Proc. Estonian Acad. Sci. Geol., 2006, **55**, 1, 67–87
https://doi.org/10.3176/geol.2006.1.04

Dolomitization and sedimentary cyclicity of the Ordovician, Silurian, and Devonian rocks in South Estonia

Aada Teedumäe, Alla Shogenova, and Toivo Kallaste

Institute of Geology at Tallinn University of Technology, Estonia pst. 7, 10143 Tallinn, Estonia; teedumae@gi.ee

Received 1 August 2005, in revised form 25 October 2005

Abstract. The distribution and composition of dolomitized rocks and stoichiometry of dolomite in southern Estonia in the Ordovician, Silurian, and Devonian were studied on the background of the facies, sedimentary cyclicity (nine shallowing-up cycles), and evolution of the palaeobasins. The composition of rocks and lattice parameters of dolomite were investigated using the X-ray diffraction, X-ray fluorescence, titration and gravimetric analyses, and porosity measurements. The formation of dolostones is directly determined by the cyclic evolution of palaeobasins. Dolomitized rocks belong to the shallow-water inner shelf or tidal/lagoonal facies belt of regressive phases of sedimentary cycles. Sediments of the deep shelf/transitional environment and transgressive phases are not dolomitized. The most stoichiometric is secondary replacive dolomite of Silurian and upper Ordovician dolostones, formed during the early diagenesis of normal-marine (saline) shallow-shelf calcitic sediments. The content of insoluble residue does not affect the stoichiometry. The changes in lattice parameters are induced by the Ca/Mg ratio in the dolomite lattice. The dolomite of the dolostones contacting limestone or containing calcite has an expanded lattice. The primary (syngenetic) dolostone of the lagoonal or tidal flat belt has also an expanded lattice. No dolomitizing effect of the waters of the Devonian palaeobasin on the underlying rocks was revealed. The whole data set of the studied dolostones is consistent with the marine water environment in the palaeobasin at the corresponding time and shows no sign of the inflow of external fluids. It suggests that the microbial model of dolomite formation may characterize the Ordovician, Silurian, and Devonian in southern Estonia. The occurrence of dolostones between undolomitized rocks limits the time of dolomitization to the early diagenetic stage.

Key words: dolomitization, sedimentary cyclicity, diagenesis, dolomite, XRD, porosity, Ordovician, Silurian, Devonian, Estonia.

INTRODUCTION

Studies on the lithology, chemical composition, and petrophysical properties of basin-related dolomitized rocks in Estonia support the idea of their diagenetic origin with differences in details (Vishnyakov 1956; Jürgenson 1970; Kiipli 1983;

Bityukova et al. 1996, 1998; Shogenova & Puura 1998; Shogenova 1999; Teedumäe et al. 1999, 2001, 2003, 2004). Various sources of magnesium have been suggested for the Silurian secondary dolostones, such as Devonian sediments (Jürgenson 1970), hypersaline lagoonal waters of the Devonian basin (Kiipli 1983), and contemporaneous Silurian seawater (Teedumäe et al. 1999, 2001, 2003, 2004).

Investigations of the facies, sedimentary cyclicity, and evolution of the Baltic Palaeobasin (Kleesment 1997; Nestor & Einasto 1997; Kaljo et al. 1998, 2001, 2004) provide a favourable basis for the estimation of the palaeoenvironmental factors of dolomitization. Previous detailed studies (Teedumäe et al. 1999, 2001, 2003, 2004) on intensive spatial pervasive dolomitization of the Silurian shallow shelf sediments support the idea of their primarily normal-saline calcareous origin and early diagenetic dolomitization, associated with the regressive phases of the development of the Baltic Palaeobasin. Bacterial sulphate reduction can be treated as the basic factor for dolomitization.

The present research constitutes a sequel to the above-mentioned papers by Teedumäe and coauthors. The main objectives are (a) to study the variability of the composition of dolomitized rocks and stoichiometry of the dolomite of deeper (transitional) facies through the Ordovician, Silurian, and Devonian, (b) to reveal the nexus of the studied parameters (d_{104} spacing, CaO, MgO, insoluble residue, Fe_2O_3, MnO, porosity) with the facies and sedimentary cyclicity, (c) to compare the evolution of the process of dolomitization in shallow shelf and transitional zones. A. Teedumäe studied the composition of dolomitized rocks and aspects of dolomitization. A. Shogenova composed the sections of the drill cores under consideration, selected samples of dolomitized rocks from the database compiled by her during the last decade, and studied the porosity. T. Kallaste performed the X-ray diffractometry (XRD). X-ray fluorescence (XRF) measurements were carried out in the All-Russian Geological Institute (St. Petersburg). Titration and gravimetric chemical analyses were made by T. Linkova. Porosity was measured by A. Jõeleht and V. Shogenov.

MATERIAL AND METHODS

Ninety-two samples of dolostone and dolomitic marlstone containing MgO > 10% (classified after Vingisaar et al. 1965) from seven drill cores of southern Estonia (Ruhnu (500), Häädemeeste (172), Taagepera, Tartu (453), Valga (10), Võru and Värska (6); Fig. 1B) were selected for combined study of the chemical composition, porosity and XRD (d_{104}) measurements. CaO, MgO were estimated by titration, the insoluble residue was measured by gravimetric chemical analyses (83 samples), and Fe and Mn were analysed by the XRF method (92 samples).

For XRF analysis 40–50 g of rock powder (50–70 μm) was dried at 105 °C temperature. Of that amount, 1.5 g was heated at 950–1000 °C to determine the loss on ignition (LOI). Then 0.6 g of dried rock powder was mixed with 7.2 g of tetra-borate of Li and meta-borate of Li in equal proportions. The mixture was put into the golden-platinum crucible and heated in a flame during 10 min (1000 °C).

Using the Claisse fluxer bis device, a glass disk 35 mm in diameter and 3 mm thick was prepared for XRF analysis performed on the spectrometer ARL9800 with 15 monochromators and a goniometer. Measurements were made in vacuum with X-ray tube voltage of 30 kV and DC of 50 mA. The exposition time was 60 s. The spectrometer was calibrated using glass disks with prepared standard samples. After the content of the glass disk was determined, the rock sample content was recalculated.

The element contents were calculated using multivariate regression of Lukas–Tus:

$$C_i = a_{0i} + I_i(a_i + \sum a_{ji} I_j), \tag{1}$$

where I_i, I_j are intensities of the determining and disturbing elements, C_i is the component content, a_{0i}, a_i, a_{ji} are correction (adjustment) coefficients.

XRD measurements were carried out on a diffractometer HZG4, using Fe-filtered Co radiation. The rock powder was mixed in a mortar with Si in the ratio 8 : 2, some drops of ethanol were added, and the mixture was evenly spread on a glass slide. The measured angular range 32–38 °2θ reveals the 104 reflection of dolomite and calcite and 111 reflection of Si. The positions of reflections were calculated as weighted average. The instrumental shift was corrected according to the Si reflection (3.1355). The precision of d_{104} measurement is ±0.0005 Å.

The molar concentration of $CaCO_3$ (m_{Ca}) in dolomite was calculated from d_{104} by the formula

$$m_{\mathrm{Ca}} = \frac{(d_{104} - 2.8840)}{0.003} + 50 \tag{2}$$

using linear dependence between these parameters (Lippmann 1973). Formula (2) is valid if the contents of Fe and Mn in dolomite lattice are low, which for the present case are close to the above-mentioned detection limit of the method.

The fix-point of ideal stoichiometric dolomite ($d_{104} = 2.8840$ Å) was calculated (Teedumäe et al. 1999) on the basis of the composition of two standards, Es-4 (Estonia) and SI-1 (former USSR). No siderite or rhodochrosite was revealed. In some samples traces of calcite were identified.

