Distribution of phosphorus in the Middle and Upper Ordovician Baltoscandian carbonate palaeobasin

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Abstract. Baltoscandian Middle and Upper Ordovician carbonate rocks are relatively poor in phosphorus, with the P_2O_5 content of 0.05–0.5%, rarely exceeding 1%. Phosphorus distribution in the Ordovician carbonate succession shows spatial and temporal variations. In the Estonian Shelf P content is the highest in the Middle Ordovician, close to the Tremadocian P-rich siliciclastic sediments, decreasing towards younger carbonate rocks. In the basinal, i.e. deep shelf, sections two intervals of elevated P contents occur: the first is similar to the shallow shelf in the lowermost Darriwilian, the second is a moderate P increase in the upper Darriwilian–Sandbian interval. The Darriwilian–Sandbian interval of elevated P content in the deep shelf sections roughly corresponds to algal kukersite accumulations in the shallow shelf. Multiple processes determined phosphorus distribution in the studied sediments. Regional processes influencing P distribution include seawater circulation, e.g. P influx by coastal upwellings, and sedimentation rate. Global oceanic variation in bioproduction ($\delta^{13}C$ trends) had no positive effect on P accumulation in the Baltoscandian epeiric sea.

Key words: phosphorus, Ordovician, Baltoscandia, kukersite.

INTRODUCTION

Phosphorus (P) is an essential element in photosynthesis. When involved in marine photosynthesis P regenerates from decomposing organic matter, recycles and tends to concentrate in deep ocean water in dissolved form. Via the upwelling, vertical water exchange and diffusion P penetrates into the photic zone and triggers primary productivity (Van Cappellen & Ingall 1994). Palaeozoic deep anoxic ocean waters must have been rich in P, as stratification in the water column impeded the water mixing. High photosynthetic activity is expected from the high P influx in upwelling regions. Nevertheless, the relationship between P and primary productivity is difficult to catch in geological sections, mainly due to organic matter loss during oxidation in the water column as well as during early diagenesis. Organic matter preserved only in suitable conditions. Indirect proxies, such as chert, barite, $\delta^{13}C$, etc., must be used to find out the enhanced primary bioproductivity (Kiipli et al. 2004). The Sandbian kukersite oil shale deposits in the Estonian shallow shelf are widely known. Investigation of the P relationship with kukersite can shed light to the problem of nutrient supply in kukersite formation.

Fixation of P in marine sediments depends on its content in primary sources, such as terrestrial income and upwelling from the ocean deep, and diagenetic conditions. Phosphorus in the Ordovician East Baltic Basin is bound into carbonate-fluorapatite, francolite (Põlma 1982). Usually apatite is scattered in the sedimentary rock as small grains, faunal debris, ooids, crusts or impregnations. Phosphorite concretions, phosphatic oolites and phosphatic discontinuity surfaces are recorded mainly in the lower part of the Ordovician carbonate succession in Estonia. The uppermost Ordovician is poor in such occurrences (Põlma 1982; Saadre 1995). Massive accumulation of phosphatic shells of inarticulate brachiopods in quartz sand of the Lower Ordovician (Tremadocian) Pakerort Stage has led to the formation of phosphorite as mineral resource in northern Estonia (Arsen′ev & Gorbunova 1979; Raudsep 1997). The high content of P is known also in the Tremadocian *Lycophoria* Formation in northern Jämtland, Sweden (Andersson 1971).

Middle and Upper Ordovician P has received less attention due to the absence of high concentrations in Baltoscandia. Though, P has been mentioned in association with pyritized detrite of the Kukruse and Haljala stages (Põlma 1982). This detrite is found in a wide area from southern Estonia to Poland (Männil 1966). Phosphorite has also been recorded in the Llanvirn (Darriwilian) condensed sections of northern Poland (Podhalańska 2002) and in the Llanvirn–Caradoc (Darriwilian–Sandbian) of the Holy Cross Mountains of southern Poland (Trela 2005).

The present work gives the results of P_2O_5 analyses from the East Baltic Ordovician succession with an aim to study the relationships between P and palaeo-environment. Phosphorus is considered to be a necessary nutrient for kukersite formation.

