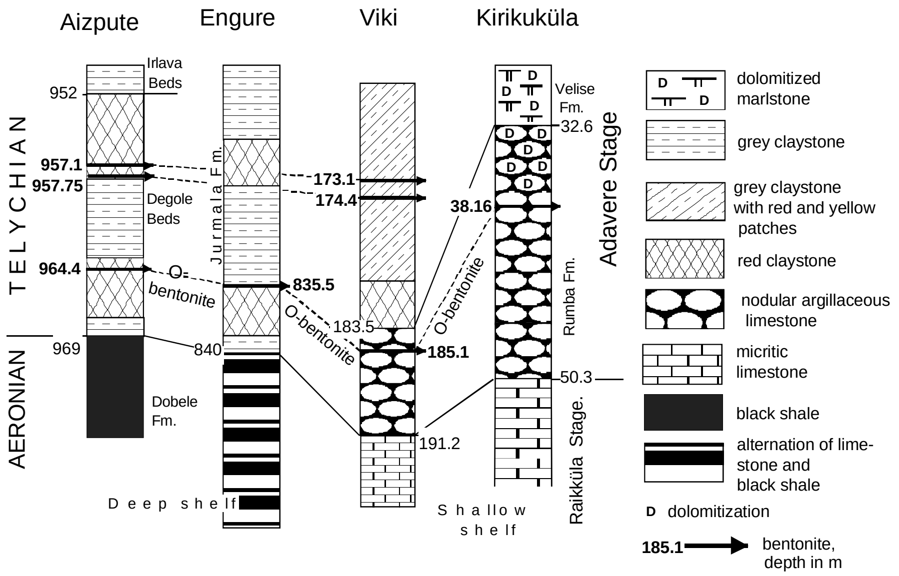

Fig. 3. O-bentonite, the Osmundsberg metabentonite, correlation between deep and shallow shelf refining the Aeronian/Telychian and Raikküla/Adavere boundaries

3. Geological background

3.1. Palaeoshelf distribution

The Swedish-Latvian Confacies Belt formed a deep shelf part with gulf-shaped 'Livonian Tongue'(Jaanusson 1972) or Yelgava Depression (Männil 1966) comprising west Latvia and south Estonia (Fig. 1). The deep shelf was rimmed by shallower zones. In Estonia the transitional zone between the deep and shallow shelf (Põlma 1982) had supposedly a steeper sea floor decline, greater sediment thickness, characteristic lithological and mineralogical features, e.g. glauconite and corrensite occurrences. The Baltic Shield and the Ukrainian Shield as the permanent areas of terrigenous sediment source were situated in the north and in the south of the Baltic Basin (according to the present-day compass-card). In the east the connection of the Baltic

Basin with the Moscow Syneclise was episodic since the late Ordovician (Kaljo 1987). In the Late Silurian these eastern areas rose and turned into land (Nikishin et al. 1996).

3.2. The end-Ordovician

The Pirgu Regional Stage, early Ashgill, revealed a wide distribution of red facies in the Swedish-Latvian Confacies Belt (Männil 1966). Red dolomitic marls of the Jonstorp Fm. were spread in the deep shelf of west Latvia and south Estonia.

The Porkuni Regional Stage, the Hirnantian, was represented by grey marlstone in the deep shelf. That was a time of glaciation at high latitudes in Gondwana causing the world-wide regression.

3.3. The early Silurian

Time corresponding to the Juuru Regional Stage, Rhuddanian below upper-*cyphus* zone (Fig. 2), was transgressional, after a period of non-deposition in the shallow shelf at the Ordovician/Silurian transition. Micritic limestones accumulated in east Latvia and Lithuania, marls in south Estonia. In the deep shelf of west Latvia the greenish-grey and red-coloured clayey sediments, the Remte Fm., formed in small thickness pointing at oxygenated conditions in the deep shelf bottom waters and sediment.

During the late Rhuddanian and Aeronian, corresponding to the Raikküla Regional Stage, micritic limestones in great thickness, up to 170 m in the Ikla core, accumulated in the transitional zone. Contemporaneous black shales with a thickness of 7-to-10 m formed in the deep shelf of west Latvia and further offshore.

Telychian, corresponding to the Adavere Regional Stage, was a time of global transgression (Johnson et al. 1991). The carbonate production decreased compared to foregoing Raikküla time, as shown by the wide distribution of marlstones and claystones of the Velise Fm. The deep shelf was represented by claystone, red-coloured in the lower Telychian sections.

4. SCIENTIFIC RATIONALE OF METHODS

4.1. Early diagenetic model

Water exchange between seawater and sediment is characteristic of early diagenesis. Early diagenetic features of the rock give the best information on synsedimentary seawater chemistry. Berner's (1971) model of early diagenetic factors, which joins into mathematical equation the sedimentation rate, concentration of oxygenating agents of marine water, concentration of organic carbon in the upper sediment layer, was taken as a theoretical ground in tracing redox conditions (Paper I). Schematically, the different pathways of organic matter degradation within the sediment (cf. Tromp et al. 1995), and the behaviour of main oxydizing agents -- the free oxygen and sulphate ion -- are given in Figure 4. The figure illustrates three main ways of behaviour of the components of the early diagenesis in the oxic and anoxic environments, characteristic of the deep shelf of the Telychian and Aeronian, correspondingly, and in the shallow shelf sedimentary environment of sulphate reduction, characteristic of most times. Within the red-coloured oxic sediment the organic carbon content reached the zero-point, whereas the pore-water oxygen stayed in excess (cf. Fig. 4 a, b and c). In the black shale environment the sulphate and oxygen were exhausted and the organic carbon stayed in excess. In the sulphate-reducing environment, when the free oxygen was exhausted, the degradation of