Measurements of rock porosity were made at room temperature and pressure in laboratories of the Geological Survey of Finland on samples with 50–200 cm^3 size (Jõeleht & Kukkonen 2002) and in the Petrophysical laboratory of the Research Institute of Earth's Crust of St. Petersburg University on cubes of 24 mm side (Priyatkin & Polyakov 1983; Shogenova & Puura 1998). Samples were dried at a temperature of 100–110 °C and the weight of dry samples (P_{d}) was determined. Next, samples were saturated with ordinary water for 7 days. The samples were then weighed in air (P_{w}) and water (P_{ww}). From the obtained measurements effective porosity (Φ) was calculated as follows:

$$\Phi = (P_{\mathrm{w}} - P_{\mathrm{d}} / (P_{\mathrm{w}} - P_{\mathrm{ww}}). \tag{3}$$

GEOLOGICAL SETTING

During the post-Tremadocian, from the Hunneberg time of the early **Ordovician** to the end of the **Silurian**, Estonia was a part of the northern flank of a shallow cratonic sea (Fig. 1) where carbonate and fine siliclastic-calcareous sediments accumulated with conformable bedding, dipping southwestwards. The part of this basin in the Baltic area is referred to as the Baltic Palaeobasin (Nestor & Einasto 1997). At the earlier stages of development this basin extended from present Norway to the Volga area and from the Fennoscandian Shield to the

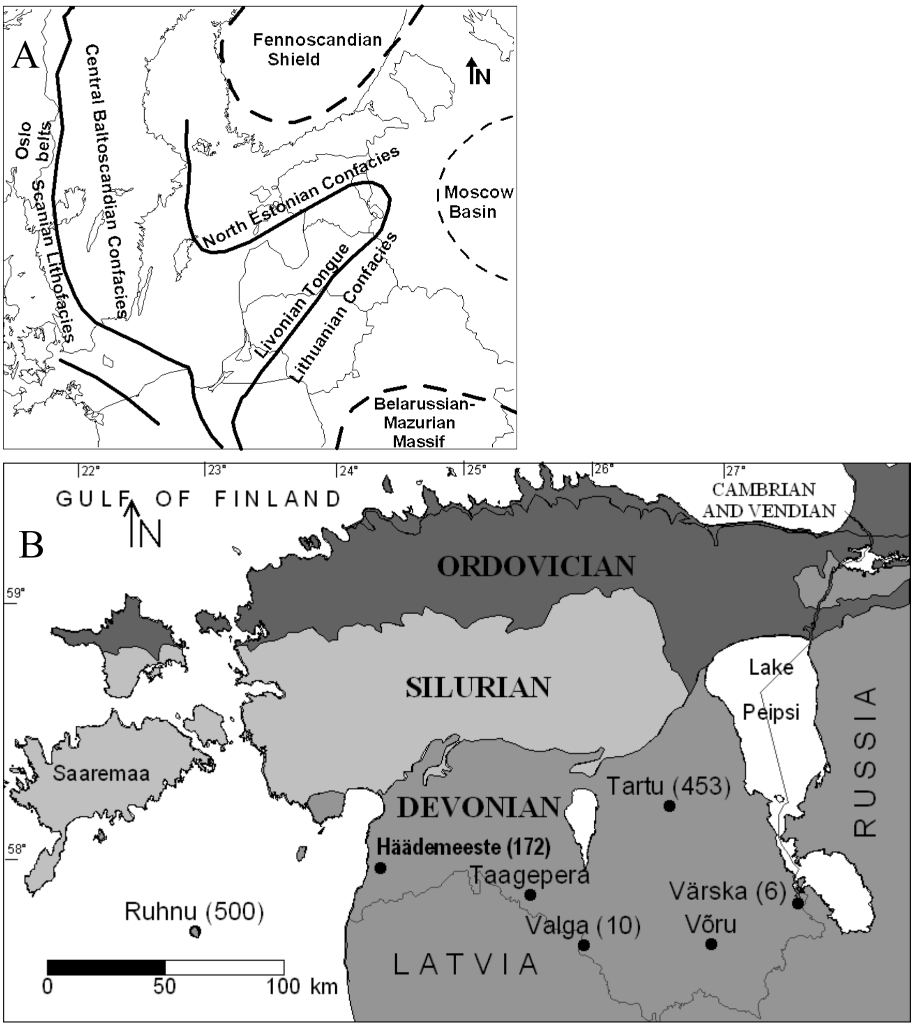

Fig. 1. (A) The main structural elements of the Baltoscandian Ordovician and Silurian basin (after Jaanusson 1995; Nestor & Einasto 1997). (B) Geological sketch map of Estonia (Kala 1995) with the location of the studied boreholes.

Precambrian Belarussian–Mazurian massif (Fig. 1A). During the final stages of development, the basin was restricted to the Baltic Syneclise in the East Baltic area and North Poland. Present-day Estonia is situated within the shelf facies belt and transitional zone (Livonian Tongue). Determined by the basin development, the limits of the main facies belts gradually shifted southwestwards up to pinching out in the southeasternmost sections (Fig. 2).

The Livonian Tongue of the central Baltoscandian Confacies Belt (Fig. 1A), formed by the marine terrigenous(siliciclastic)-carbonate sediments, extended far to the east. These sediments occur between the hemipelagic organic-rich muds on the continental margin and carbonate sediments on the shallow shelf plateau – North Estonian Confacies Belt. Against the background of the ocean/continent palaeogeography they can be treated as transitional facies (Einasto 1995).

Drastic climatic changes took place during the Ordovician and Silurian. The continent of Baltica drifted northwards from the temperate climatic zone of the high latitudes in the Southern Hemisphere and reached the subtropical-tropical zone in the Late Ordovician (Oandu Stage) (Jaanusson 1973; Harris & Fettes 1988; Webby & Laurie 1992; Nielsen 2004; Kaljo et al. 2004). It amalgamated to the Avalonian continent in the mid-Caradoc (Keila Stage) and Laurentia in the early Silurian. The widely documented Hirnantian glacial sea-level drop in the Porkuni Stage (Harris et al. 2004) marked the end of the Ordovician. The tropical climate period was characterized by more intense cyclic accumulation of calcareous mud and the beginning of reef-formation in the basin. From the late Llandovery (Adavere Stage) onwards, the influx of clay material (weathering products of rising Caledonides) increased gradually.

Nestor & Einasto (1997) differentiated nine high-rank shallowing-up sedimentary cycles in the development of the Baltic post-Tremadocian Ordovician and Silurian basin (Fig. 2). The sedimentary cyclicity reflects the cumulative impact of the sedimentation rate, geotectonic movements, and eustatic oscillation: transgression at the beginning and regression at the end of the cycles. The cycles are separated from each other by subregional sedimentation breaks of variable duration, increasing in the onshore direction.

In the Early and Middle Ordovician the western part of the East European Platform as far as the Moscow Syneclise was slowly subsiding and covered by a shallow epicontinental sea with comparatively weak bathymetric differentiation.

During the eustatic high stands at the beginning of Billingen, Kunda, Haljala, Oandu (Ordovician), Juuru, Adavere, and Jaani (Silurian) times (Fig. 2), the Palaeobaltic basin turned into an epicontinental strait-sea, temporarily connected via the Moscow Syneclise (Fig. 1A) with the Uralian Ocean (Einasto 1995). This connection was closed during eustatic low stands at the end of Volkhov, Keila, Porkuni (Ordovician), and Raikküla (Silurian) times and it turned into a pericontinental gulf-like basin. An extensive sea-level drop in Volkhov time caused the retreat of the sea from the entire open shelf (upper ramp) area and an erosional surface with deep corroded pockets and furrows developed on the top of the Volkhov Stage on a spacious area (Nestor & Einasto 1997). The magnitude of the sea-level drop at the Volkhov–Kunda boundary was supposedly 30–40 m (Dronov 2004).

