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Linkage of diagenesis to depositional environments and stratigraphy in the northern part of the Baltic basin

Anne Kleesment[a], Kalle Kirsimäe[b], Tõnu Martma[a], Alla Shogenova[a], Kristjan Urtson[a] and Kazbulat Shogenov[a]

[a] Institute of Geology at Tallinn University Technology, Ehitajate tee 5, 19086 Tallinn, Estonia; kleesmen@gi.ee
[b] Department of Geology, University of Tartu, Ravila 14a, 50411 Tartu, Estonia

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Abstract. The spatial and temporal distribution of carbonate cementation was investigated in Devonian siliciclastic rocks of the northern part of the Baltic basin, using geochemical (oxygen and carbon stable isotope, microprobe and bulk chemical analyses), optical, scanning electron and cathodoluminescence microscope methods. Carbonate cementation in the studied rocks is dolomitic and only rarely calcitic. Dolomite cementation occurs as laterally persistent zones, lenses or concretionary forms. Carbonate-cemented beds are the most common at the level of the maximum flooding surface and within the regressive system tract sediments. Levels of concretionary cementation with dolocrete features possibly mark the position of subaerial unconformities.

Interpretation of dolomite $\delta^{13}C$ and $\delta^{18}O$ values suggests marine and/or mixed marine-meteoric origin of diagenetic fluids. Marine origin of fluids is interpreted in the diagenetic alteration of siliciclastic interlayers in the Leivu and Kernave sequences that were cemented penecontemporaneously with early diagenetic dolomitization of carbonate rocks. The siliciclastic intervals of the Vadja Formation and partly of the Leivu Formation were cemented somewhat later with dolomite precipitated from mixed marine-meteoric pore water. Carbon isotopic values suggest that carbon was mainly derived from marine sources, except in the Pärnu Formation where negative $\delta^{13}C$ values of dolomite indicate that carbon was derived from oxidation of organic materials.

Key words: siliciclastic rocks, dolomite cementation, diagenesis, stable isotopes, Devonian, Baltic basin.

INTRODUCTION

Carbonate cementation of siliciclastic rocks is widespread within sedimentary basins and has a major impact on the physical and reservoir properties of sedimentary successions. Carbonate cementation processes span the entire diagenetic history of rocks from early to late diagenesis (Benito et al. 2006; El-ghali et al. 2006; Van den Bril & Swennen 2009). Carbonate cements supply valuable information on palaeoenvironments of the diagenetic alteration, chemical composition and flow patterns of fluids in sedimentary basins. Carbonate-cemented sandstone bodies range from isolated concretions to laterally persistent cemented layers occurring frequently in shallow-marine sandstones (Van den Bril & Swennen 2009). Diagenetic alterations (incl. cementation) largely modify the porosity and permeability of rocks and so affect the reservoir-quality of sequences (Morad et al. 2000, 2010; Taylor et al. 2000; Taylor & Gawthorpe 2003; Al-Ramadan et al. 2005; Salem et al. 2005; El-ghali et al. 2006; Sliaupa et al. 2008). Diagenetic alteration and particularly carbonate cementation have recently gained significant interest in the context of the sequence stratigraphic framework (Ketzer et al. 2002, 2003; Zamanzadeh et al. 2009; Morad et al. 2010; Taylor & Machent 2010).

The present study focuses on the carbonate-cemented siliciclastic rocks of the Devonian Baltic Basin (DBB) in the interval from the Early Devonian (Emsian) Rezekne Formation (Fm) to the Burtnieki Fm of the Middle Devonian (lower part of the Givetian) in the northern part of the DBB (Figs 1–3). Various types of carbonate-cemented rocks occur as laterally persistent layers, lens-shaped bodies and concretionary (globular) dolomite cements in the studied section. The aim of this paper is to document and discuss the distribution and origin of carbonate cementation in the siliciclastic sequence of the Devonian sediments in the DBB.

GEOLOGICAL SETTING

The studied rocks occur in the northwestern part of the DBB of the East European Platform in Estonia (Fig. 1). The DBB was a restricted shallow epeiric sea that developed in association with the Scandinavian Caledonides (Plink-Björklund & Björklund 1999) in the western part of the Baltica Plate on the margin of the