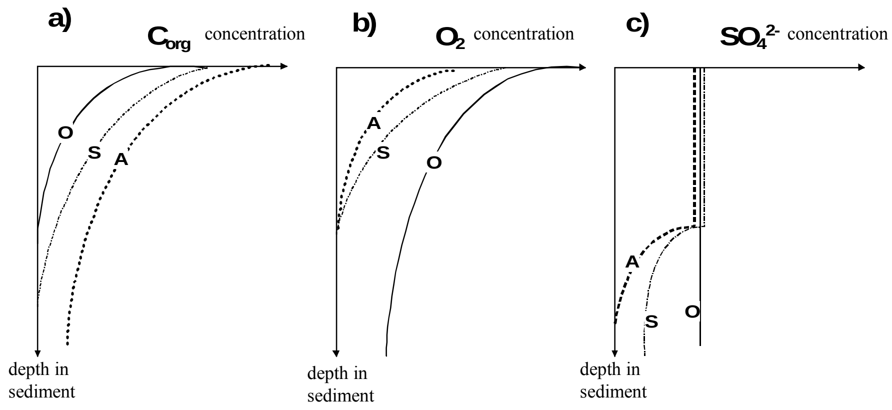

Fig. 4. Early diagenesis in anoxic (A), oxic (O) and sulphate-reducing (S) sedimentary environments. Modified after Tromp et al. (1995). Concentration profiles within sediment of a) organic carbon, b) free oxygen and c) sulphate ion. Explanations in text

organic matter was carried on by sulphates (Froelich et al. 1979), which might stay in excess when the process of organic matter remineralisation ended.

In the Telychian case the formation of red beds at the deep shelf was supported by thick oxygenated water column allowing degradation of most of the dead organic matter in its journey to the sea bottom. Together the small sedimentation rate, low content of organic carbon reaching the sea-floor, and enough free oxygen created oxygenating conditions of early diagenesis. In the Aeronian the black shale formation at the deep shelf was facilitated by great flux of organic carbon. The degradation of organic carbon utilized the free oxygen of water column and sulphate-bound oxygen within the sediment (Fig. 4 b, c).

4.2. Proxies for early diagenetic factors

To estimate the role of each early diagenetic factor the proxies for them were needed, as direct measurement of the ancient parameters was not possible. The $\delta^{13}C$ data from the publications of earlier investigators (Kaljo ja Martma 2000), records of authigenic silica and barite occurrences and of barium contents in the rock sections were considered as indexes of primary bioproductivity. SiO_2/Al_2O_3 and K_2O/Al_2O_3 ratios were used as proxies for grain size, transgressions—regressions, and admittedly for sedimentation rate. Based on analyses from the Aizpute-41 core the overall sea stand was higher in the early Silurian compared to the late Ordovician (Fig. 5), shown by SiO_2/Al_2O_3 and K_2O/Al_2O_3 ratios. Approximate calculation of the sedimentation rate for the whole Telychian of the Aizpute-41 core yielded a mean rate of 4 cm/ky (Paper I).

Trace metal and organic matter contents of Aeronian black shale were indexes of anoxic environment (Paper II). Hematite, goethite (Paper III) and chalcopyrite (Kiipli, Kiipli ja Kallaste 2000), investigated in Telychian red beds, helped □amet trace the redox developments within fresh sediment being, at the □amet ime, indicators of sea bottom water chemistry.

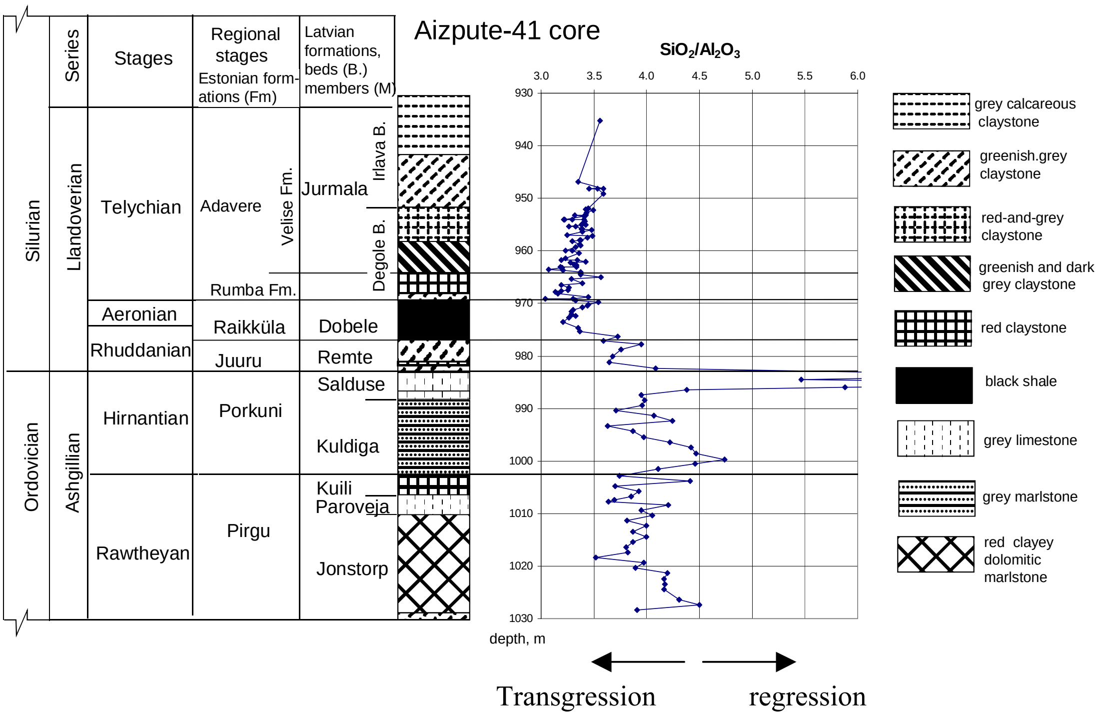

Fig. 5. Lithology and stratigraphy of the Aizpute-41 core with SiO_2/Al_2O_3 ratio describing transgressions-regressions