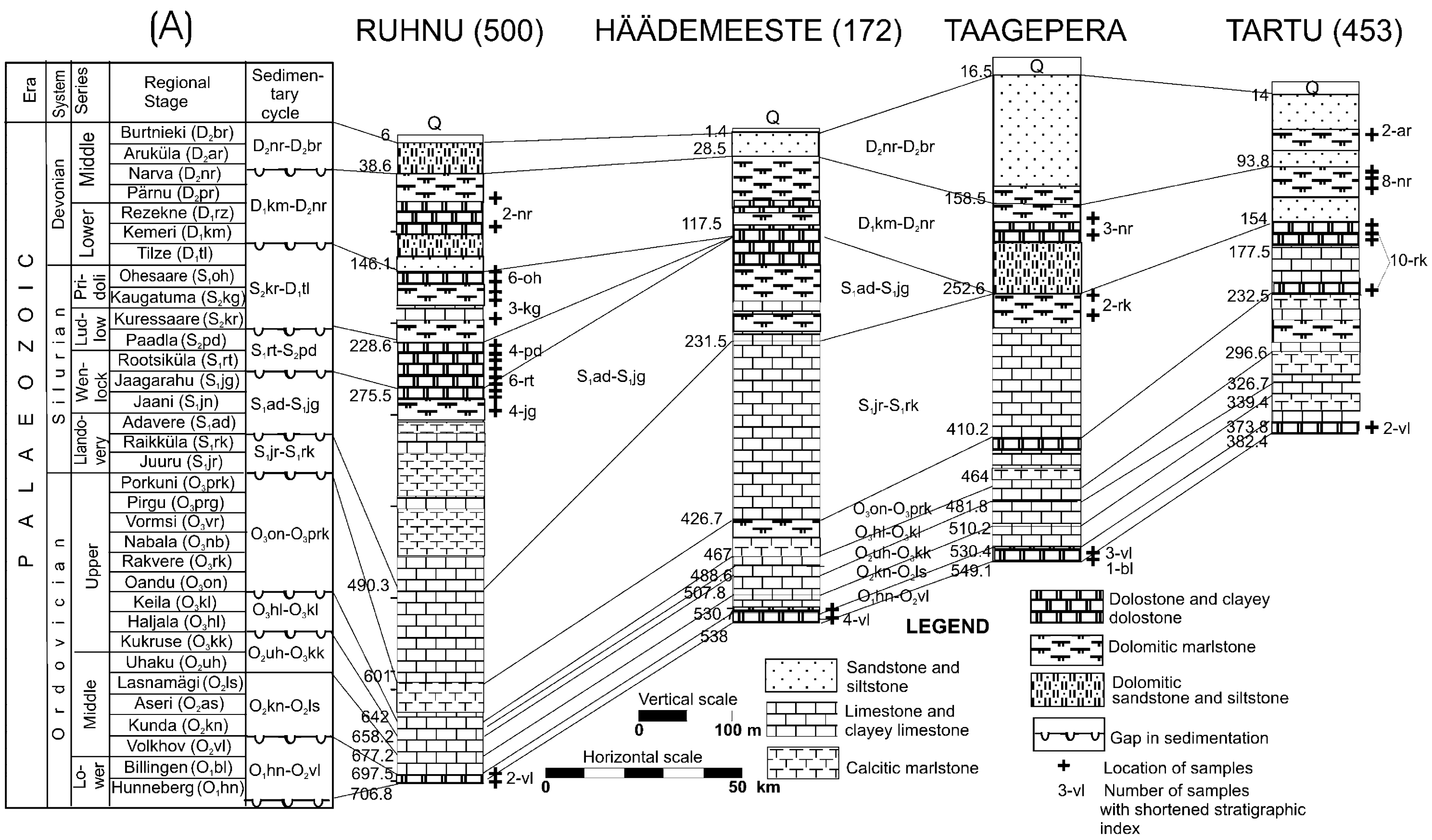

Fig. 2. Generalized lithological logs and sedimentary cycles of the studied sections. Limestone and clayey limestone – insoluble residue 0–25%, MgO 0–10%; dolomite and clayey dolomite – insoluble residue 0–25%, MgO > 10%; calcitic marlstone – insoluble residue 25–50%, MgO 0–10%; dolomitic marlstone – insoluble residue 25–50%, MgO > 10%; dolomitic sandstone and siltstone – terrigenous component >50%, MgO > 10% (Vingisaar et al. 1965, pp. 3–15).

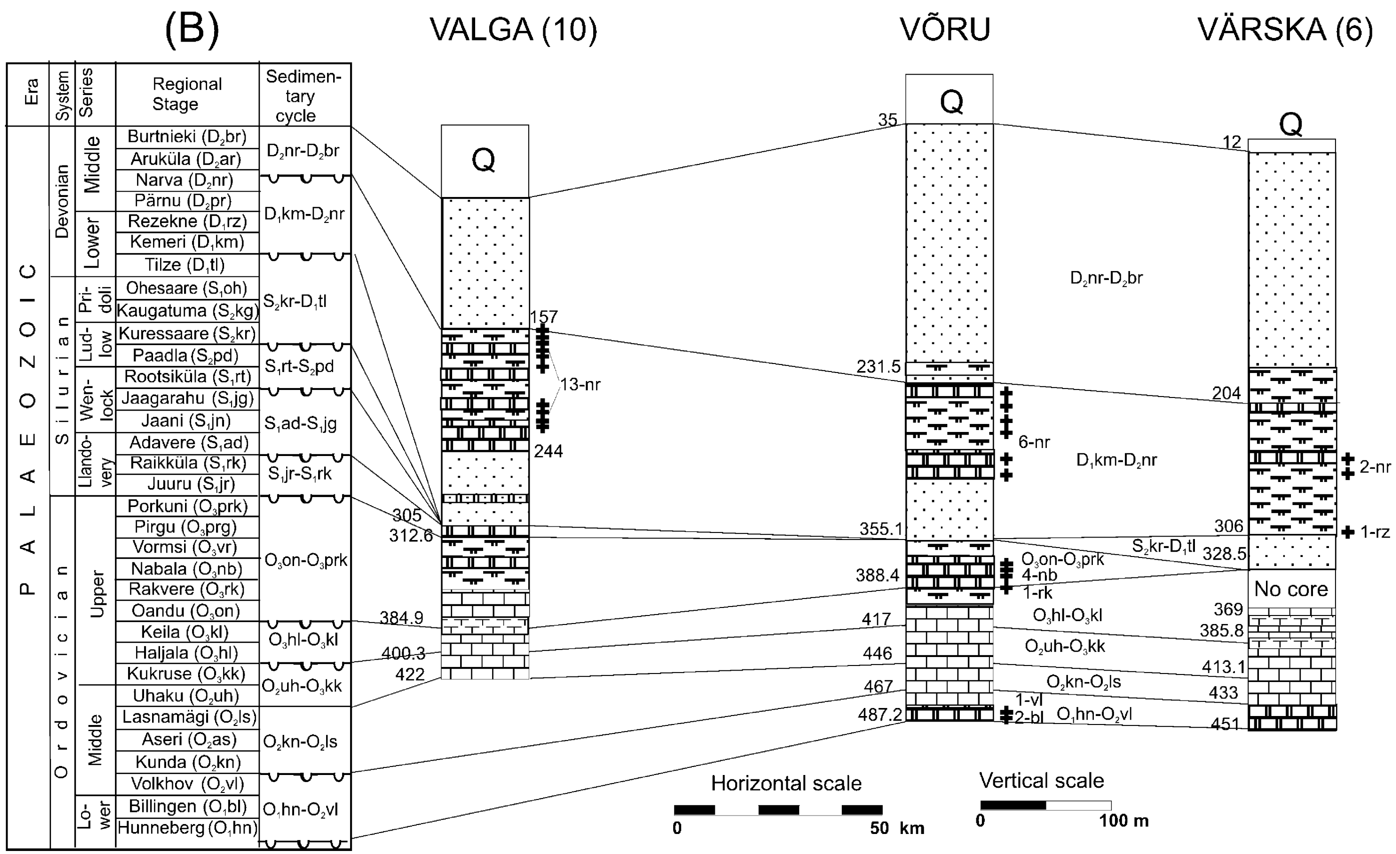

Fig. 2. *Continued.*

The extremely rapid middle Wenlock (Jaagarahu time) regression, likely induced by the progressing rise of the Caledonides, transformed the Baltic Palaeobasin into a gulf-like pericratonic sea (Nestor & Einasto 1997). At the end of the Wenlock the basin retreated southwestwards from the continental part of Estonia, and thus Ludlow and Přidoli sediments occur only on southern islands (e.g. Ruhnu).

Differences between the development of the shelf (North Estonian Confacies) and transitional area (Livonian Tongue, southern Estonia) are more noticeable during the regressive stages, when the bathymetric differentiation of the basin was the greatest. In the northern shallow shelf area (Teedumäe et al. 2004) some evidences of temporal dislocation of the regressive parts of cycles to the earlier time have been noticed, as the duration of sedimentation brakes is increasing in the onshore direction (Nestor & Einasto 1997). The same can be followed in the Võru and Valga drill core sections in the late Ordovician (Fig. 2B). A great number of stratigraphic hiatuses of the shelf area are filled in the transitional area, but there occur discontinuity surfaces (hardground), sometimes impregnated, marking gaps in sedimentation and sedimentary cyclicity (Fig. 2A,B**)**.

Carbon isotope studies (Kaljo et al. 1997, 1998, 2001; Kaljo & Martma 2000; Ainsaar et al. 2004) of the Ordovician and Silurian carbonate rocks show a good correlation of positive $\delta^{13}C$ excursions with lows of the global sea-level curve and support the primary role of climatic or climatically triggered oceanic processes in the general pattern of carbon isotope changes. However, positive $\delta^{13}C$ excursions have no obvious lithological preference, correlate with depositional facies and through them with the sedimentary cyclicity. The positive $\delta^{13}C$ excursions in carbonate sections and increased micritic limestone accumulation give evidence of a primary bioproductivity rise. The micritic limestone does not contain organic carbon. Only fine-dispersed pyrite evidences the primary origin of organic carbon, remineralized by early diagenetic bacterial sulphate reduction. Chertification and barite occurrences also hint at an increase in the primary bioproductivity (Kiipli et al. 2004).