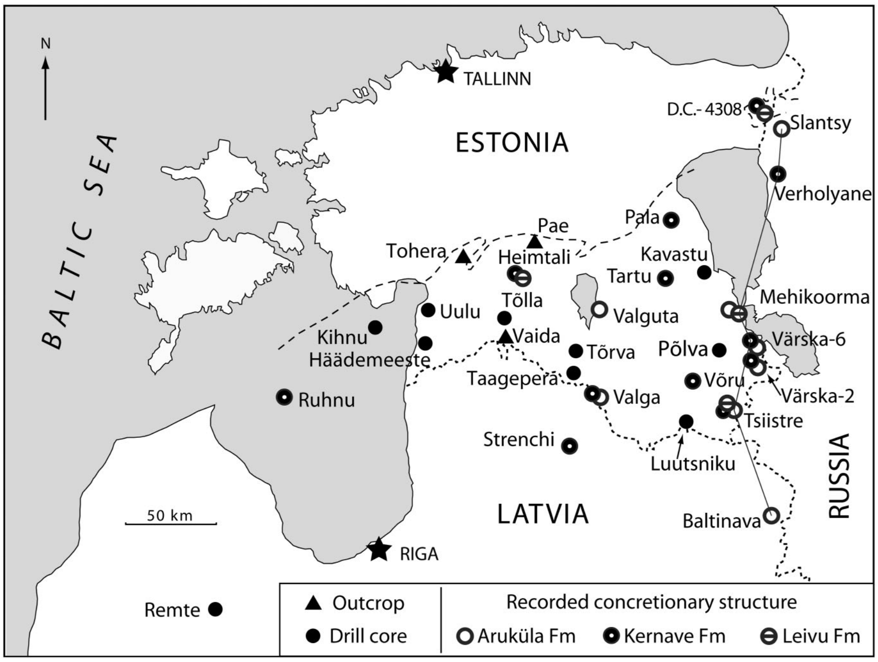


Fig. 1. Location of the studied drill cores and occurrence of concretionary structures.

Series	Stage	Regional Stage	Formation	Member	Main lithology
UPPER DEVONIAN	Frasnian	Amata	Amata		Sandstone
MIDDLE DEVONIAN	? Givetian	Gauja	Gauja	Lode	
				Sietini	
		Burtnieki	Burtnieki	Abava	Sandstone
				Koorküla	
				Härma	
		Aruküla	Aruküla	Tarvastu	
				Kureküla	
				Viljandi	Sand- and siltstone
	Eifelian	Narva	Kernave		
			Leivu		Dolomitic marl- and dolostone
			Vadja		
		Pärnu	Pärnu		Sandstone
LOWER DEVONIAN	Emsian	Rezekne	Rezekne		
	Pragian	Kemeri	Kemeri		
	Lochkov	Tilze	Tilze		

Fig. 2. Devonian stratigraphy of Estonia with main lithology of the units (modified from Kleesment 2009).

Laurussia supercontinent staying at an equatorial position during Devonian time (Cocks & Torsvik 2006).

The Devonian succession of the basin is composed of mixed carbonate-siliciclastic sediments. Siliciclastic deposits are found in the DBB from the latest Early Devonian (Pragian) until the end of the Middle Devonian (end of the Givetian). During the second part of the Eifelian, in Narva time, transgressive tidally influenced, mixed carbonate-siliciclastic subtidal to supratidal shallow marine deposits partially filled the DBB (Tänavsuu-Milkeviciene et al. 2009; Tänavsuu-Milkeviciene & Plink-Björklund 2009). The Narva transgression was followed by a regressive southward progradation of tide-dominated deltaic to estuarine deposits that continued through the Middle Devonian, up to the end of the Givetian (Kuršs 1992; Kleesment 1997; Plink-Björklund & Björklund 1999; Pontén & Plink-Björklund 2007; Tänavsuu-Milkeviciene & Plink-Björklund 2009).

The stratigraphic interval under consideration (Fig. 2) comprises rocks that formed in various depositional environments. The mainly siliciclastic sequence contains carbonate-dominated units, interlayers, and seams of mixed carbonate-siliciclastic rocks (Figs 2, 3; Kleesment & Mark-Kurik 1997). Dolostones and dolomitic marlstones (commonly aphano- and finely crystalline varieties) are mostly found in the Leivu and Vadja formations (Fms; Kleesment & Shogenova 2005). The siliciclastic rocks are mainly poorly cemented, well- to medium-sorted, fine- to very fine-grained sandstones. Interbeds of medium-grained sandstones occur in the Rezekne, Pärnu, Burtnieki and Gauja Fms, those of siltstones in the Kernave and Aruküla Fms. Besides dolomite-cemented rocks, also gypsum, late diagenetic calcite (Kleesment & Shogenova 2005) and Fe-hydroxide-cemented (Shogenova et al. 2009) interlayers are found.

The present-day burial depths in the studied area are up to 480 m (Kleesment & Mark-Kurik 1997). However, they reach 900 m in the southern drill cores in Latvia.