4.3. Carbonate system

Atmospheric Pco_2 drives the carbon cycle of sea water — the carbonate chemistry and primary bioproductivity. Numerical models of sea water carbonate system go back 100 Ma (Tyrrell ja Zeebe 2004). Data on the whole Phanerozoic are episodic and incomplete, though several seawater components, e.g. Mg, Ca and sulphate concentrations (Horita et al. 2002; Lowenstein et al. 2001), and atmospheric Pco_2 (Berner ja Kothavala 2001; Royer et al. 2004) have been proposed. Our reconstruction of carbonate formation—dissolution in the East Baltic shelf (Paper IV) bases on use of the general considerations of carbonate system, and atmospheric CO_2 estimations by Royer et al. (2004). The $\delta^{18}O$ data by Heath et al. (1998), measured in the brachiopods of the Ruhnu core, enabled to elucidate the Hirnantian and Llandovery relative temperatures implying atmospheric Pco_2 change. The Ca concentration was taken constant through late Ordovician and early Silurian, though this simplification would need further confirmation. We proceeded from the distribution of carbonate minerals and their diminishing amount in the profile from shallow to deep shelf (Paper IV Fig. 2) using calcite—dolomite—terrigenous matter contents calculated from chemical analyses

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4.4. Low pH proved by metabentonite composition

Metabentonites were used as one argument for the relatively low Ph of the deep shelf bottom water in the Ph-model. These layers of altered volcanic ash contained kaolinite, in the deep shelf of both the Telychian and Aeronian. In geological sections from corresponding shallower facies the metabentonites consisted of illite-smectite, and in the shallowest shelf of K-feldspar (Paper VI). The metabentonites of the Adavere stage of the Viki core consisted of illite-smectite without kaolinite. Kaolinite formation at lower Ph than illite-smectite and K-feldspar (at limited variation of concentration of dissolved silica) (Helgeson & Mackenzie 1970) indicated the low Ph of sea bottom water, decreasing in accordance with water deepening (Paper VI).

5. MATERIAL AND ANALYTICAL METHODS

5.1. Material

The material comes from the west Latvian Aizpute-41 core of the deep shelf facies, and from several cores of the transitional zone and shallow facies. The Aizpute core was sampled from the lower Ashgillian to upper Telychian. The lithology, stratigraphy and sampling points are given in Figure 5. The figure also gives the SiO_2/Al_2O_3 ratio used as a proxy for sea level fluctuations. The other cores were sampled in narrower intervals depending on the research tasks, discussed in the presented papers. Metabentonites, studied for correlations on the basis of trace elements (Paper VII) and pyroclastic sanidine composition (Kiipli & Kallaste 2002), were collected from available Estonian and Latvian cores.

5.2. Analytical methods

The rock samples were analysed for major and trace elements by X-ray fluorescence method in the laboratory of the Institute of Geology, using discs fused with Li-tetraborate, and pressed-powder pellets. The main chemical elements were measured from fused discs, trace elements and sulphur from pressed-powder pellets. Calibration was done after international and Estonian rock reference materials (Kiipli, T. et al. 2000). Measuring of loss on ignition (LOI) at 450^{o}C as a rapid method for estimation of the content of organic matter was applied.

X-ray diffractometry (XRD) measurements were carried out for determination of the concentration of the $NaAlSi_3O_8$ component in pyroclastic sanidine of metabentonites. This method by Kiipli and Kallaste (2002) was used in the present work. Different XRD techniques were applied for determination of hematite and goethite contents in Telychian red beds (Paper III), identification of authigenic silica in Aeronian sections (Paper VIII), and study of main minerals of metabentonites (Paper VI).

6. THE MODELS

6.1. The redox model

Aeronian black shales and overlying Telychian greenish grey and red claystones of the deep shelf of the East Baltic Basin indicate at difference in synsedimentary redox conditions of the bottom-water of the sea. In the Aeronian the primary bioproductivity rise was responsible for the accumulation of organic-rich black shale in the deep shelf, and formation of light-grey microcrystalline limestone with chertification, chert nodules and barite in shoreward areas (Paper VIII). The bottom waters of the deep shelf were anoxic with oxygen-poor denitrifying layer transitional to the oxygenated wave-mixing zone above (Paper II). In the early Telychian the bioproductivity decreased. This conclusion comes from the absence of indicators characteristic of high primary bioproductivity of Aeronian (Paper I). In early Telychian the red beds formed in the deep shelf indicating at oxygenated conditions in the bottom water and within the sediment. Eustasy was not the primary cause of redox condition change at the Aeronian--Telychian boundary though it was able to shift the existing facies. Such a shift of red facies took place at the Rumba--Velise transition, in accord with the second transgressive pulse in the early Telychian.

Sedimentation rate did not influence the alteration of redox regime of the deep shelf, as it was low for both the Aeronian and Telychian.

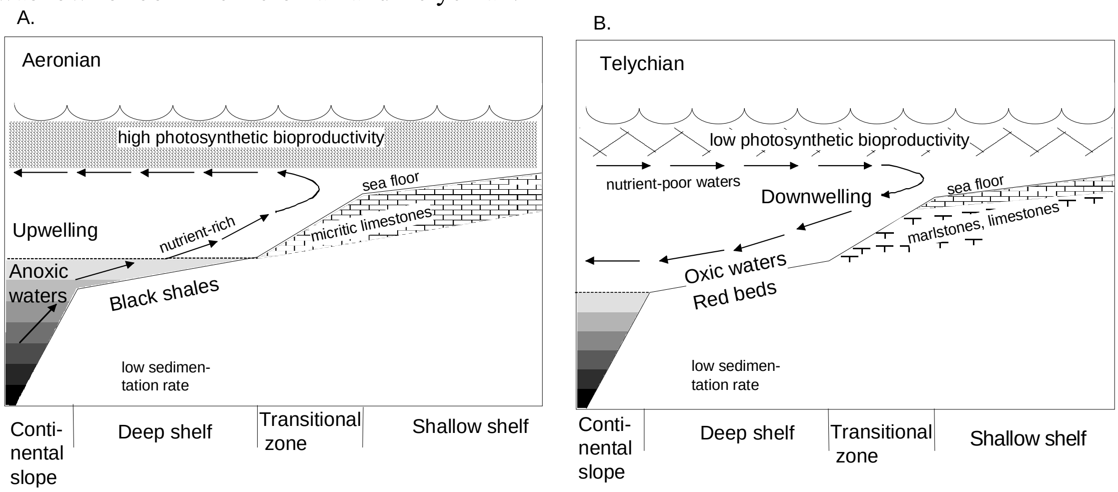

Fig. 6. Model of (A) wind-induced upwelling responsible for anoxic conditions in deep shelf bottom waters and sediment; (B) wind-induced downwelling responsible for oxic conditions in deep shelf bottom waters and sediment