At the beginning of the **Devonian** the Baltic depression became completely filled with sediments (Nestor & Einasto 1997). Only a remnant lagoon-like body of water was preserved in its southeastern part. The regression, which had started in the Silurian and continued with short interruptions also in the lower Devonian (Ķemeri time), marks the geocratic period separating the Caledonian and Herzynian tectonic stages (Nestor & Einasto 1997). During this period the older sediments of the Baltic Palaeobasin were subject to denudation. The sediments of the lower Devonian (Tilže and Ķemeri stages) occur in a restricted area of southeastern Estonia – Võru, Valga, and Värska boreholes (Fig. 2B).

In the Devonian Estonia belonged to the northwestern part of the Main Devonian Field of the East European Platform where epicontinental shallow sea sediments accumulated (Kleesment 1997). The end of the lower Devonian (Rezekne time) marked the beginning of a new westerly transgression (Kleesment 1997). The northern part of this basin extended to the Estonian territory where mainly near-shore sandy sediments accumulated. The gradual deepening of the sea resulted in the accumulation of carbonate sediments in southeastern Estonia. At the beginning of the middle Devonian (Pärnu time and the beginning of Narva time) the basin retreated (Kleesment 1997). The succeeding transgression reached the maximum in the middle of Narva time when dolomitic muds of variable clay content accumulated. The occurrence of syneresis cracks suggests episodic subareal conditions (Kleesment 1997). The arid climate, comparatively scarce relicts of fauna, and presence of gypsum indicate increased salinity of the basin (Kuršs 1992, pp. 145–161). A more extensive influx of fresh water from the north at the end of Narva time temporarily changed the water salinity to normal seawater (Kleesment 1997). The character of sediments (alternation of silty clays with silty dolostones, the presence of sandy material) suggests sedimentation in the tidal belt (Hettinger 1995). The end of Narva time marks the beginning of the pulsatory regression period, which lasted up to the end of the middle Devonian and was represented by sandy-silty sediments. A new, late Devonian transgression started from the east (Moscow Syneclise). Carbonate sedimentation reached only a restricted area in southeastern Estonia (Kleesment 1997) and is not revealed in the studied drill cores.

RESULTS AND DISCUSSION

The sedimentation environment as well as diagenesis determine the crystallographic ordering of mineral dolomite. The composition of dolomite-bearing rocks – dolostones – is a direct source providing information about environmental conditions during the formation of dolomite.

The $\boldsymbol{d_{104}}$ **spacing** of dolomite in the studied rocks varies from 2.8860 to 2.9045 Å (Fig. 3). It is mainly between 2.886 and 2.891 Å, being the lowest (below 2.888 Å) for the upper Ordovician and Silurian dolostones. The d_{104} value of the dolomite of Devonian dolostone is higher, ranging mainly between 2.887 and 2.891 Å. The d_{104} values of dolomite exceeding 2.892 Å characterize the dolostones near the contact with limestones or containing calcite more than 0.5%. The increase in the d_{104} value of dolomite coexisting with calcite has been widely observed since Lippmann (1973). This suggests that the Ca-rich environment interrupts the crystallographic ordering of dolomite in contacting sediments. The increase in the d_{104} spacing of dolomite near the contact with limestone is typical of both secondary (Vingisaar & Utsal 1978; Kiipli 1983; Kallaste & Kiipli 1995; Teedumäe et al. 1999, 2001, 2003, 2004) and primary (synsedimentary) dolomite (Teedumäe et al. 2003) in all studied sections in Estonia. From above it follows that the changes in the d_{104} spacing of the studied dolomite are induced by the Ca/Mg ratio in the dolomite lattice.

The results of titration analyses also show a positive correlation between the d_{104} spacing of mineral dolomite and CaO/MgO ratio of rock (Fig. 3). The d_{104} spacing calculated by formula (1) for 50 mol% $CaCO_3$ is 2.884 Å, for 52 mol% – 2.890 Å, and for 54 mol% – 2.896 Å. The d_{104} spacing does not depend on the content of insoluble residue (Fig. 4). This fact indicates the early dolomitization of nonlithified sediment near the sediment–water interface, as stabilization of calcium-rich dolomite to a more ideal type will mostly take place by dissolution and reprecipitation. The different content of insoluble residue of lithified sediment (rock) in all probability could not have provided equal permeability for dolomitizing fluid (seawater) for solid-state diffusional processes, operating only at a submicron scale (Tucker & Wright 1994).

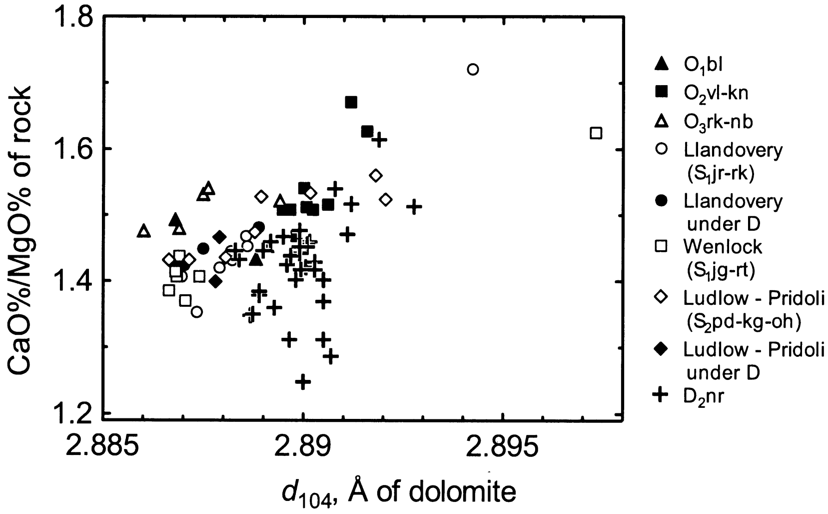

Fig. 3. d_{104} of mineral dolomite vs. CaO/MgO of rock.

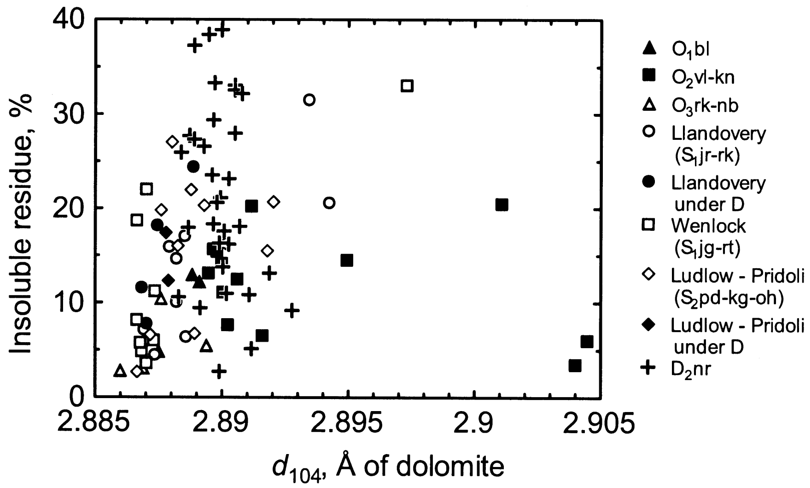

Fig. 4. d_{104} of mineral dolomite vs. insoluble residue of rock.

The content of **Fe compounds** shows a clear positive correlation with the content of insoluble residue (Fig. 5) for all types of studied dolostones of all ages. This indicates the primary sedimentary, prior to dolomitization, origin of Fe compounds and suggests the internal source (seawater) of Mg and early, prior to lithification, dolomitization. The dolostones of the alternation zones near tectonic disturbances, which have dolomitized after lithification, do not show this correlation (Bityukova et al. 1996).

The possible average concentration of Fe in the dolomite lattice (Fig. 5, trendline) is 0.84% Fe_2O_3 (0.98 mol% $FeCO_3$). It corresponds to an increase in the d_{104} value of about 0.0005 Å and is equal to the precision of the method (Teedumäe et al. 2004). Most of the above-mentioned amount of Fe, not connected with insoluble residue, in all probability occurs in the Fe compounds soluble in acid. The concentrations of Fe compounds are the highest in the dolostones of the Volkhov and Kunda stages near the impregnated (pyrite, goethite, hematite, etc.) discontinuity surface or dolostones containing glauconite. Four samples from these levels and one sample from the Narva Stage (Devonian), with $Fe_2O_3 > 5.0\%$, were excluded from Fig. 5 to avoid the impact of the anomalously high content of Fe_2O_3 on the trendline.