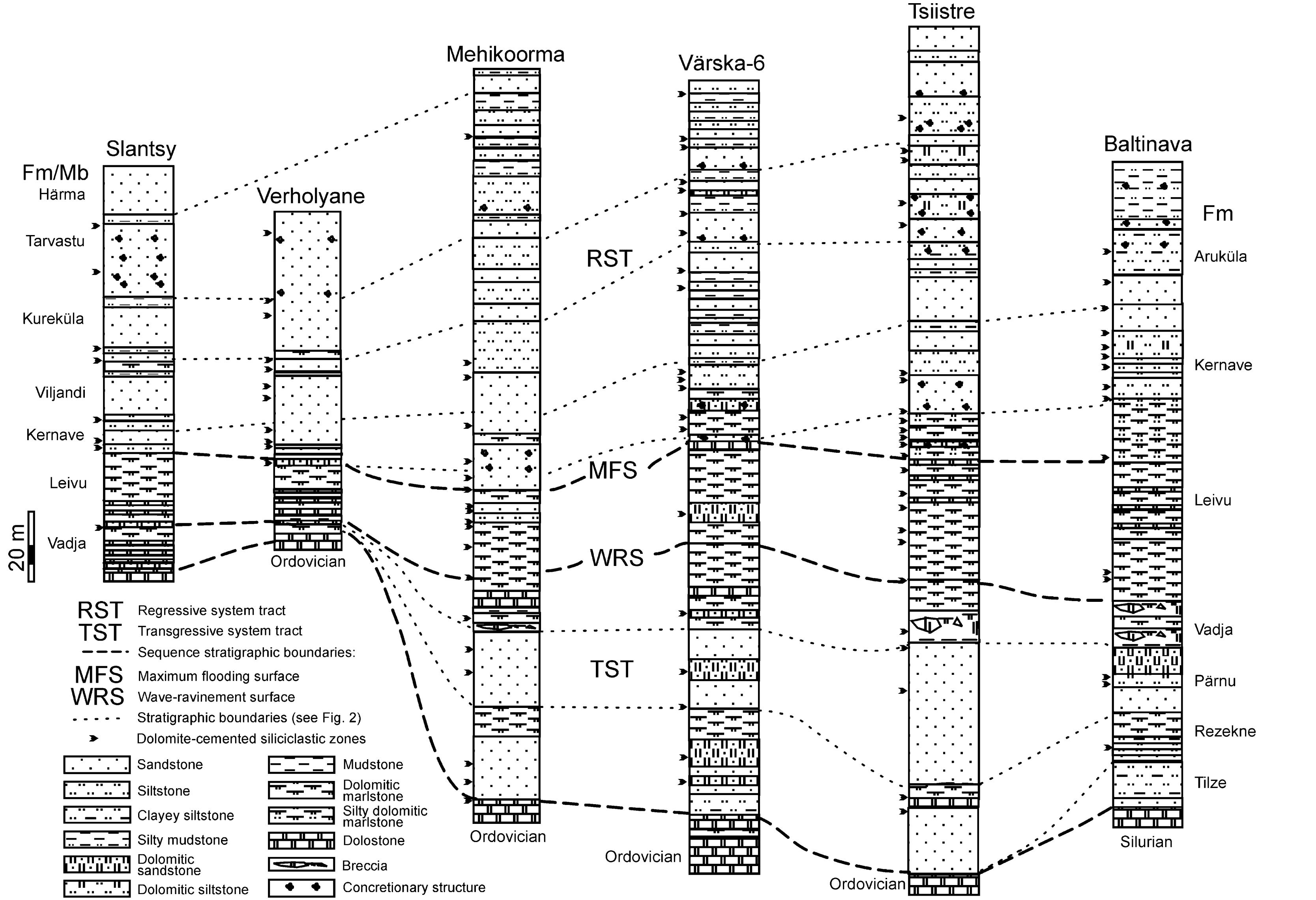


Fig. 3. Correlation of stratigraphical and lithological logs with sequence stratigraphic interpretation. Levels of dolomite-cemented interlayers and concretionary structures are marked. For location of drill cores and cross section see Fig. 1, for explanation of stratigraphic terms see Fig. 2.

DEPOSITIONAL FACIES AND SEQUENCE STRATIGRAPHY

In the studied stratigraphic interval, up to 240 m thick, the siliciclastic-dominated and carbonate-dominated lithofacies are intercalated (Figs 2, 3). The sequence comprises a lower transgressive phase consisting of an overall deepening succession and an upper regressive phase consisting of an overall shallowing succession. The lowermost part of the sequence, Rezekne and Pärnu Fms, occur in the transgressive system tract (TST) during which shallow-marine, open-coast tidal flat and tide-influenced estuarine deposits accumulated (Tovmasyan et al. 2008). Weakly-cemented siliciclastic rocks contain rare interlayers of dolostone and dolomitic marlstone. Palaeocurrent indicators, such as cross stratifications and channel axis orientation in the fluvial and deltaic sandstone, indicate sediment supply from the north (Plink-Björklund & Björklund 1999).