GEOLOGICAL BACKGROUND

The Ordovician Baltoscandian Basin was an epi-continental sea opened to the ocean in the west and south. The axial part of the palaeobasin comprising S Estonia, W Latvia and NW Lithuania formed a gulf-shaped deep shelf, called the 'Livonian Tongue' (Fig. 1). The passing of the deep shelf to the transitional zone and shallow Estonian Shelf was smooth in the northern direction in the first half of the Ordovician. In the Late Ordovician the deep shelf became differentiated from the shallow shelf (Nestor & Einasto 1997). The ocean in the Ordovician was redox-stratified, with alternating oxygen-rich and oxygen-poor states (Berry et al. 1989). Probably, the anoxic deep waters of the ocean flooded the deepest part of the Baltoscandian palaeobasin, which is shown by widespread black shales in Scania and Västergötland (Männil 1966). The upper Darriwilian–Sandbian, lower Upper Ordovician, reveals a particular type of organic-matter-rich shale, kukersite. The industrially exploited kukersite deposits formed in NE Estonia and NW Russia in Kukruse time, but thinner seams occur also in the older Kunda and Uhaku and younger Haljala–Keila stages. Kukersite contains 10–60% organic matter, carbonate and siliciclastic terrigenous component, and accessory authigenic minerals, such as pyrite (Bauert & Kattai 1997). The main biologic component of kukersite is the extinct photosynthetic organism *Gloeocapsomorpha prisca*, which is represented by selectively preserved highly aliphatic, resistant biomacromolecules from its outer cell walls (Derenne et al. 1990; Mastalerz et al. 2003).

MATERIALS AND METHODS

Five drill cores were studied for the P content (Fig. 1) – Laeva-13 in Estonia, Aizpute-41 in Latvia, Kurtuvenai-161 and -166 in Lithuania and När in Sweden. For the Estonian Mehikoorma and Ruhnu cores the P_2O_5 data from Shogenova (2003, 2005) and stratigraphy from Põldvere (2003, 2005) were used. Phosphorus was measured in whole-rock samples by the X-ray fluorescence method. The lower limit of P_2O_5 detection is 0.05%. The samples were collected from the cores at about 1-m step. The average P distribution in the shallow Estonian Shelf sections (Fig. 2) was calculated by using the database of the Estonian Geological Survey (see Kiipli 2005). The total number of analyses of the Estonian Geological Survey was 382, collected from 24 cores and 4 outcrops.

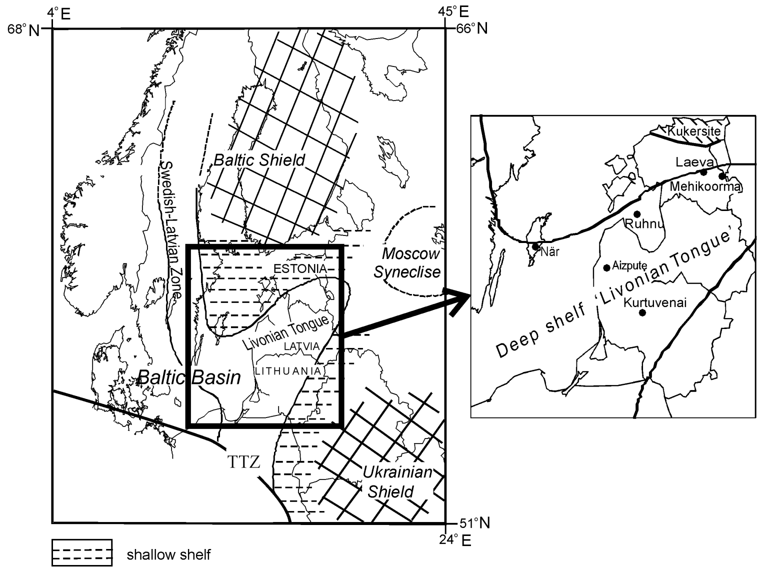

Fig. 1. Location of boreholes and facies setting. TTZ – Teisseyre–Tornquist Line.