The **concentration of Mn** in dolostones of different ages is variable (Fig. 6), being in general 2000–3000 ppm in the Ordovician, 300–1000 ppm in the Silurian, and 1000–2000 ppm in the Devonian. Two dolostone samples of the Volkhov Stage and one sample of the Kunda Stage (Ruhnu drill core), collected near the impregnated discontinuity surface between them, show the highest contents of Mn – 5300, 7500, and 6500 ppm, respectively (Fig. 6). Manganese, which is highly

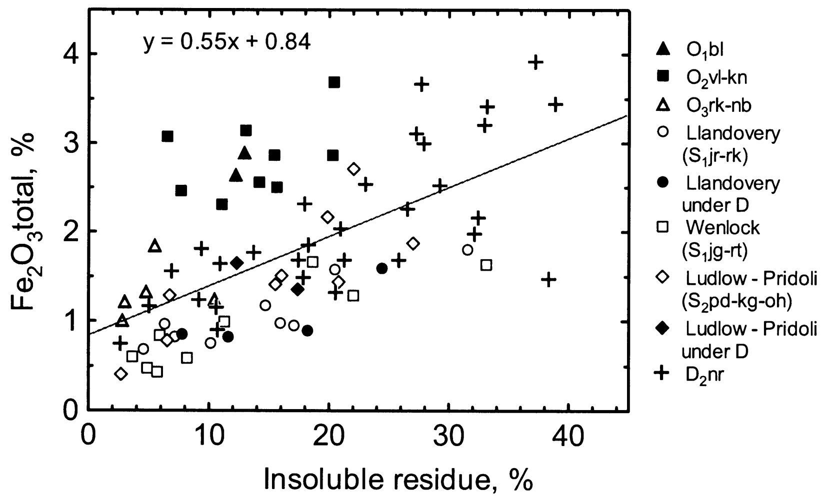

Fig. 5. Insoluble residue vs. Fe_2O_3total of rock.

soluble in an anoxic environment, is dissolved in the reducing sediment sections. It diffuses in pore water and forms peaks of Mn-oxide concentration as soon as oxygen is available, recording the depth of the redox boundary (Richter & Turekian 1993; Mangini et al. 2001). Within the studied area and sequence the highest concentrations of Mn are registered in the dolostone of the Volkhov and Kunda stages in the westernmost and deepest-water Ruhnu (500) and Häädemeeste (172) sections. In all probability they result from the sharp variation in oxygenating conditions during the extensive sea-level drop in the middle Ordovician Volkhov time as well as from the increased content of Mn in deeper marine environments. The limestone–dolostone interbedding in the section of the Volkhov Stage also indicates fluctuation in the availability of oxygen. Kiipli (1983) described anomalously high Mn concentrations in the dolostone contacting limestone. A marked increase in Mn content from shallow to deep marine lithofacies has been observed within the carbonates of the Middle Ordovician sequence in Eastern Tennessee (Shanmugam & Benedict 1983). Such an origin-induced difference in the Mn content between shallow- and deeper-water lithofacies has stayed unaffected by later diagenesis.

The concentration of Fe compounds is also high in Mn-rich samples (Fig. 7). Most likely this is caused by a higher primary supply of Mn and Fe, as iron–manganese minerals are characteristic of the glauconitic carbonates of this zone (Jürgenson 1988, pp. 74–79). A general positive correlation occurs between Mn and Fe compounds (Fig. 7), but no correlation is observed between the concentration of Mn with d_{104} and insoluble residue (Figs 6, 8). This indicates a possible concurrence of acid-soluble iron and manganese compounds.

The **porosity** of the studied dolomitized rocks varies in a wide range (1.3–24.5%), showing a general positive correlation with insoluble residue (Fig. 8). Such correlation is characteristic of all types of carbonate rocks in Estonia (Shogenova 1998; Shogenova & Puura 1997, 1998) and can be interpreted as primary porosity

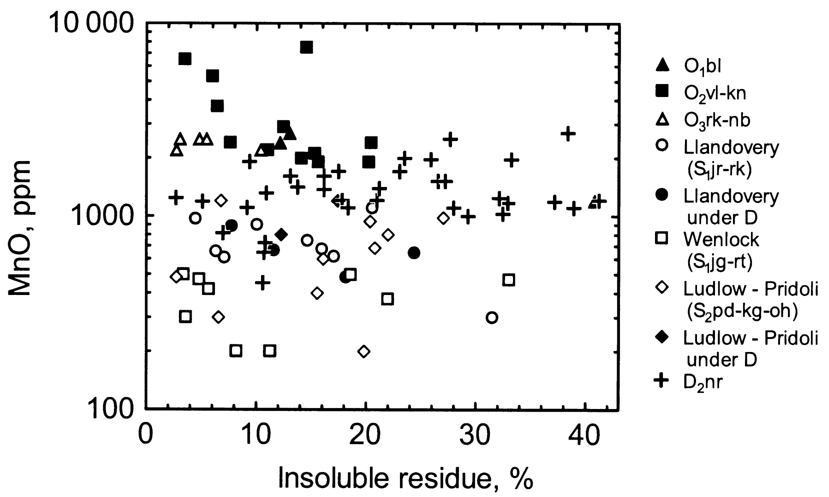

Fig. 6. Insoluble residue vs. MnO of rock.

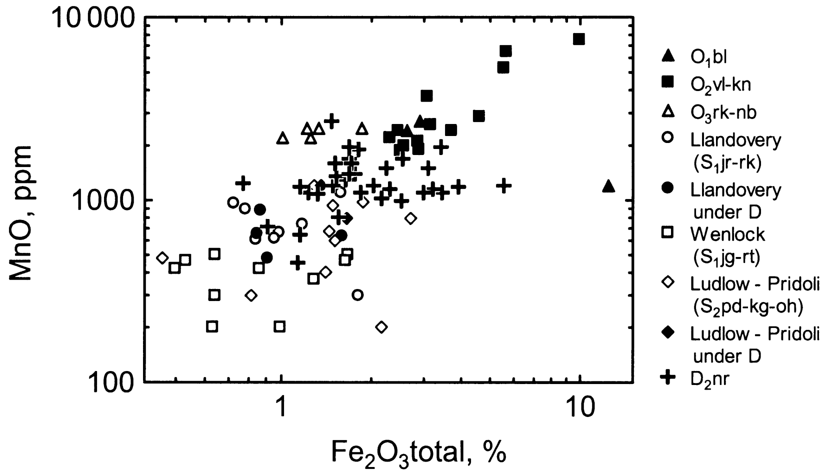

Fig. 7. Fe_2O_3total vs. MnO of rock.

(Schön 1996, p. 25), controlled by the content and composition of the insoluble residue of the sediment. The above-mentioned dependence supports the idea of early diagenetic dolomitization of the studied rocks. The higher porosity, which is out of the porosity/insoluble residue correlation, is interpreted as secondary porosity, associated with late diagenesis of lithified sediment – rock (Shogenova & Puura 1997, 1998; Shogenova 1998; Shogenova et al. 2003; Kleesment & Shogenova 2005).

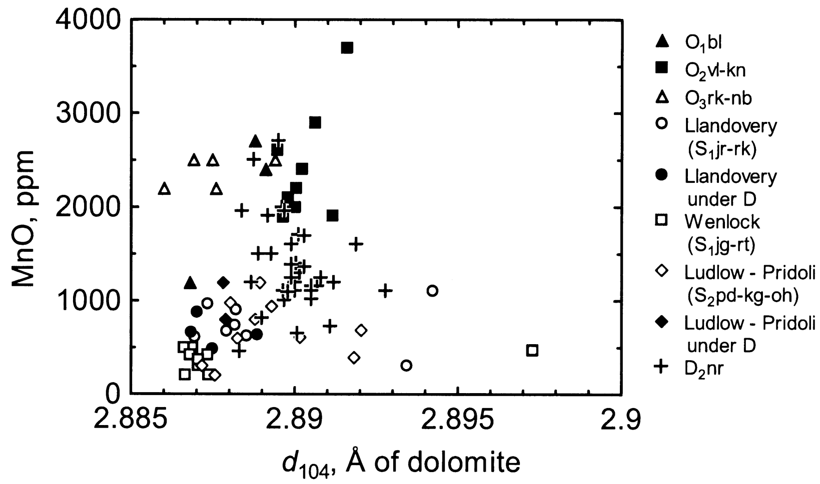

Fig. 8. d_{104} of mineral dolomite vs. MnO of rock.

Dolomitic rocks of different ages vary in porosity (Fig. 9). Lower and middle Ordovician dolostones (O_1bl, O_2vl-kn) have the lowest porosity in the range of 1.3–10% for the insoluble residue of 3.5–20.2%. Upper Ordovician dolostones have also low porosity of about 1.5–4.4% for the insoluble residue of 5.3–10.4%. These rocks are rather pure early diagenetic dolostones of primary porosity.