The middle Eifelian time marks an abrupt change from siliciclastic-dominated sedimentation to carbonate-dominated sedimentation (Nikishin et al. 1996). Tänavsuu-Milkeviciene et al. (2009) suggested that the DBB expanded first from southwest to northeast and, later during the transgression, also to the north, south and east. The first part of the transgression was characterized by muddy deposition. Carbonate-rich sabkha and supratidal to subtidal carbonate tidal-flat sediments were deposited in the northern and northwestern part and silt- and sand-rich tidal delta deposition in the southern and southwestern part of the DBB. The early phase of the transgression was punctuated by a short wave ravinement event on the level of the Vadja and Leivu Fms boundary (WRS, Fig. 3). During that event a short break in carbonate sedimentation occurred in the northern part of the DBB, which is in places marked by a sandstone layer with a mature mineral composition and high roundness of minerals (Kleesment 1997, 2009). In the course of the following deposition of subtidal carbonate-rich and subtidal mixed-facies mudstones, the amount of siliciclastic material increased in the northern and central parts of the basin (Tänavsuu-Milkeviciene et al. 2009). We interpret the maximum flooding surface (MFS) to be within the upper part of the Leivu Fm, which overlies the transgressive shallow-marine, intertidal to supratidal flats and is overlain by prodeltaic facies of the regressive system tract (RST; Fig. 3).

The upper part of the examined sequence (Kernave, Aruküla, Burtnieki and Gauja Fms) is represented by silty to fine-grained siliciclastic sediments, considered to be deposited in shallow-marine and deltaic settings (Kleesment 1997; Plink-Björklund & Björklund 1999; Pontén & Plink-Björklund 2007; Tänavsuu-Milkeviciene & Plink-Björklund 2009). The sand-rich progradational part is composed of several depositional units starting with sandstones and grading upwards into mudstones and siltstones, presumably indicating sea-level fluctuations (Kleesment 1997; Kleesment & Mark-Kurik 1997). The distinguished cycles are observed over a large area and are specified as members on a stratigraphic scale (Figs 2, 3; Kleesment 1994, 1995). Similarly, on the basis of vertical and lateral changes in the facies associations, Tänavsuu-Milkeviciene & Plink-Björklund (2009) recognized in the same section several stratigraphical units representing gradationally based progradational to aggradational vertically stacked cyclic packages that fine upwards in the Kernave and Aruküla Fms. The siliciclastic material was fluvially transported to the DBB from the northern and northwestern margins of the basin and later redistributed by tidal currents (Kleesment 1997; Plink-Björklund & Björklund 1999; Tänavsuu-Milkeviciene et al. 2009; Tänavsuu-Milkeviciene & Plink-Björklund 2009).

The Kernave Fm has been interpreted as shallow marine tidal flat and tidal bar deposits intercalated by tide-dominated deltaic formations (Kleesment 1997) or as being deposited in a tide-dominated deltaic setting that consists of prodelta mudstones, delta front tidal bar deposits intercalated by delta plain tidal flat and distributary channel deposits, which is also the characteristic depositional environment for the Aruküla Fm (Tänavsuu-Milkeviciene & Plink-Björklund 2009). The Kernave and Aruküla Fms and rarely the Leivu Fm contain peculiar concretionary-cemented interlayers. In the Kernave and Aruküla deposits the distribution area of concretionary-cemented interlayers expands to the south down to the Riga–Baltinava zone (Figs 1, 3, 4).

The overlying siliciclastic deposits of the Burtnieki Fm accumulated in the conditions of the continuing regressive trend in fluvially dominated subaqueous delta plain environment, which was repeatedly interrupted by short subaerial periods due to low-amplitude eustatic influences

Fig. 4. Example of concretionary cement in the Kernave Fm, Tsiistre drill core.

(Kleesment 1997). The regressive trend continued during the Gauja Age when subaqueous to subaerial tide-influenced delta plain and delta front deposits accumulated (Pontén & Plink-Björklund 2007). From the Burtnieki Age upwards the redeposition and recycling of siliciclastic particles has notably increased the roundness of grains and maturity of mineral composition (Kleesment 2009).

COMPOSITION OF SILICICLASTIC ROCKS

The composition of siliciclastic rocks varies from quartzarenite in coarser grain sizes (>0.1 mm) to subarcose and arcose in fine grain sizes (<0.1 mm). The TST sandstones are mineralogically quartzose and feldspathic arenite with the quartz content of 70–85%. Garnet dominates among heavy minerals. The lower part of the RST (Kernave and Aruküla Fms) is dominated by arcosic arenites (quartz content usually 50–70%) with a considerably high content of mica minerals. Upwards in the section the maturity and roundness of the sediment particles increase significantly. In the Gauja Fm the quartz content is up to 95%. Also, among heavy minerals the content of zircon increases upwards in the succession of the RST (Kleesment & Mark-Kurik 1997). The grain size and mineralogical composition of weakly cemented and dolomite-cemented rocks are similar, but the content of cement is clearly different – typically 5–10% in weakly cemented sand- and siltstones and 20–50% in dolomite-cemented siliciclastic rocks. Weakly cemented sandstones contain mainly clay-muddy cement of illite-chlorite composition. Kaolinite and mixed-layer illite-smectite are present in siliciclastic rocks of the TST (Pärnu and Rezekne Fms), whereas large amounts of kaolinite occur in siliciclastic rocks of the Burtnieki and Gauja Fms – in the uppermost part of the RST (Kleesment 1995).