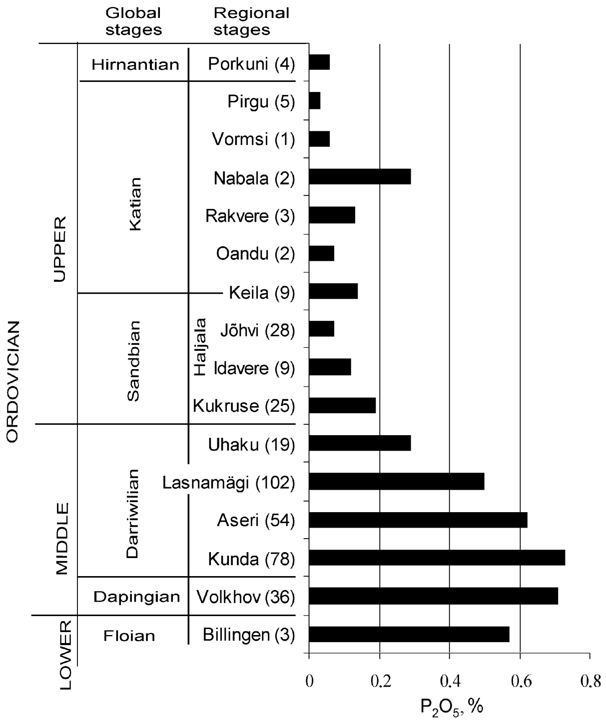

Fig. 2. Distribution of average P_2O_5 contents through the post-Tremadocian Ordovician of the shallow Estonian Shelf. The number of analyses is given in parentheses. P_2O_5 data from the electronic database of the Estonian Geological Survey (Kiipli 2005).

RESULTS

The measured P_2O_5 contents of Middle and Upper Ordovician carbonate rocks vary mainly between 0.05% and 0.5%, reaching occasionally 4%. These are higher in the Dapingian–Sandbian interval, whereas the uppermost Ordovician is P-poor (Figs 2–4). The highest values in the Ordovician succession, about 10%, occur in the Tremadocian siliciclastic *Obolus*-phosphorite (Raudsep 1997). In the North Estonian sections the P_2O_5 content decreases from 10% in the Pakerort Stage to an average of 0.7% in the Volkhov and Kunda stages, to 0.2% in the Kukruse Stage and below 0.1% in the Haljala Stage and upwards. Short-term increase is recorded in the Nabala Stage (Fig. 2). Viira et al. (2004) detected the reworking of P-rich sediments in the Hunneberg–Billingen stages, which indicates that part of the high P content in the Floian–early Darriwilian interval may come from the underlying Tremadocian sediments. The occurrences of Hunneberg–Billingen lingulates (Puura 1996) also point to elevated P in seawater of that time. Kiipli et al. (1984) suggested re-deposition of lower Ordovician sediment in early Kunda time.

Two intervals of elevated P contents occur in the cores from the transitional zone and deep shelf. The Dapingian–lower Darriwilian can be considered as a diminishing succession of the Tremadocian phosphorus ‘high’, with the minimum P_2O_5 contents in the mid-Darriwilian Aseri Stage (Figs 3, 4). The late Darriwilian–Sandbian interval, from the Lasnamägi Stage to the Keila Stage, revealed a moderate elevation of P_2O_5, up to 0.5% and more (Figs 3, 4). The Upper Ordovician Katian and Hirnantian are poor in P_2O_5, with the average content between 0.05% and 0.1%. As an exception, slight increase in P_2O_5, up to 0.3%, was recorded in the Kurtuvenai-161 and Aizpute-41 cores in the Mossen, Mõntu or Fjäcka formations (Katian Stage), whereas Mossen and Fjäcka are black shale intervals. A similar elevation of P contents was observed in the approximately corresponding carbonate sections of the Rakvere, Nabala and Vormsi stages in the Laeva-13, Mehikoorma, Ruhnu and När cores (Figs 3, 4). The post-Tremadocian P contents are the highest in the westernmost studied section, the När core of Gotland (Fig. 4). The increased P_2O_5 level in the late Darriwilian–Sandbian of the basinal sections roughly corresponds to contemporary kukersite deposition in the shallow Estonian Shelf. The obtained P content data were compared to Al content to find out whether the risen siliciclastic input caused an increase in P. However, no correlation was recognized, which points to an alternative route of P.