The suggested mechanism regulating the primary bioproductivity and oxygen content of bottom-waters and sediment of the deep shelf was the alternation of wind-induced up- and downwellings (Fig. 6). Upwelling in the Aeronian brought nutrient-rich and oxygen-depleted waters from ocean deep to the shelf generating high primary productivity and anoxic deep shelf environment. This caused the black shale formation in the deep shelf. Downwelling in the Telychian gathered nutrient-poor but oxygen-rich surface waters causing low primary bioproductivity and oxygenation of bottom-waters and sediment. This caused the red bed formation in the deep shelf.

6.2. The pH model

In the late Ordovician--early Silurian the calcite formed in the shallow shelf and dissolved in the deep shelf (Paper IV Fig. 2). The dolomite content diminished offshore, but was not subject to total dissolution. Very likely the dolomite formed in the deep shelf environment *in situ*. The calcite production--preservation was temporally different. This was a response to global and local changes, the eustatic movements, decrease and increase in seawater CO_2 and, correspondingly, increase and decrease in pH (Fig. 7).

The Pirgu-Porkuni lower sea-level stand caused a wider offshore deposition of calcite (Paper IV Fig. 2A, 2B). A lower atmospheric CO_2 of ice-age supported calcite formation at the warm low latitudes. Since the beginning of the Silurian the stress of atmospheric CO_2 increased (Royer et al. 2004) causing decrease of pH of ocean waters. The $\delta^{18}O$ data of the Llandovery section of the Ruhnu core reveal about 1‰ negative trend, which was considered by Heath et al. (1998) as a rise in temperature. Recent studies of isotope partitioning during Ca-carbonate precipitation allow another interpretation relative to $\delta^{18}O$ and pH interaction (Zeebe 1999). Nevertheless, we agree with Heath et al. (1998) and Royer et al. (2004) about the post-glacial rise in temperature and atmospheric CO_2. Relationships between pCO_2 and seawater pH are given in the Figure 7. The influence of high atmospheric pCO_2 to the calcite formation--dissolution was greatest in the Adaver time, the Telychian. Also the low photosynthetic activity did not maintain the higher pH of the sea surface. This resulted in low carbonate production in the shallow shelf, and the carbonate dissolution in the deep shelf or even shallower, in the transitional zone.

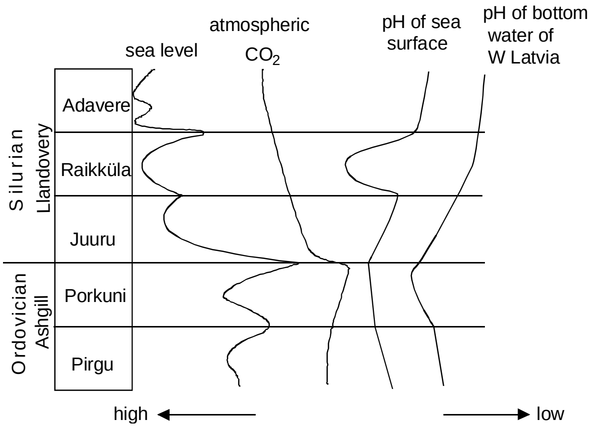

Fig. 7. Schematic sea-level curve, pCO_2 and pH of sea surface and bottom waters. Base on the Aizpute-41 core SiO_2/Al_2O_3 ratios, carbonate distribution on the East Baltic shelf (Paper IV Fig. 2), $\delta^{18}O$ data of the Ruhnu core by Heath et al. (1998) and global pCO_2 model by Royer et al. (2004)

In the Raikküla time, the Aeronian, the carbonate production was supported, as a local rise in the primary bioproductivity at the sea surface (Paper VIII) compensated the damaging effect of increasing atmospheric CO_2. In the deep shelf the great organic carbon flux, in turn, enhanced the dissolution of calcite in the Aeronian (Paper IV). The Aeronian upwelling lifted the dissolved carbonate components, the Ca^{2+} and CO_3^{2-}, back to the shallow shelf additionally supporting the carbonate formation. In Telychian the downwelling carried the dissolved compounds away from the shelf, thereby still decreasing the carbonate saturation on the shelf.

The oceanic anoxic waters (Railsback et al. 1990) affected the deepest part of the seawater pH profile. Supposedly dissolved CO_2, forming below the oxic/anoxic interface in the course of remineralisation of dead organic matter, concentrated due to weak water circulation, and lowered the pH.

6.3. Palaeogeographic prerequisites

The East Baltic Basin was situated in the south-western part of the Baltica Craton, located at 20-30^{o} of southern latitude in the end-Ordovician and early Llandovery (Cocks 1993; Kiessling et al. 2003). By the Wenlock the Baltic Craton had drifted to the equator (Torsvik et al. 1992; McKerrow 1988; Ziegler et al. 1977). During the Ordovician--Silurian the Baltic Basin moved from the region of North-westerlies to South-easterly Trade winds performing a counterclockwise rotation. The changing wind regime in the coastlines of the Baltic Basin might have generated an alternation of upwellings and downwellings (Fig. 8). Parrish (1982) and Moore et al. (1993) pointed out in their models that upwellings were characteristic of western coasts of continents. In the Aeronian the East Baltic Basin probably filled these preconditions if we presume the closure of the connection with the Moscow Syneclise.