MATERIAL AND METHODS

The studied material includes carbonate-cemented siliciclastic layers sampled in drill cores and outcrops from various lithostratigraphical units, depositional facies and system tracts in the northern part of the DBB (Figs 1–3). More than 300 samples were collected, mainly from siliciclastic rocks and for comparison from some carbonate units.

Petrographic examination was performed on 123 thin sections of both clay-muddy and carbonate-cemented siliciclastic rock samples from 17 sections (D.C.4308, Verholyane, Pala, Tartu, Valguta, Värska-2, Värska-6, Võru, Tsiistre, Valga, Taagepera, Tõlla, Uulu, Häädemeeste, Ruhnu, Tilleoja, Vaida; Fig. 1). Surface morphology of quartz grains from selected clay-cemented and dolomite-cemented siliciclastic rocks was examined with a Zeiss EVO MA 15 scanning electron microscope (SEM). The elemental composition of cements and grain surface features were determined with the energy dispersive spectrometer (EDS) INCAx-Act (Oxford Instruments Plc). Cathodoluminescence (CL) studies of thin sections were performed using the cold cathode CL stage CL8200 Mk5 (Cambridge Image Technology Ltd) attached to an optical microscope.

Fifty-seven samples (26 samples of dolomite-cemented rocks, 1 sample of calcite-cemented siliciclastic rocks and 30 samples of dolostones) were studied for stable carbon and oxygen isotopes. Carbon and oxygen isotope analyses were performed in the Laboratory of Mass Spectrometry of the Institute of Geology at Tallinn University of Technology (IG TUT) with the GasBench II preparation line connected to the Thermo Scientific Delta V Advantage mass spectrometer. The material was powdered and treated with 99% phosphoric acid at 70 °C for 2 h. The results are presented in the usual δ-notation, as per mil deviation from the VPDB standard. Reproducibility of replicate analyses was generally better than 0.1‰.

The bulk chemical composition of 160 rock samples was determined by XRF spectrometry in the All-Russian Geological Institute (VSEGEI) of St. Petersburg and at the IG TUT. The effective porosity of 82 rock samples was measured on cubes of 24 mm side, or on cylinders, 25.4 mm in diameter and 27–28 mm high. The measurements were performed at room temperature and pressure by the water saturation method (Jõeleht & Kukkonen 2002).