DISCUSSION

For the shelf seas two sources of P can be considered: terrigenous input from the weathering area and the oceanic source – mainly upwelling of dissolved components (Föllmi et al. 1993). Variations in terrestrial input of the weathered material, including nutrients, could be related to climate’s humidity-aridity and sea level changes controlling the area of weathering. Elevated late Darriwilian–Sandbian P concentrations in basinal facies of Baltoscandia coincide with large-scale global rise in sea level (Haq & Schutter 2008), but the influence of regional Baltoscandian sea level changes (Hints et al. 2010) on P distribution is not obvious. Rapid short-term sea level falls with increase in siliciclastic input, like Hirnantian glacioeustatic events, do not show increase in P concentration. These processes, together with missing correlation between the P and Al contents in sediments, support the idea that terrestrial input is not the main P source in the intervals of elevated P.

Coastal upwellings are supposed to be effective suppliers of P to the carbonate shelf. In the North American Midcontinent the Late Ordovician estuarine circulation system resulted in an influx of deep, cool,

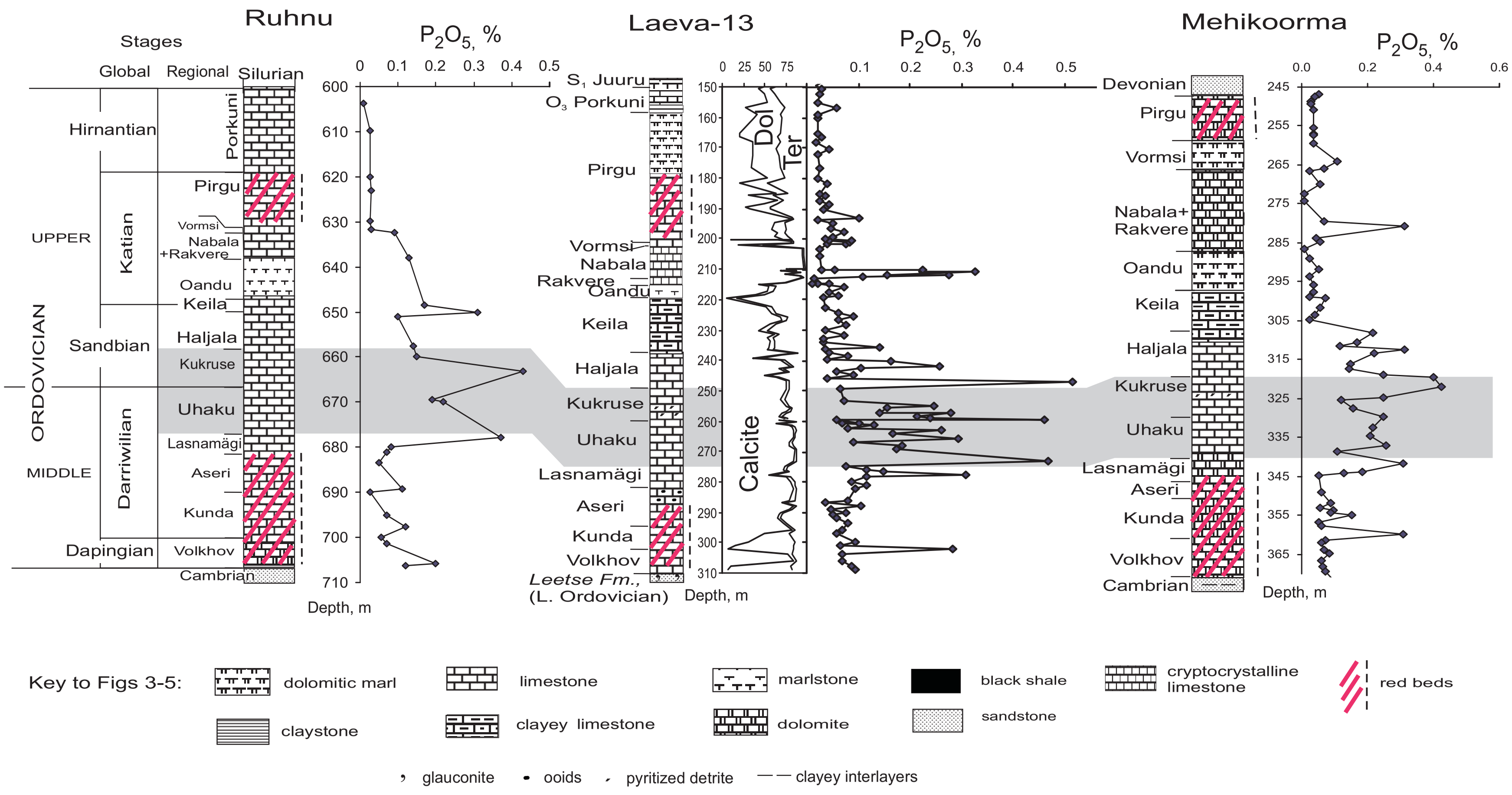

Fig. 3. P_2O_5 contents of rocks in the Ruhnu, Laeva-13 and Mehikoorma core sections. The Ruhnu stratigraphy is from Põldvere (2003) and P_2O_5 data are from Shogenova (2003). The Mehikoorma stratigraphy is from Põldvere (2005) and P_2O_5 data are from Shogenova (2005). The grey area marks the late Darriwilian–Sandbian interval (Uhaku and Kukruse stages) of maximum kukersite accumulation in the shallow shelf.

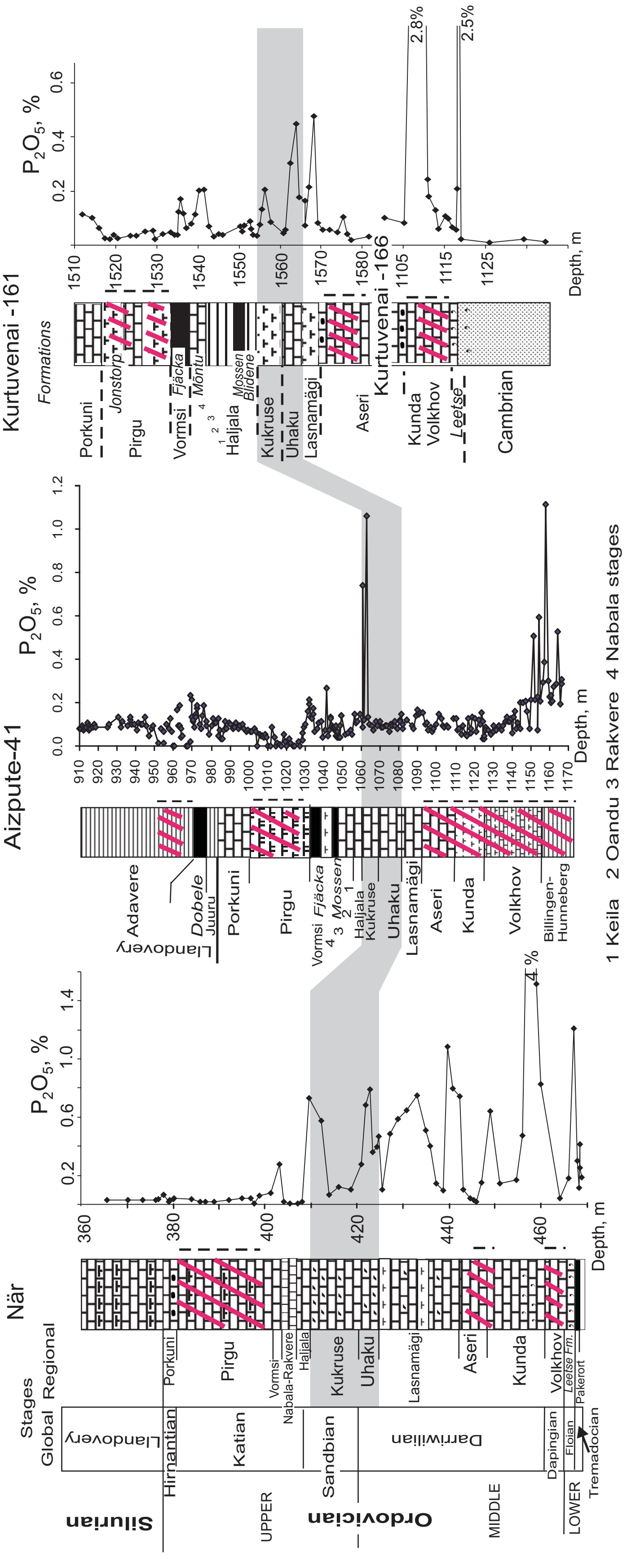

Fig. 4. P_2O_5 contents of rocks in the När, Aizpute-41 and Kurtuvenai-161 and -166 core sections. For lithology see Fig. 3.