The porosity of Silurian rocks from the Llandovery varies in the range of 2.9–13.4% for the insoluble residue of 4.5–31.5%. It is higher on average but may also be lower than the porosity of Ordovician rocks for the given insoluble residue content. The porosity of Silurian rocks from the Wenlock, Ludlow, and Přidoli is 5–21% for the insoluble residue of 2.7–33%. It is higher than the porosity of Llandovery rocks and may sometimes (Ruhnu drill core) be of secondary origin.

Devonian rocks have the widest range of porosity (2.5–24.5%) and insoluble residue (2.7–41.2%). Their porosity has similar to Silurian rocks scatter (Fig. 9) and in some cases has evidently been developed during different stages of diagenesis.

Clear dependence of porosity on the content of insoluble residue in the studied rocks indicates their early diagenetic origin, predating lithification. The exceptional samples (Fig. 8) may display, besides specific lithological characteristics (crystal or grain size, etc.), the secondary character of porosity, formed during the late diagenetic alterations of already lithified rock. This concerns part of the Wenlock, Ludlow, and Přidoli samples of the Ruhnu drill core, and the Devonian samples. Leaching, karstification, and other processes that took place in the pre-Devonian continental period or during the Devonian might have altered the corresponding rocks in some places, possibly under subareal or near-surface conditions.

Lippmann (1973) recognized the fact that dolomite could not be a normal product of marine carbonate precipitation because of kinetic obstacles. The

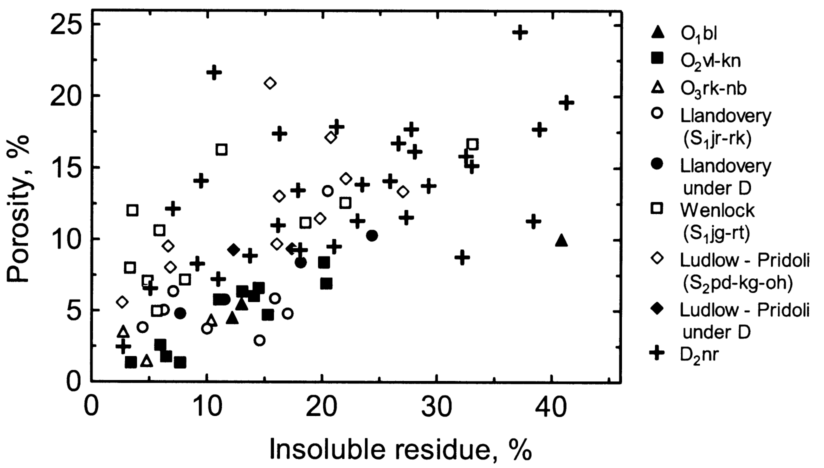

Fig. 9. Insoluble residue vs. porosity of rock.

microbial dolomite model invoked by a number of researchers (Garrison et al. 1984; Baker & Burns 1985; Slaughter & Hill 1991; Bernasconi 1994; Vasconcelos & McKenzie 1997; Wright 1997, 2000; Brehm et al. 2002; Rao et al. 2003) and demonstrated by the results of laboratory experiments (Warthman et al. 2000) provides an opportunity to view the geological history of dolomite formation from a new perspective. The main component of the model is the presence of sulphate-reducing bacteria. The majority of extensively dolomitized successions on ancient carbonate platforms contain evidence of fossil bacteria, suggesting that the "seed" for ancient dolomite in shallow-water carbonate successions may be microbial dolomite (Burns et al. 2000). In particular, this explains the cyclicity in the occurrence of dolostones (Teedumäe et al. 2003) in the geological sequence as well as their spatial distribution through the Palaeozoic in Estonia. The Ordovician, Silurian, and Devonian carbonate rocks of Estonia show a rather unique preservation of primary sedimentary and biogenic structures. Since their formation the rocks have been covered with a comparatively thin sedimentary cover (Fig. 2) and have not been subject to deep burial diagenesis or other alternations, except for the restricted zones of tectonic disturbances.

The supposition that the waters of the Devonian basin had a dolomitizing effect on underlying sediments (Vishnyakov 1956; Jürgenson 1970; Kiipli 1983) was not proved by the present study. No differences were recorded in the stoichiometry or other parameters of contemporaneous Silurian dolomites regardless whether they contact Devonian sediments or not (Figs 3–8).

DISTRIBUTION OF DOLOSTONES

Burns et al. (2000) have identified large peaks in the distribution of dolostones during the last 570 Ma, namely in the Early Ordovician–Middle Silurian. A marked and overall negative correlation exists between the abundance of dolostones and the modelled atmospheric O_2 levels, implying that periods of low oxygen levels of seawater might be more favourable for massive dolomite formation. Depth is a determining criterion for dolomitization. In the Ordovician–Silurian dolomitization has been the most intensive in the shallow shelf area of the North Estonian Confacies Belt (Fig. 1), where in places dolomitized rocks form the entire section of the regressive phases (Haas 1991; Teedumäe et al. 2004). In general, the occurrence of dolomitized rocks in the transitional zone of the basin is limited to the Volkhov, Porkuni (Ordovician), Jaagarahu (Silurian), and Narva (Devonian) regional stages, the upper parts of sedimentary cycles (Fig. 2) in areas of shallow shelf environment.

Lower Ordovician dolostones have a continuous spatial distribution all over the northern shelf zone and the transitional area (Livonian Tongue). At this early stage of development the floor of the palaeobasin formed an evenly and weakly tilted ramp (Nestor & Einasto 1997). The evenness of the basin floor determined during the extensive regression in Volkhov time a uniform environment for dolomitization on the entire studied territory (Figs 1B, 2A,B) and a spacious area outside it. The dolostone layer reaches the northern limits of the Volkhov Stage in Estonia and western Russia (Fig. 1B). During the whole of the middle Ordovician tectonic and eustatic stillstand the Livonian Tongue was a typical transitional zone, where different muddy (carbonate–siliciclastic) sediments accumulated. No dolomitization is noticed (Fig. 2A,B), which suggests that dolomitization does not take place in a deeper environment. From the upper Ordovician onwards, the bathymetric profile of the basin differentiated and the facies zonation obtained a more distinct shape. However, the facies belts were transforming according to the fluctuation of sea level and oscillation of shoreline. During the regressive stages the floor of the basin was the most differentiated. In the peripheral parts of the Palaeobaltic Basin (Taagepera, Tartu, Valga, and Võru drill cores) upper Ordovician dolostones occur in the shallow shelf facies, where they are cross-cutting neighbouring facies and depositional sequences or interbedding with limestones (Fig. 2A,B).

Silurian sediments are found only in the westernmost Ruhnu and Häädemeeste sections (Fig. 2A). From Jaagarahu time upwards, gradual shallowing of the basin continued, interrupted by short deepening episodes (Nestor & Einasto 1997). It resulted in the extension of the shallow-water environment, favourable for dolomitization westwards.

In the northern marginal part of the Baltic Palaeobasin dolomitic rocks occur at the levels mentioned above, but have a much wider lateral and vertical distribution. Such a direct spatio-temporal relationship with the evolution of the sedimentary basin is a principal argument for early dolomitization (Teedumäe et al. 2003).

In the Devonian, dolostones are associated with terrigenous rocks and sedimentary breccia; they have fragmentary distribution and are present only in the northern sections (Ruhnu, Häädemeeste, Taagepera, and Tartu) of lagoonal and tidal facies. These dolomites, barren of fossils, can be treated as synsedimentary (lagoonal) or early diagenetic.

Secondary dolomitization has changed the primary composition of rocks, but the skeletal remains of fossils, and lithological and geological characteristics suggest the mainly normal-marine origin of sediments and early diagenetic or syndepositional dolomitization of all studied dolostones. Less often lagoonal primary dolomites were formed.

The selective character of secondary dolomitization can be related to the activity of sulphate-reducing bacteria. It has been proposed (Rao et al. 2003) that dolomite should be considered as a biomineral. The sedimentological data (interbedding of dolostone with limestone, marl, and siliclastic rocks) indicate that dolomite probably formed close to the water–sediment interface in the sulphate reduction zone of organic matter diagenesis. The localization/migration of this zone depends on a great number of factors: favourable environmental conditions, availability of organic matter, depth of water, etc. The absence of one of the factors excludes the process, and sections of concurrent cycles, situated nearby, may differ in terms of dolomitization.