RESULTS

Character of cement and its spatial distribution

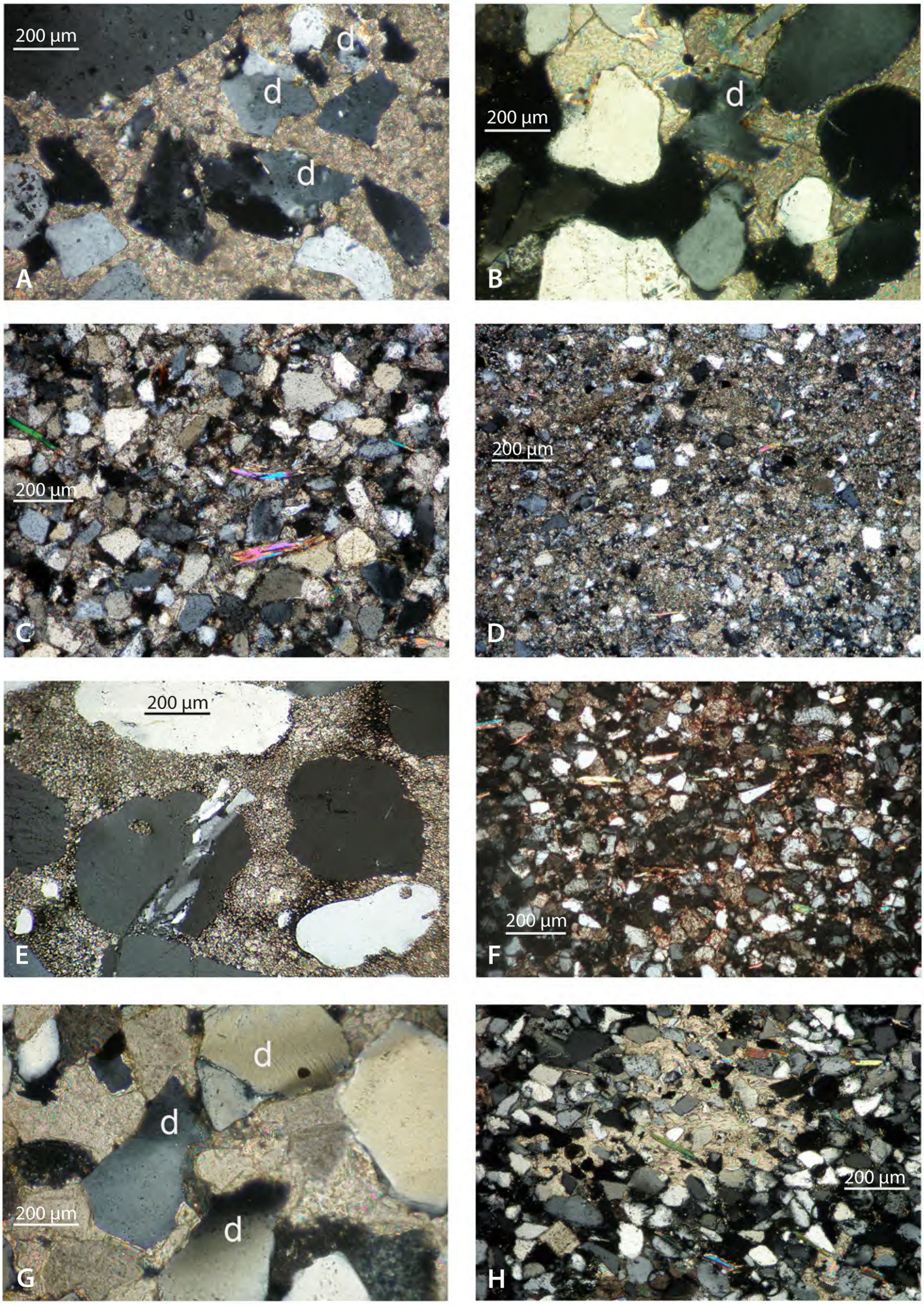
Weakly clay-cemented siliciclastic rocks contain 20–50 cm thick dolomite-cemented tabular and wedge planar intervals, commonly forming 5–10% of the Rezekne, Pärnu and Aruküla Fms and being only rare in the Burtnieki and Gauja Fms. Lense-shaped dolomite-cemented zones have in many places uneven surfaces, occur above claystone beds or surfaces in the upper part of the Aruküla Fm, and in the Burtnieki Fm.

Dolomite-cemented zones are relatively rare in the lower part of the TST (Rezekne, Pärnu and Vadja Fms) occurring mainly next to carbonate interlayers. These zones are more frequent in the Rezekne Fm in the Värska core (up to 20%), the upper part of which consists of dolomitic rocks (Fig. 3). Carbonate cement in the studied section is mainly found as dolomite, and calcite-cemented zones are rare. Dolomite cement occurs as euhedral to subhedral crystals filling pore spaces and is rimming detrital grains. This type of cement makes up 20–50% of the total volume of the analysed siliciclastic samples. The crystal size of pore-filling dolomite cement varies considerably, mostly from 5 to 300 µm, rarely up to 1 mm. The crystal size commonly increases towards the centre of the pores. The cement crystals rimming detrital grains are usually smaller than those of the cements precipitated in the remaining pore space – 5–20 µm (Figs 5A–C, 6A1). Some dolomite crystals are zoned (Figs 5A, 6B), sometimes with a dull red core and a brighter red edge in cathodoluminescence (Fig. 6B2). Energy dispersive spectrometry revealed Fe (0.4–0.5%) and K (0.25–0.3%) in dolomite cement in addition to major Mg and Ca. No differences in the composition of the core and rim of zoned dolomite crystals were determined. Some dolomite-cemented layers of the Pärnu and Rezekne Fms are rich in ooids (Figs 6B2, 7A; Stinkulis 1999). Similar to detrital particles, dolomitic ooids with lamellar texture are surrounded by fine (10–15 µm) zoned dolomite rhombs. Pore-filling dolomite is somewhat coarser (20–40 µm). Ooids are non-luminescent in cathodoluminescence, while all rimming and pore-filling particles show a bright zoned structure (Fig. 6B2). The chemical composition of dolomite cement and dolomitic ooids is similar – Mg/Ca ratios 0.24 and 0.21 with a minor Fe content (0.4–0.5%). Ooids were probably precipitated together with detrital material and later penecontemporaneously cemented.

Zones of sliliciclastic rocks with calcite cement are present in the Vadja, Leivu and Rezekne Fms in a restricted area in southeastern Estonia (Värska, Võru and Tsiistre cores). Calcite cement occurs as clear euhedral and subhedral medium- to coarse-crystalline (160–300 µm) grains (Fig. 6C1). Calcite crystals rimming the quartz grains are finer, 20–50 µm (Fig. 6C1), in cathodoluminescence exhibiting a brighter luminescence colour than the pore-filling crystals (Fig. 6C2). Energy dispersive spectrometry of calcite cement revealed pure $CaCO_3$ composition. Calcite cementation is accompanied by iron-rich patches in the basal part of the Värska-6 core, and also a unique sulphide-cemented pocket (2 mm in diameter) was recorded in this rock. Sulphide occurs as zigenite ($(Co, Ni)_3S_4$), which is rarely found in the sedimentary rocks, with minor quantities of galenite (PbS) and pyrite (FeS_2). The EDS analyses showed 13–26 wt% Co and 6–15 wt% Ni. The sulphide matrix corroded the calcite rims surrounding the grain (Fig. 7B). According to EDS analyses, iron-rich patches (2–4 mm in size) contain 20–30% Fe, which occurs as iron oxide coating on detrital grains.