P-rich waters through the Sebree Trough from the Iapetus Ocean to the carbonate platform, causing widespread distribution of phosphorite, phosphatic carbonates and phosphatic discontinuity surfaces (Kolata et al. 2001). Some authors have doubted in the occurrence of coastal upwellings in the Ordovician of Baltoscandia because of the low bottom relief and shallowness of the sea (Põlma 1982; Nordlund 1989). However, there is some morphological similarity between the Sebree Trough in North America and the Livonian Tongue in Baltoscandia, suggesting the possibility of a similar circulation system. The palaeogeographic position of the Baltic Craton was favourable for upwelling of deep P-rich waters from the western open ocean in the Tremadoc, Early Ordovician (Wilde et al. 1989). The gradual decline in the P content from the post-Tremadoc to the mid-Darriwilian could be explained by declining upwelling activity and a lesser reworking of old P-rich sediment, initially coming from the Tremadocian phosphorite. The late Darriwilian–Sandbian interval of elevated P in the basinal sections might have resulted from the revival of upwelling. The time of this upwelling matches between two periods of faster water movements, the Floian–lower Darriwilian southerly current and the westerly late Sandbian current (Kiipli et al. 2008, 2009). Some indicators, such as the distribution of P-rich rock in Poland (Podhalańska 2002; Trela 2005), point to a possible southerly direction of upwelling. However, the Kurtuvenai-161 and Aizpute-41 sections from the most southern areas do not reveal a very strong P rise (Fig. 4). At the same time, the westernmost När section exhibits much higher values, pointing to the westerly direction of upwelling. Therefore, the areal distribution of P needs more investigation to give evidences of the course of upwelling. Decline in P content to the minimum in Katian and Hirnantian time could be explained by closure of the Tornquist Sea (Cocks & Torsvik 2005) which terminated the upwelling circulation.

Elevated input of nutrients to the epeiric seas could have resulted in increased bioproduction, accompanied by increase in organic material burial. Three organic material accumulation intervals can be followed in the Middle and Upper Ordovician succession of Baltoscandia. The black shale beds of the Mossen and Fjäcka formations, which were distributed in the deeper basin, and the nearly corresponding Rakvere, Nabala and Vormsi stages from the shallow shelf reveal small increase in P contents. The late Darriwilian–Sandbian interval of elevated P contents of deep shelf sections (Figs 3, 4) is approximately contemporaneous with the main kukersite-bearing interval in the shallow shelf. As algae need P for the build-up of their organism, and P is recorded in the deep shelf sediment of the same time, a link is assumed to exist between kukersite and P. Kukersite deposits have a very low P content (<0.1%; Pets et al. 1985). Probably, the upwelling rose P to the shallow shelf. In the photic zone P was consumed by the photosynthetic organism *G. prisca*, recycled several times, but did not concentrate in sediments. The small P content of kukersite points to the preferential regeneration of P in the process of organic matter degradation (see, e.g., Ruttenberg 2007). When calculating the C : P ratio of kukersite using data by Pets et al. (1985), and comparing the 1000 : 1 C : P ratio of kukersite with the Redfield ratio 106 : 1 (characteristic of atomic ratios of C and P of marine photosynthetic plankton), the faster removal of P is obvious. Probably, the labile organic matter and P remineralized and moved away, and the preserved part, the cell walls of *G. prisca* (Derenne et al. 1990), contained initially fewer P. This explanation reveals a reason for the low content of P in kukersite. The relationship of kukersite seams to the hardground facies suggests that thick deposits of oil shale formed in the shallow marine area. With the help of storms organic matter was transported from tidal zone algal mats into near-coastal areas *post mortem* (Männil et al. 1986; Kõrts 1992; Bauert 1993). Increased nutrient influx to the shelf might stimulate the growth of algal mats in the near-coastal zone. Kukersite accumulation on the shallow shelf was accompanied by a low sedimentary rate of carbonate in offshore facies. Still, there remain questions about the absence of the contemporaneous black shale facies on the deeper shelf and low P content in kukersite-bearing sediments.