CONCLUSIONS

The formation of dolostones in the studied transitional area was directly determined by the cyclic evolution of palaeobasins. Dolostones definitely belong to the shallow-water environment and, in general, with the exception of the marginal parts of the palaeobasin, represent the uppermost sediments of the regressive phases of sedimentary cycles. Sediments of deeper environments are not dolomitized.

The most stoichiometric is the secondary (replacive) dolomite of Silurian and upper Ordovician dolostones, formed during the most shallow-water periods. The primary (syngenetic) dolomite of Devonian lagoonal or tidal flat dolostones is less stoichiometric. The changes in the d_{104} spacing of dolomite are induced by the Ca/Mg ratio. The dolomite of dolostones containing calcite or contacting limestone has an expanded lattice. The content of insoluble residue does not affect the stoichiometry of dolomite. The porosity and content of iron compounds of the studied dolomitized rocks show a general positive dependence on insoluble residue, suggesting their early diagenetic origin. No dolomitizing effect of the Devonian palaeobasin waters on underlying rocks was revealed. The whole set of the studied components of dolostones is consistent with the marine water environment in the palaeobasin of the corresponding time. No signs of the inflow of external fluids were observed, which suggests that a microbial model for dolomite formation may be relevant for the origin of mineral dolomite in Ordovician, Silurian, and Devonian marine sediments in southern Estonia. The occurrence of dolostones between the undolomitized rocks limits the time span of dolomitization to early diagenesis.

ACKNOWLEDGEMENTS

The present study was financed by the governmental target-funding project No. 0332088s02. We are grateful to the referees L. Ainsaar and S. Šliaupa for constructive reviews. We thank A. Kleesment for consulting us on Devonian sedimentary cyclicity and geology, D. Kaljo and H. Nestor for reading the manuscript and useful comments, and H. Kukk for linguistic help.

REFERENCES

Ainsaar, L., Meidla, T. & Martma, T. 2004. The middle Caradoc facies and faunal turnover in the Late Ordovician Baltoscandian palaeobasin. *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, **210**, 119–133.

Baker, P. A. & Burns, S. J. 1985. The occurrence and formation of dolomite in organic-rich continental margin sediments. *Bull. Am. Ass. Petrol. Geol.*, **69**, 1917–1930.

Bernasconi, S. M. 1994. Geochemical and microbial controls on dolomite formation in anoxic environments: a case study from the Middle Triassic (Ticino, Switzerland). In *Contributions* *to Sedimentology*, Vol. 19 (Füchtbauer, H., Lisitzyn, A. P., Millimann, J. D. & Seibold, E., eds), pp. 1–81. Schweizerbart'sche Verlagsbuchhandlung (Nägele u. Obermiller), Stuttgart.

Bityukova, L., Shogenova, A., Puura, V., Saadre, T. & Suuroja, K. 1996. Geochemistry of major elements in Middle Ordovician carbonate rocks: comparative analysis of alternation zones, North Estonia. *Proc. Estonian Acad. Sci. Geol.*, **45**, 78–91.

Bityukova, L., Shogenova, A. & Götze, H.-J. 1998. Influence of chemical composition on petrophysical properties of Early-Palaeozoic rocks in Estonia. *Phys. Chem. Earth*, **23**, 309–316.

Brehm, U., Gasiewicz, A., Gerdes, G. & Krumbein, W. E. 2002. Biolaminoid facies in a peritidal sabkha: Permian platy dolomite of Northern Poland. *Int. J. Earth Sci.*, **91**, 260–271.

Burns, S. J., McKenzie, J. A. & Vasconcelos, C. 2000. Dolomite formation and biochemical cycles in the Phanerozoic. *Sedimentology*, **47**, 49–61.

Dronov, A. V. 2004. Magnitude of sea-level changes in the Ordovician of Baltoscandia. In *WOGOBOB-2004, 8th Meeting of the Working Group on the Ordovician Geology of Baltoscandia, May 13–18, 2004 Tallinn and Tartu, Estonia. Conference Materials* (Hints, O. & Ainsaar, L., eds), pp. 21–22, Tartu.

Einasto, R. 1995. "Liivi keele" omapärast Baltika arenguloos. In *Second World Meeting of Estonian Geologists, Tartu 3–6th October 1995. Geology of Livonia* (Meidla, T., Jõeleht, A., Kalm, V. & Kirs, J., eds), pp. 23–32, Tartu.

Garrison, R. E., Kastner, M. & Zenger, D. H. 1984. Dolomites of the Monterey Formation and other organic-rich units. *Soc. Econ. Paleont. Mineral., Pacific Section*, **41**.

Haas, J. 1991. A basic model for Lofer Cycles. In *Cycles and Events in Stratigraphy* (Einsele, G., Ricken, W. & Seilacher, A., eds), pp. 722–728. Springer-Verlag, Berlin.

Harris, A. L. & Fettes, D. J. (eds). 1988. The Cambrian–Appalachian Orogen. *Geol. Soc. Spec. Publ.*, 38.

Harris, M. T., Schultz, T., Sheehan, M., Ainsaar, L., Hints, L., Männik, P., Nõlvak, J. & Rubel, M. 2004. Upper Ordovician sequences of western Estonia. *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, **210**, 135–148.

Hettinger, R. D. 1995. Sedimentological descriptions and depositional interpretations, in sequence stratigraphic context, of two 300-meter cores from the Upper Cretaceous Straight Cliffs Formation, Kaiparowits Plateau, Kane County, Utah. *Bull.U.S. Geol. Surv.*, 2115-A, 1–32.

Jaanusson, V. 1973. Aspects of carbonate sedimentation in the Ordovician of Baltoscandia. *Lethaia*, **6**, 11–34.

Jaanusson, V. 1995. Confacies differentation and upper Middle Ordovician correlation in the Baltoscandian basin. *Proc. Estonian Acad. Sci. Geol.*, **44**, 73–86.

Jõeleht, A. & Kukkonen, I. T. 2002. Physical properties of Vendian to Devonian sedimentary rocks in Estonia. *GFF*, **124**, 65–72.

Jürgenson, E. 1970. Secondary alternation of rocks. In *Silur Éstonii* (Kaljo, D., ed.), pp. 96–100. Valgus, Tallinn (in Russian).

Jürgenson, E. 1988. *Osadkonakoplenie v silure Pribaltiki.* Valgus, Tallinn (in Russian).

Kala, E. 1995. Geological map of Estonia. Scale 1 : 2 500 000. Geological Survey of Estonia, Tallinn.

Kaljo, D. & Martma, T. 2000. Carbon isotopic composition of Llandovery rocks (East Baltic Silurian) with environmental interpretation. *Proc. Estonian Acad. Sci. Geol.*, **49**, 267–283.

Kaljo, D., Kiipli, T. & Martma., T. 1997. Carbon isotope event markers through the Wenlock–Pridoli sequence at Ohesaare (Estonia) and Priekule (Latvia). *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, **132**, 211–224.

Kaljo, D., Kiipli, T. & Martma., T. 1998. Correlation of carbon isotope events and environmental cyclicity in the East Baltic Silurian. *New York State Mus. Bull.*, **491**, 297–312.

Kaljo, D., Hints, L., Martma, T. & Nõlvak, J. 2001. Carbon isotope stratigraphy in the latest Ordovician of Estonia. *Chem. Geol.*, **175**, 49–59.

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. *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, **210**, 165–185.

Kallaste, T. & Kiipli, T. 1995. Discrete dolomite phases in carbonate rocks: results of the mathematical treatment of X-ray diffraction peaks. *Proc. Estonian Acad. Sci. Geol.*, **44**, 211–220.

Kiipli, E., Kiipli, T. & Kallaste, T. 2004. Bioproductivity rise in the East Baltic epicontinental sea in the Aeronian (Early Silurian). *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, **205**, 255–272.

Kiipli, T. 1983. On the genesis of Ordovician and Silurian dolomites at the contact with Devonian deposits. *Eesti NSV TA Toim. Geol.*, **32**, 110–117 (in Russian).

Kleesment, A. 1997. Devonian sedimentation basin. In *Geology and Mineral Resources of Estonia* (Raukas, A. & Teedumäe, A., eds), pp. 205–208. Estonian Academy Publishers, Tallinn.

Kleesment, A. & Shogenova, A. 2005. Lithology and evolution of Devonian carbonate and carbonate-cemented rocks in Estonia. *Proc. Estonian Acad. Sci. Geol.*, **54**, 153–180.

Kuršs, B. M. 1992. *Devonskoe terrigennoe osadkonakoplenie na glavnom devonskom pole*. Zinatne, Riga.

Lippmann, F. 1973. *Sedimentary Carbonate Minerals.* Springer-Verlag, Berlin.