In the upper part of the TST (Leivu Fm) the content of dolomite-cemented siliciclastic rocks is 5–20% (Fig. 3). These zones are 0.1–0.6 m thick and intercalate with claystone and dolomitic marlstone. Dolomite cement occurs in most cases in 30–50% of the total volume of the siliciclastic rock as finely crystalline dolomite (Fig. 6D, E). In the RST siliciclastic-dominated rocks the number of dolomite-cemented interlayers decreases upwards (Fig. 3). In the Kernave Fm, represented by frequent intercalation of siliciclastic and dolomitic rocks, the content of dolomite-cemented siliciclastic rocks is 10–20%, in the upper part

Fig. 5. Photomicrographs of thin sections in cross-polarized light. (**A**) Fine-grained, moderately sorted dolomite-cemented sandstone. Matrix (25–30%) is composed of semitransparent euhedral and subhedral finely to medium-crystalline (20–70 µm) dolomite. Abundant deformed quartz grains (d). Tõlla core, Pärnu Fm, GIT 441-114. (**B**) Fine-grained, moderately sorted dolomite-cemented sandstone. Matrix (30–40%) is composed of semitransparent euhedral crystals of medium- to coarse-crystalline (100–300 µm) dolomite. Quartz grains are surrounded by very finely crystalline (5–10 µm) dolomite rims. Some quartz grains are deformed (d). Värska-2 core, Rezekne Fm, GIT 441-68. (**C**) Fine-grained dolomite-cemented sandstone. Matrix (about 20%) is composed of semitransparent subhedral crystals of finely to medium-crystalline (50–120 µm) dolomite. Quartz grains are surrounded by very finely crystalline (5–10 µm) dolomite rims. Tsiistre core, Vadja Fm, GIT 550-36. (**D**) Dolomite-cemented siltstone. Matrix (40–50%) is composed of cloudy finely crystalline (about 10 µm) dolomite. Tsiistre core, Leivu Fm, GIT 550-25. (**E**) A 10 cm thick dolomite-cemented sandstone interlayer in dolomitic marlstone. Dolomite matrix (40–50%) is composed of very finely crystalline cloudy dolomite (5–10 µm). The siliciclastic part is represented by coarse rounded quartz grains (0.3–1 mm) with some amount of fine particles (0.03–0.1 mm). Some quartz grains are crushed and splinters of quartz occur in cement. Värska-2 core, Leivu Fm, GIT 441-56. (**F**) Dolomite-cemented silty sandstone. Matrix (20–25%) is composed of finely to medium-crystalline (50–90 µm) semitransparent dolomite rhombs, part of them zoned. Mehikoorma core, Aruküla Fm, Viljandi Mb, GIT 550-42. (**G**) Medium-grained, moderately to poorly sorted dolomite-cemented sandstone. Matrix (40%) is represented by semitransparent finely to medium-crystalline (50–150 µm) subhedral to anhedral dolomite. Many quartz grains are deformed (d), some of them corroded. Vaida outcrop, Aruküla Fm, Tarvastu Mb, GIT-443-187. (**H**) Very fine-grained clay-cemented sandstone containing abundant irregular calcite-cemented lumps (0.3–1.0 mm). Medium-crystalline (50–150 µm) euhedral to subhedral calcite in lumps forms 30–40%, whereas the bulk of clay cement in adjacent areas is 10–15%. Clay matrix contains some euhedral calcite crystals. Tsiistre core, Leivu Fm, GIT 550-22.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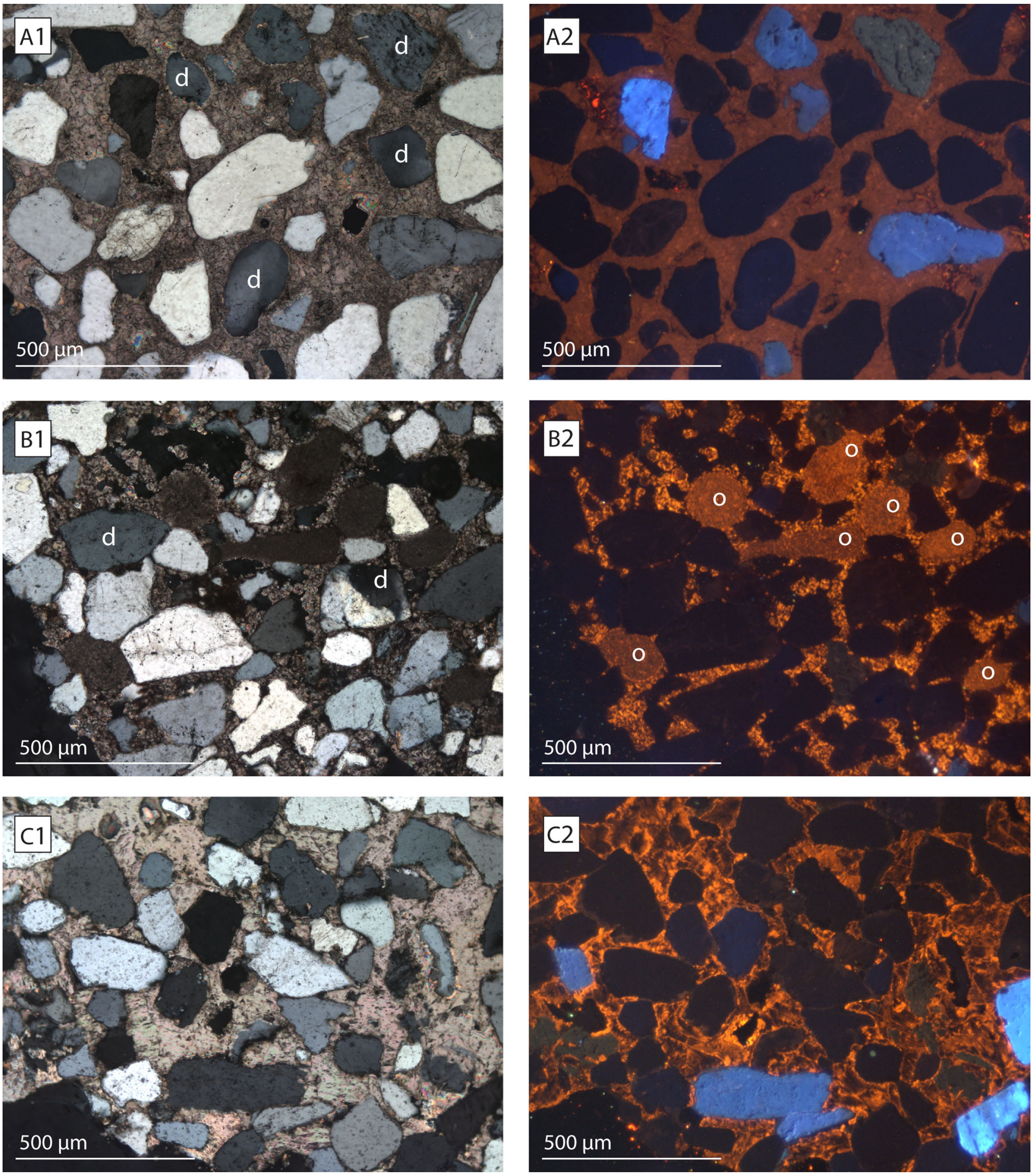