We tested the hypothesis that increased input of marine P to the epeiric sea might be correlated with global variations in oceanic bioproductivity. Positive $\delta^{13}C$ excursions in the Ordovician sections are interpreted as times of enhanced primary bioproductivity, or/and enhanced organic matter burial. The $\delta^{13}C$ curves are considered globally synchronous (Saltzman 2005; Kaljo et al. 2007; Ainsaar et al. 2010). For example, the end-Ordovician global climatic cooling would have led to the ventilation of deep ocean and rise in P in seawater, increase in bioproductivity in the photic zone and prominent $\delta^{13}C$ positive excursion in the Hirnantian (Brenchley et al. 1994; Saltzman 2005; Kaljo et al. 2007). The phosphate content in two southern Estonian sections is compared with $\delta^{13}C$ curves (Kaljo et al. 2007; Ainsaar et al. 2010) in Fig. 5. According to this comparison, the Darriwilian–Sandbian interval of elevated P contents does not have positive correlation with $\delta^{13}C$ in bulk carbonate rocks. On the contrary, the interval with the most negative $\delta^{13}C$ values in the Kukruse Stage corresponds to the elevated P content and the highest Hirnantian $\delta^{13}C$ excursion to the minimum P content. Baltic carbonate rocks from the Katian–Hirnantian interval, corresponding to the high-bioproductivity P-limited

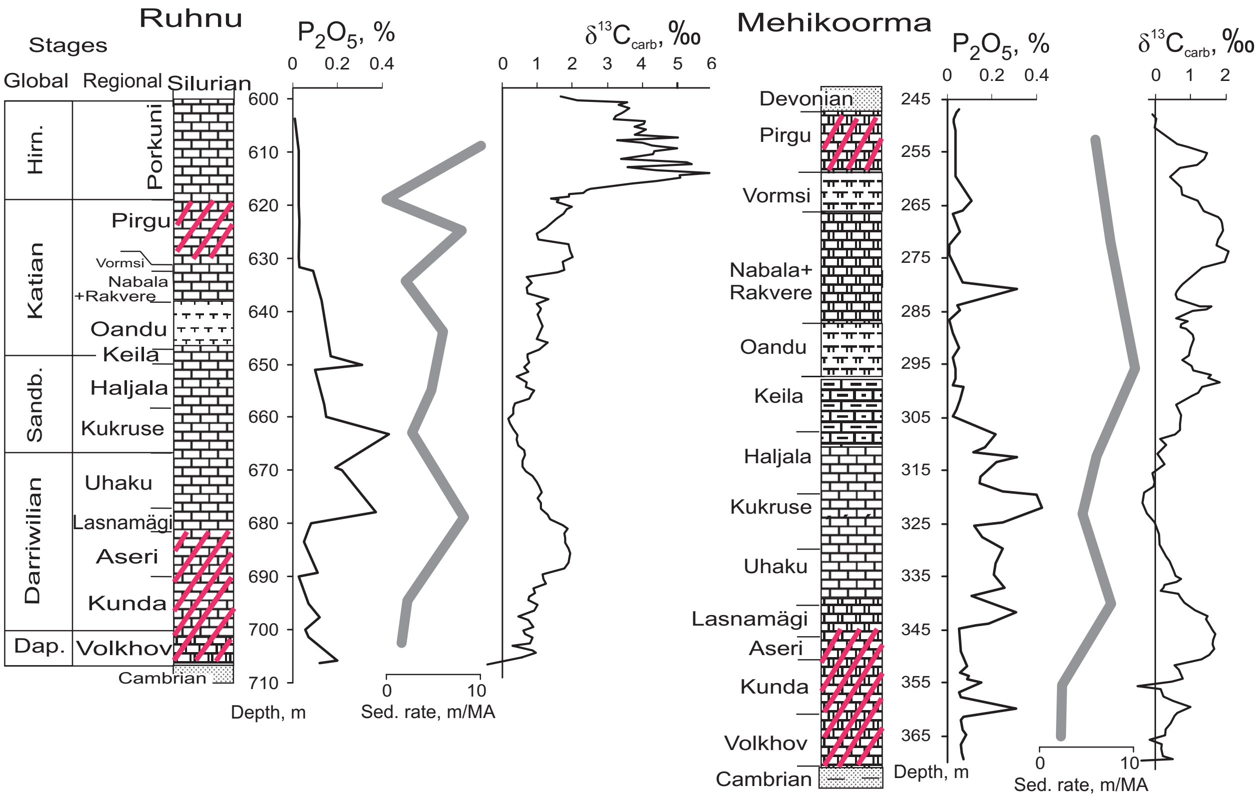

Fig. 5. Comparison of the P_2O_5 content, stable carbon isotope composition $\delta^{13}C$ (Kaljo et al. 2007; Ainsaar et al. 2010) and sedimentation rate (grey line; calculated as the ratio of unit thickness to time duration; timescale by Webby et al. 2004) in the Ruhnu and Mehikoorma core sections. Hirn., Hirnantian; Sandb., Sandbian; Dap., Dapingian. For lithology see Fig. 3.