In accord with the wander of the Baltica Plate from cold climates to the tropics the carbonate production accelerated through the Ordovician and achieved high sedimentation rate in the Silurian. Unfavourable conditions hindered carbonate formation at intervals, such as the Velise time of the Telychian.

7. CONCLUSIONS

Several features for dynamic climatic and environmental conditions of the Palaeo-Baltic area in the late Ordovician – early Silurian are presented. The Aeronian and Telychian of the East Baltic Basin differed from each other by the oxygen regime of deep shelf bottom waters, primary bioproductivity of surface waters, organic carbon preservation in deep shelf sediments, carbonate accumulation, and eustasy-related water depth.

Wind-driven coastal up- and downwellings regulated the nutrient and oxygen supply in the East Baltic shelf and were responsible for most of the redox changes at the Aeronian/Telychian boundary. Eustasy shifted the facies boundaries, but causal connection between transgression--regression and redox change at the Aeronian/Telychian transition in the Paleo-Baltic basin can not be stated.

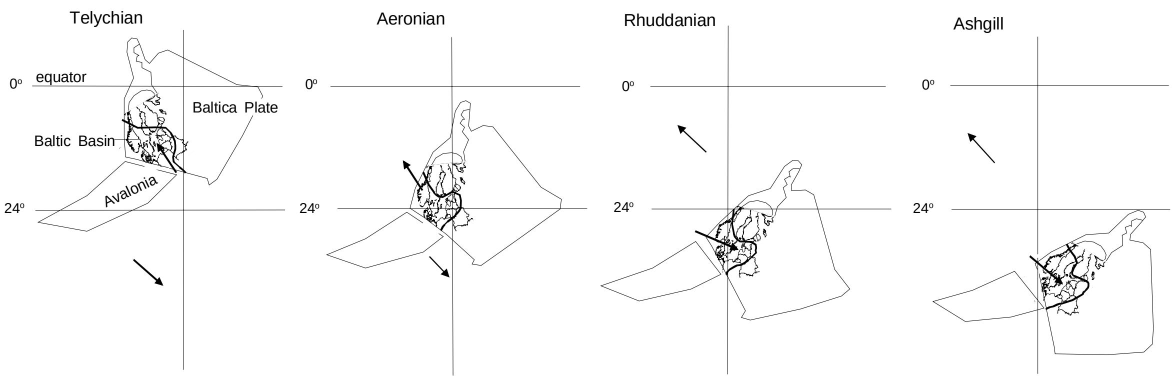

Fig. 8. Drift of the Baltica Plate in Ordovician-Silurian (developed according to models of Kiessling et al. 2003; Torsvik et al. 1992; Cocks 1993; McKerrow 1988; Ziegler et al. 1977). Prevailing wind directions are shown by arrows. Upwelling was characteristic of the Aeronian when the Baltic Basin was supposedly between the zones of Westerlies and Easterly Trade Winds. Downwelling took place in the Telychian when the Trade Winds blew into the Basin

Carbonate distribution varied between stages from the late Ordovician to early Silurian. Ca-carbonate production was most prominent in Aeronian, the mid-Llandovery. In Telychian, the late Llandovery, the production diminished. This can be explained by a rise in atmospheric CO_2, culminating in the late Llandovery. The influence of pCO_2 on the seawater pH was modified by primary bioproductivity. Up- and downwelling governed the primary bioproductivity. They also increased and decreased, correspondingly, the concentration of carbonate and calcium ions in the shallow shelf, regulating the carbonate saturation state.

Dissolution of the carbonates in the deep shelf was due to relatively low pH. Low pH of deep waters was also suggested by independent evidences, the kaolinitic composition of bentonite layers, found in Telychian as well as in Aeronian deep shelf sections.

Modelling of processes enables to draw parallels between different geological times and regions. Upwelling has been considered as a trigger of formation of black shale, the precursor of oil (Parrish 1982; Moore et al. 1993), associated phosphorites and several metals. Marine red beds, the result of downwelling-induced conditions in our model, can concentrate Cu. Chalcopyrite occurrences, pointing to this possibility, have been found in Telychian red rocks (Kiipli et al. 2000). The carbonate formation-dissolution and related carbonate system of seawater involves an important climate regulator, the atmospheric pCO_2. The increasing climate warming of recent years has already had an impact on marine calcite-producing planktic organisms (Feely et al 2004). Carbonates are a potential buffer avoiding dramatic climate fluctuations.

Investigating the past is the key to the future.

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REFERENCES

Bergström, S. M., Huff, W. D. & Kolata, D. R. 1998. The Lower Silurian Osmundsberg K-bentonite. Part I: stratigraphic position, distribution, and palaeogeographic significance. *Geological Magazine 135*, 1-13.

Berner, R. 1971. Principles of chemical sedimentology. McGraw- Hill, N. Y., 223 pp.

Berner, R. A. & Kothavala, Z. 2001. GEOCARB III: a revised model of atmospheric CO_2 over Phanerozoic time. *American Journal of Science 30*, 182-204.

Cocks, L. R. M. 1993. Triassic pebbles, derived fossils and the Ordovician to Devonian palaeogeography of Europe. *Journ. of the Geol. Soc. London 150*, 219-226.

Feely, R. A., Sabine, C. L., Lee, K., Berelson, W., Kleypas, J., Fabry, V. J. & Millero, F. J. 2004. Impact of anthropogenic CO_2 on the $CaCO_3$ system in the oceans. *Science 305*, 362-366.

Froelich, P. N., Klinkhammer, G. P., Bender, M. L., Luedtke, N. A., Heath, G. R., Cullen, D., Dauphin, P., Hammond, D., Hartman, B. & Maynard, V. 1979. Early oxidation of organic matter in pelagic sediments of the eastern equatorial Atlantic: suboxic diagenesis. *Geochim. Cosmochim. Acta*, **43**,1075-1090.