Mangini, A., Jung, M. & Laukenman, S. 2001. What do we learn from peaks of uranium and of manganese in deep sea sediments? *Marine Geol.*, **177**, 63–78.

Nestor, H. & Einasto, R. 1997. Ordovician and Silurian carbonate sedimentation basin. In *Geology and Mineral Resources of Estonia* (Raukas, A. & Teedumäe, A., eds), pp. 192–204. Estonian Academy Publishers, Tallinn.

Nielsen, A. T. 2004. Ordovician sea-level changes: a Baltoscandian perspective. In *The Great Ordovician Biodiversification Event* (Webby, B. D., Paris, F., Droser, M. L. & Percival, G., eds), pp. 84–93. Columbia University Press, New York.

Priyatkin, A. & Polyakov, E. 1983. *Petrofizicheskie metody issledovaniya gornykh porod*. Leningradskij Universitet, Leningrad (in Russian).

Rao, V. P., Kessarkar, P. M., Krumbein, W. E., Krajevsky, K. P. & Schneiders, R. J. 2003. Microbial dolomite crusts from the carbonate platform of western India. *Sedimentology*, **50**, 819–830.

Richter, F. M. & Turekian, K. K. 1993. Simple models for the geochemical response of ocean to climatic and tectonic forcing. *Earth Planet. Sci. Lett.*, **119**, 121–131.

Schön, J. H. 1996. Physical properties of rocks: fundamentals and principles of petrophysics. *Seismic Explor.*, **18**.

Shanmugam, G. & Benedict, G. L. 1983. Manganese distribution in the carbonate fraction of shallow and deep marine lithofacies, Middle Ordovician, Eastern Tennessee. *Sedim. Geol.*, **35**, 159–175.

Shogenova, A. 1998. Electrical properties of lower Paleozoic carbonate rocks and their relationships with porosity in Estonia. In *Research in Petroleum Technology* (Middleton, M., ed.), *Nordic Petroleum Technology Series*, IV, 17–45. Nordisk Energi-Forskningsprogram, Ås, Norway.

Shogenova, A. 1999. The influence of dolomitization on the magnetic properties of Lower Palaeozoic carbonate rocks in Estonia. In *Palaeomagnetism and Diagenesis in Sediments* (Tarling, D. H. & Turner, P., eds), *Geol. Soc. London, Spec. Publ.*, **151**, 167–180.

Shogenova, A. & Puura, V. 1997. Petrophysical changes caused by dolomitization and leaching in fracture zones of lower Paleozoic carbonate rocks, North Estonia. In *Second Nordic Symposium on Petrophysics, Fractured Reservoirs* (Middleton, M., ed.), *Nordic Petroleum Technology Series*, I, 155–185. Nordisk Energi-Forskningsprogram, Ås, Norway.

Shogenova, A. & Puura, V. 1998. Composition and petrophysical properties of Estonian Early Palaeozoic carbonate rocks. In *Research in Petroleum Technology* (Middleton, M., ed.), *Nordic Petroleum Technology Series*, IV, 183–202. Nordisk Energi-Forskningsprogram, Ås, Norway.

Shogenova, A., Kleesment, A., Jõeleht, A., Shogenov, V. & Vaher, R. 2003. Physical properties and composition of Devonian carbonate and siliciclastic rocks from Estonia. In *Abstracts Volume 2, 65th EAGE Conference and Technical Exhibition, Stavanger, European Association of Geoscientists & Engineers*, 258.
Slaughter, M. & Hill, R. J. 1991. The influence of organic matter in organogenic dolomitization. *J. Sedim. Petrol.*, **61**, 296–303.
Teedumäe, A., Kallaste, T. & Kiipli, T. 1999. Dolomites of the Muhu Formation (Silurian) in mainland Estonia: aspects of dolomitization, properties, and prospects of utilization. *Proc. Estonian Acad. Sci. Geol.*, **48**, 213–227.
Teedumäe, A., Kallaste, T. & Kiipli, T. 2001. Aspects of dolomitization of the Mõhküla beds (Silurian, Estonia). *Proc. Estonian Acad. Sci. Geol.*, **50**, 190–205.
Teedumäe, A., Kallaste, T. & Kiipli, T. 2003. Comparative study of dolomites of different genesis (Raikküla Formation, Silurian; Estonia). *Proc. Estonian Acad. Sci. Geol.*, **52**, 113–127.
Teedumäe, A., Kallaste, T. & Nestor, H. 2004. Sedimentary cyclicity and dolomitization of the Raikküla Formation in the Nurme drill core (Silurian, Estonia). *Proc. Estonian Acad. Sci. Geol.*, **53**, 42–62.
Tucker, M. E. & Wright, V. P. 1994. *Carbonate Sedimentology*. Blackwell Scientific Publications, London.
Vasconcelos, C. & McKenzie, J. A. 1997. Microbial mediation of modern dolomite precipitation and diagenesis under anoxic conditions (Lagoa Vermelha, Rio de Janeiro, Brazil). *J. Sedim. Res.*, **67**, 378–390.
Vingisaar, P. & Utsal, K. 1978. On Estonian Palaeozoic rockforming carbonate minerals. *Sov. geol.*, **12**, 107–115 (in Russian).
Vingisaar, P. A., Oraspõld, A. L., Einasto, R. E. & Jürgenson, E. A. 1965. *Karbonaatkivimite ühtne klassifikatsioon ja legend*. Tallinn (in Estonian and Russian).
Vishnyakov, S. G. 1956. Genetic types of dolomitic rocks in the northwestern margin of the Russian Platform. *Tr. geol. in-ta AN SSSR*, **4**, 209–255 (in Russian).
Warthman, R., van Lith, Y., Vasconcelos, C., McKenzie, J. A. & Karpoff, A. M. 2000. Bacterially induced dolomite precipitation in anoxic culture experiments. *Geology*, **28**, 1091–1094.
Webby, B. D. & Laurie, J. R. (eds). 1992. *Global Perspectives on Ordovician Geology*. Rotterdam.
Wright, D. T. 1997. An organogenic origin of widespread dolomite in the Cambrian Eilean Dubh formation, north-western Scotland. *J. Sedim. Petrol.*, **67**, 54–64.
Wright, D. T. 2000. Benthic microbial communities and dolomite formation in marine and lacustrine environments – a new dolomite model. In *Marine Authigenesis from Global to Microbial* (Glenn, C. R., Lucas, J. & Prevot, L., eds), *SEPM Spec. Publ.*, **66**, 7–20.

Lõuna-Eesti Ordoviitsiumi, Siluri ja Devoni kivimite dolomiidistumine ning settimise tsüklilisus

Aada Teedumäe, Alla Šogenova ja Toivo Kallaste

On uuritud dolomiidistunud kivimite koostist ning omadusi Ordoviitsiumi, Siluri ja Devoni paleobasseinide arengufaaside ning settimise tsüklilisuse (üheksa tsüklit) taustal eesmärgiga selgitada dolomiidistumise eripära üleminekufaatsiese (Liivi Keel) tingimustes. Seitsme puursüdamiku proovide andmebaasist on valitud proovid, mille MgO sisaldus on üle 10%, ja nendes on määratud lisaks andmebaasis olevale (CaO, MgO, lahustumatu jääk, MnO, Fe_2O_3, poorsus) ka dolomiidi

võre parameeter d_{104}. Dolomiidistumise seos basseini arengu ja settimise tsüklilisusega on ilmne. Dolomiidistunud on ainult basseini arengu regressiivsetel perioodidel suhteliselt madalaveelistes tingimustes kujunenud lubisetted. Sügavamate faatsieste ja transgressiivsete perioodide setendid dolomiidistunud ei ole. Kõige täiuslikuma võrega on Ordoviitsiumi ja Siluri dolokivide dolomiit. Lahustumatu jäägi sisaldus võre parameetreid ei mõjuta. Nende muutused on tingitud Ca/Mg suhtest dolomiidis. Lubjakiviga kontakteeruvas dolokivis ja dolokivis, mis sisaldab kaltsiiti, on dolomiidi võre laienenud. Kogu uurimisandmestik kinnitab, et nii primaarne (süngeneetiline) laguunne kui ka sekundaarne dolomiit on kujunenud merelises keskkonnas. Mingeid ilminguid ülisoolsuse või basseiniväliste lahuste sissevoolu kohta ei ole. Dolomiidistunud kivimite leviku fatsiaalne ning ajaline seaduspära ja nende vaheldumine geoloogilises läbilõikes mittedolomiidistunud kivimitega võimaldab väita, et basseinisisene sekundaarne dolomiidistumine toimus litifitseerumata lubisette varase diageneesi staadiumis sulfaatredutseerivate bakterite toimel.