ocean by Saltzman (2005), are extremely poor in P. Possibly the regional seawater circulation system led to P input and fixation in the sediments, independent of the global oceanic trends in carbon isotopic composition and bioproductivity changes.

Besides the P input, its content in the rock may be influenced by the sedimentation rate. The 'diluting' effect of carbonate sedimentation plays a role in the case of terrestrial influx of P. If upwelling is the P source, then the sedimentation rate of both siliciclastic matter and carbonate may cause depletion or enrichment. Indeed, the sedimentation rate in the Baltoscandian palaeobasin was relatively low in the Early and Middle Ordovician (Nestor & Einasto 1997), coinciding with higher P concentrations in the Floian–lower Darriwilian succession. The sedimentation rates were very low also in early Sandbian time, in the interval of elevated P content in this deeper basinal area (Fig. 5). Phosphorus was concentrated on the numerous impregnated discontinuity surfaces in the Middle and early Late Ordovician sections (Põlma 1982; Nordlund 1989; Saadre 1993), also suggesting connection between the slow discontinuous sedimentation and elevated P concentration.

In the late Ordovician the carbonate sedimentation rate increased due to the drift of Baltica towards tropical latitudes, and the P content of the sediment decreased. The ratio of P to terrigenous matter shows low values as well, pointing to the low P content of seawater.

CONCLUSIONS

Phosphorus distribution has spatial and temporal variations in the Baltoscandian Middle and Upper Ordovician carbonate section. In the Estonian Shelf P_2O_5 contents are the highest in the lower part of the carbonate succession, in the Floian–lower Darriwilian interval, decreasing towards younger rock. Two intervals of elevated P contents occur in the deeper basinal sections. The first is a diminishing succession of the Tremadocian high P, and the second is a moderate increase in the upper Darriwilian–Sandbian interval. The Sandbian kukersite accumulation on the Estonian Shelf roughly corresponds to the interval of elevated P in the deep shelf.

Multiple factors determined the P distribution in the studied sediments. Regional processes influencing the P distribution include seawater circulation, e.g., P influx by coastal upwellings, and the sedimentation rate. Upwelling became less favourable towards the end-Ordovician due to changes in the palaeogeographic position of the Baltica Craton. At the same time the sedimentation rate of carbonate increased, causing the decline in the P content in core sections. There is no positive correlation between the changes in global oceanic bioproductivity shown by $\delta^{13}C$ variation and P fixation in carbonate sediments, which points to the leading role of regional seawater circulation in the P distribution in Baltoscandia.

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Fosfori jaotus Baltoskandia paleobasseini Kesk- ja Ülem-Ordoviitsiumi kivimites

Enli Kiipli, Tarmo Kiipli, Toivo Kallaste ja Leho Ainsaar

P_2O_5 sisaldust mõõdeti mitmes Balti basseini sügava šelfi ja üleminekutsooni puursüdamikus. Madala ja sügava šelfi sisalduste jaotuses on erinevusi. Madalal šelfil langeb keskmine fosforisisaldus 0,7%-st Volhovi ja Kunda lademes alla 0,1% Haljala lademes ning kõrgemal. Üleminekutsooni ja sügava šelfi läbilõigetes järgneb Alam-Ordoviitsiumi suurte fosforisisalduste intervallile langus ja uus väiksem tõus Lasnamäe lademest Haljala lademeni. P_2O_5 kontsent-ratsioon kasvab keskmiselt 0,5, harvem 1 protsendini. Lasnamäe-Haljala intervalli sisse jääb kukersiidi maksimaalse esinemise tase Kukruse lademes. Fosfori jaotust Ordoviitsiumi karbonaatses basseinis on kontrollinud nii globaalsed okeanograafilised protsessid (kliima, veetase) kui ka regionaalsed arengud (veetsirkulatsioon, settekiirused).