Heath, R. J., Brenchley, P. J. & Marshall, J. D. 1998. Early Silurian carbon and oxygen stable-isotope stratigraphy of Estonia: implications for climate change. *In* Landing, E. & Johnson, M. E. (eds.) Silurian cycles. *New York State Museum Bulletin 491*, 313-326.

Helgeson, H. C. & Mackenzie, F. T. 1970. Silicate - sea water equilibria in the ocean system. *Deep-sea Research 17*, 877-892.

Horita, J., Zimmermann, H. & Holland, H. D. 2002. Chemical evolution of seawater during Phanerozoic: implications from the record of marine evaporites. *Geochim. Cosmochim. Acta 66*, 3733-3756.

Jaanusson, V. 1972. Aspects of carbonate sedimentation in the Ordovician of Baltoscandia. *Lethaia 6,* 11-34.

Johnson, M. E., Baarli, B. G., Nestor, H., Rubel, M. & Worsley, D. 1991. Eustatic sea-level patterns from the Lower Silurian (Llandovery Series) of southern Norway and Estonia. *Geological Society of America Bulletin 103*, 315-335.

Kaljo, D. (ed.), 1987. *Reshenya mezhvedomstvennogo stratigraficheskogo soveschaniya po ordoviku i siluru Vostochno-Evropeyskoi platformy 1984. g. s regional'nymi stratigraficheskimi schemami.* Leningrad, 114 pp. (in Russian).

Kaljo, D., & Martma, T. 2000. Carbon isotopic composition of Llandovery rocks (East Baltic Silurian) with environmental interpretation*: Proceedings of the Estonian Academy of Sciences, Geology 49/4*, 267-283.

Kiessling, W., Flügel, E. & Golonka, J. 2003. Phanerozoic carbonate platform sedimentation. *Lethaia 36*, 195-225.

Kiipli, E., Kiipli, T. & Kallaste, T. 2000. Early diagenetic chalcopyrite occurrences in Telychian marine red beds of West Estonia and West Latvia. *Proc. Estonian Acad. Sci. Geol. 49*, 294-307.

Kiipli, T. & Kallaste, T. 2002. Correlation of Telychian sections from shallow to deep sea facies in Estonia and Latvia based on the sanidine composition of bentonites. *Proc. Estonian Acad. Sci. Geol. 51*, 143 - 156.

Kiipli, T., Batchelor, R. A., Bernal J. P., Cowing, C., Hagel-Brunnström, M., Ingham, M. N., Johnson, D., Kivisilla, J., Knaack, C., Kump, P., Lozano, R., Michiels D., Orlova, K., Pirrus, E., Rousseau, R. M., Ruzicka, J., Sandström, H. & Willis, J. P. 2000. Seven sedimentary rock reference samples from Estonia. *Oil Shale 17*, 215-223.

Lowenstein, T. K., Hardie, L. A., Timofeeff, M. N. & Demicco, R. V. 2003. Secular variation in seawater chemistry and the origin of calcium chloride basinal brines. *Geology 31*, 857-860.

Loydell, D. K., Männik, P. & Nestor, V. K. 2003. Integrated biostratigraphy of the lower Silurian of the Aizpute-41 core, Latvia. *Geol. Mag. 140*, 205-229.
McKerrow, W. S. 1988. The development of the Iapetus Ocean from the Arenig to the Wenlock. *In* Harris, A. L., & Fettes, D. J. (eds.) The Caledonian-Appalachian orogen. *Geological Society special Publication 38*, 405-412, Blackwell Scientific Publication, Oxford.
Moore, G. T., Hayashida, D. N. & Ross, C. A. 1993. Late Early Silurian (Wenlockian) general circulation model -- generated upwelling, graptolitic black shales, and organic-rich source rocks – An accident of plate tectonics? *Geology 21*, 17-20.
Männik, P. & Viira, V. 1990. Conodonts. *In* Kaljo, D. & Nestor, H. (eds.) Field Meeting, Estonia, 1990. An Excursion Guidebook, 84-89. Institute of Geology, Estonian Academy of Sciences, Tallinn.
Männil, R. 1966. Evolution of the Baltic basin during the Ordovician (in Russian with English summary). Valgus Publishers, Tallinn, 201 pp.
Nestor, H. 1997. Silurian. *In* Raukas, A. & Teedumäe, A. (eds.) Geology and mineral resources of Estonia. 89-106. Estonian Academy Publishers, Tallinn.
Nestor, H., Einasto, R., Männik, P. & Nestor, V. 2003. Correlationof lower-middle Llandovery sections in central and southern Estonia and sedimentation cycles of lime mud. *Proc. Estonian Acad. Sci. Geology 52*, 3-27.
Nikishin, A. M., Ziegler, P. A., Stephenson, R. A., Cloetingh, S. A. P. L., Furne, A. V., Fokin, P. A., Ershov, A. V., Bolotov, S. N., Korotaev, M. V., Alekseev, A. S., Gorbachev, V. I., Shipilov, E. V., Lankreijer, A., Bembinova, E. Y., Shalimov, I. V. 1996. Late Precambrian to Triassic history of the East European Craton: dynamics of sedimentary basin evolution. *Tectonophysics 268*, 23-63.
Nõlvak, J. 1997. The Ordovician of Estonia, Table 7. *In* Raukas, A. & Teedumäe, A. (eds.) Geology and mineral resources of Estonia. 54-55. Estonian Academy Publishers, Tallinn.
Parrish, J. T. 1982. Upwelling and petroleum source beds, with reference to Paleozoic. *Am. Ass. Petroleum Geologists Bull. 66*, 750-774.
Põlma, L. 1982. Comparative lithology of the Ordovician carbonate rocks in the northern and middle East Baltic (in Russian with English summary) Valgus Publishers, Tallinn, 164 pp.
Railsback, L.B., Ackerly, S.C., Anderson, T.F., and Cisne, J.L., 1990. Palaeontological and isotope evidence for warm saline deep waters in Ordovician oceans. *Nature 343*, 156-159.
Royer, D. L., Berner, R. A., Montanez, I. P., Tabor, N. J. & Beerling, D. J. 2004. CO_2 as a primary driver of Phanerozoic climate. *Geological Society of America Today 14*, 4-10.
Tyrrell, T. & Zeebe, R., 2004: History of carbonate ion concentration over the last 100 million years. *Geochimica et Cosmochimica Acta 68*, 3521-3530.
Torsvik, T. H., Smethurst, M. A., Van der Voo, R., Trench, A., Abrahamsen, N. & Halvorsen, E. 1992. Baltica. A synopsis of Vendian-Permian palaeomagnetic data and their palaeotectonic implications. *Earth-Science Reviews 33*, 133-152.
Tromp, T. K., Van Cappellen, P. & Key, R. M. 1995. A global model for the early diagenesis of organic carbon and organic phosphorus in marine sediments: *Geochim. Cosmochim. Acta 59*, 1259-1284.
Ziegler, A. M., Hansen, K. S., Johnson, M. E., Kelly, M. A., Scotese, C. R. & Van Der Voo, R. 1977. Silurian continental distributions, paleogeography, climatology, and biogeography. *Tectonophysics 40*, 13-51.
Zeebe, R. E. 1999. An explanation of the effect of seawater carbonate concentration on foraminiferal oxygen isotopes. *Geochim. Cosmochim. Acta* 63, 2001-2007.

ABSTRACT

The models describing seawater chemistry base on lithology, mineralogy and chemical composition of the rock. Two aspects of seawater chemistry are considered, 1) the oxygenation of deep shelf waters, yielding the Eh-model, and 2) the carbonate system responsible for calcite -- dolomite formation -- dissolution, giving the pH-model.

The Eh-model was worked out on the basis of the Raikküla Regional Stage, the Aeronian, and Adavere Regional Stage, the Telychian, the Llandovery Series of early Silurian. The pH model deals with times from the late Ordovician Pirgu Regional Stage, the Ashgill Series, to the early Silurian Adavere Regional Stage.

The Aeronian and Telychian of the East Baltic basin differed from each other by the oxygen regime of deep shelf bottom waters, primary bioproductivity of surface waters, organic carbon preservation in deep shelf sediments, carbonate accumulation, and eustasy-related water depth. Wind-driven coastal up- and downwellings regulated the nutrient and oxygen supply in the East Baltic shelf and were responsible for most of the redox changes at the Aeronian/Telychian boundary.

Carbonate distribution varied between stages from the late Ordovician to early Silurian. Ca-carbonate distribution was widest in the late Ashgill, its production was most prominent in the mid-Llandovery. In the Telychian, the late Llandovery, the carbonate production diminished. This can be explained by the rise in atmospheric CO_2 culminating in the late Llandovery.

Dissolution of the carbonates in the deep shelf was due to relatively low pH coming from high atmospheric CO_2. Primary bioproductivity modified the influence of atmospheric CO_2 on the seawater pH. The Aeronian great primary bioproductivity created favourable conditions for carbonate formation in the surface waters of the shallow shelf, but great organic carbon flux enhanced the dissolution of calcite in deep waters. Up- and downwelling increased and decreased, correspondingly, the concentration of carbonate and calcium ions in the shallow shelf, additionally regulating the carbonate saturation state.

MEREVEE KEMISMI MODELLEERIMINE HILISORDOVIITSIUMI JA VARASILURI IDA-BALTI BASSEINIS

Kokkuvõte

Käesolevas töös on merevee kemismi vaadeldud hapnikusisalduse ja karbonaatse süsteemi aspektist. Vastavaid mudeleid on nimetatud Eh- ja pH-mudeliks. Modelleerimine lähtub hilisordoviitsiumi ja varasiluri kivimite litoloogilisest ja mineraalsest koostisest. Eh-mudel tugineb varasiluri kesk-ja ülem-Llandovery sügavaveelistel läbilõigetel. Tugipuurauguks ja mitmete keemiliste ning mineraloogiliste andmete allikaks on olnud lääne-Läti Aizpute-41 puursüdamik. Sügavaveelistes läbilõigetes tuleb selgelt esile merevee hapnikusisalduse ja sellega seotud teiste keskkonnatingimuste erinevus eri ajalõikude vahel. Kesk-Llandovery on esindatud musta kilda 7-10 m paksuse intervalliga, mis viitab hapnikuvaestele tingimustele merevee põhjalähedases osas. Samavanuselisteks kivimiteks madala shelfi suunal on afaniitsed lubjakivid 100 kuni 170 m paksuses. Lubjakivid sisaldavad ränimugulaid ja teisi ränistumisnähtusi, samuti on siin leitud barüüti. Iseloomuliku fatsiaalse järgnevuse ja mineraloogia alusel on kogu seda tunnuste kompleksi vaadeldud kui suurenenud fotosünteetilise bioproduktsiooni tulemust. Suurenenud primaarne bioproduktsioon oli ühe kindla protsessi, *upwelling'*u ehk mere tõusevhoovuse, tagajärg. *Upwelling*, mis tõusis shelfile Paleozoikumi hapnikuvaestest süvavetest, tõi enesega kaasa toitaineid, põhjustas suure planktoonse bioproduktsiooni ja merevee hapnikupuuduse. Hapnikupuudus tuli esile lainetuse segunemistsoonist sügavamal, kus tekkis musta kilt.

Hilis-Llandovery on, vastandina eelkirjeldatud kesk-Llandovery'le, vähese primaarse bioproduktsiooniga ja hapnikurikaste vetega. Seda tõendab süvaveelise shelfi kivimite punavärvilisus ja nii sügava kui madala shelfi kivimites suure bioproduktsiooni indikaatorite puudumine. Punavärvilisuse kandjaks on saviosakesi kattev peendispersne hematiit ja vähemal määral esinev götiit. Juhtivaks protsessiks merevee hapnikurezhiimi kujundamisel oli *downwelling,* ehk merevee langevhoovus. Langevhoovuse teke oli seotud kliima ja valdava tuulesuuna muutusega Balti mandriplaadi liikumise tõttu ekvaatori suunas. Passaatide vööndis kandis tuul ookeani pindmise hapnikurikka, kuid toitainetevaese veekihi Ida-Balti Basseini. Selle tagajärjel langes primaarne bioproduktsioon ja vesi muutus hapnikuküllaseks. Aeglase settimiskiirusega sügaval shelfil avaldus see punavärviliste setete kujunemises.

Karbonaatne sedimentatsioon hilisordoviitsiumis ja varasiluris toimus madalal shelfil erineva intensiivsusega, sügaval shelfil karbonaadid lahustusid. Hilisordoviitsiumis nihkus karbonaatne faatsies globaalse regressiooni tõttu avamere poole, mistõttu lahustumine sügavas vees on vähesem kui varasiluris. Karbonaatide tekkimise-lahustumise jaotuspilt ja andmed temperatuuri ning atmosfääri CO_2 sisalduse kohta erinevate uurijate tööde põhjal võimaldas välja eristada karbonaatse süsteemi muutuvad tegurid eri geoloogilistel aegadel. Põhiline globaalne faktor, atmosfääri CO_2 sisaldus, saavutas oma suurima mõju hilis-Llandovery's. Kõrgenenud CO_2 sisaldus põhjustas merevee pH languse, mis vähendas pinnakihis karbonaatide teket ja soodustas sügavamal põhjalähedases vees lahustumist. Hilis-Llandovery's oli ka fotosünteetiline CO_2 sidumine Ida-Balti Basseinis vähenenud, mistõttu pinnakihi pH oli tundlik atmosfääri CO_2 mõjudele. Downwellingu-tüüpi veetsirkulatsioon basseinis viis lahustunud kaltsiumi ja karbonaatioonid shelfilt ookeani, vähendades sellega veelgi karbonaatide küllastusastet ja sadenemist madalal shelfil. Vastavalt nendele tingimustele kujunesid Balti shelfil Velise eal valdavalt merglid ja sügavamal savikivimid. Kesk-Llandoverys oli atmosfääri CO_2 sisaldus veel mõõdukas. Suurenenud fotosünteesi ja CO_2 sidumise tõttu oli merevee pindmine kiht suurema pH-ga soodustades karbonaatide teket. Sügaval shelfil, vastupidi, lisandus lagunevast orgaanilisest ainest täiendavat CO_2, mis vähendas pH-d ja soodustas karbonaatide lahustumist.

Upwelling tõstis lahustunud Ca ja karbonaatiooni tagasi madalale shelfile, kus see uuesti karbonaadina välja sadenes. Kõigist nimetatud asjaoludest tingituna ongi Raikküla eal madalal shelfil ja üleminekutsoonis paks lubjakivide lasund, sügava shelfi must kilt aga on karbonaadivaene.

Tänapäevaga võrreldes on ordoviitsiumi-siluri merevesi olnud erinev nii hapniku jaotuse kui karbonaatse süsteemi osas. Ainult üksikutes maailmamere paikades võib tänapäeval leida analooge muistsele ookeanis laialt levinud anoksilisele keskkonnale. Tänapäeva hapnikurikkad ookeaniveed ja laialt levinud punavärvilised ookeani setted esinesid piiratult ordoviitsiumi-siluri ajal shelfil. Seoses Mesozoikumis karbonaatide tekke nihkumisega shelfilt ookeani pinnakihti on muutunud atmosfääri süsihappegaasi ja karbonaatse sette tasakaal. Tõenäoliselt on suurenenud ookeani puhverdusvõime, mis stabiliseerib kliimat, kui inimtegevusest lähtuv kasvuhoonegaaside õhkupaiskamine ei muutu liiga kiireks.

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Kiipli, E. 2004. Redox changes in the deep shelf of East Baltic Basin in Aeronian and early Telychian (Early Silurian). *Proceedings of the Estonian Academy of Sciences Geology 53*, 94-124.

Paper II

Kiipli, E. 1997. Geochemistry of Llandovery black shales in the Aizpute-41 core, West Latvia. *Proceedings of the Estonian Academy of Sciences Geology 46*, *3*, 127-145.

Paper III

Kiipli, E., Kallaste, T. & Kiipli, T. 2000. Hematite and goethite in Telychian marine red beds of the East Baltic. *GFF 122*, 281-286.

Paper IV

Kiipli, E. & Kiipli, T. Calcite-dolomite distribution in the East Baltic deep shelf in late Ordovician - early Silurian implying carbonate system (*submitted)*.

Paper V

Kiipli, E., Kiipli, T. & Kallaste, T. 2002. Correlation between deep and shallow shelf on the basis of O-bentonite, East Baltic. In *The Fifth Baltic Stratigraphical Conference "Basin Stratigraphy—Modern Methods and Problems", September 22-27, 2002, Vilnius, Lithuania: Extended Abstracts* -- Vilnius, 77-80.

Paper VI

Kiipli, T., **Kiipli, E.** & Kallaste, T. 1997. Metabentonite composition related to sedimentary facies in the lower Silurian of Estonia. *Proceedings of the Estonian Academy of Sciences Geology 46*, *2*, 93-104.

Paper VII

Kiipli, T., Männik, P., Batchelor, R. A., **Kiipli, E.,** Kallaste, T. & Perens, H. 2001. Correlation of Telychian (Silurian) altered volcanic ash beds in Estonia, Sweden and Norway. *Norwegian Journal of Geology (Norsk Geologisk Tidsskrift) 81,* 179-194.

Paper VIII

Kiipli, E., Kiipli, T. & Kallaste, T. 2004. Bioproductivity rise in the East Baltic epicontinental sea in the Aeronian (Early Silurian). *Palaeogeography, Palaeoclimatology, Palaeoecology 205*, 255-272.