Fig. 6. Paired microphotographs in crossed polars (1) and cathodoluminescence (2). (**A1**) Poorly sorted dolomite-cemented sandstone. Cement (35–40%) is composed of finely to medium-crystalline (80–130 µm) transparent subhedral crystals. Clastic grains are rimmed by finely crystalline (30–40 µm) dolomite crystals. Some quartz grains are corroded, part of them are deformed (d). (**A2**) The same view under cathodoluminescence microscope. Dolomite cement exhibits dull red luminescence with no zoning. Taagepera core, Pärnu Fm, GIT 550-271. (**B1**) Fine-grained moderately to poorly sorted dolomite-cemented sandstone. Cement makes up about 20% and is represented by semitransparent, finely crystalline (20–40 µm) euhedral dolomite. The rock contains abundant cloudy dolomite ooids (0.1–0.25 mm) with stratified structure. Clastic grains and ooids are often surrounded by thin dolomite overgrowths. Some clastic grains are corroded, some are deformed (d). (**B2**) The same view under cathodoluminescence microscope, showing that ooids (o) and cement were formed at different times. Dolomite rhombs in cement are zoned, displaying a cloudy core and a brighter luminescent edge. In the colour figure quartz grains are dark grey, feldspar is blue. Mehikoorma core, Pärnu Fm, GIT 550-54. (**C1**) Fine- to medium-grained moderately sorted calcite-cemented sandstone. Cement accounts for 20–30% and is represented by medium-crystalline (160–300 µm) clear subhedral calcite crystals. (**C2**) The same view under cathodoluminescence, showing two phases of cementation. Detrital grains (in the colour figure quartz is dark grey, feldspar blue) are surrounded by bright rims. Värska-6 core, Rezekne Fm, GIT 550-209.

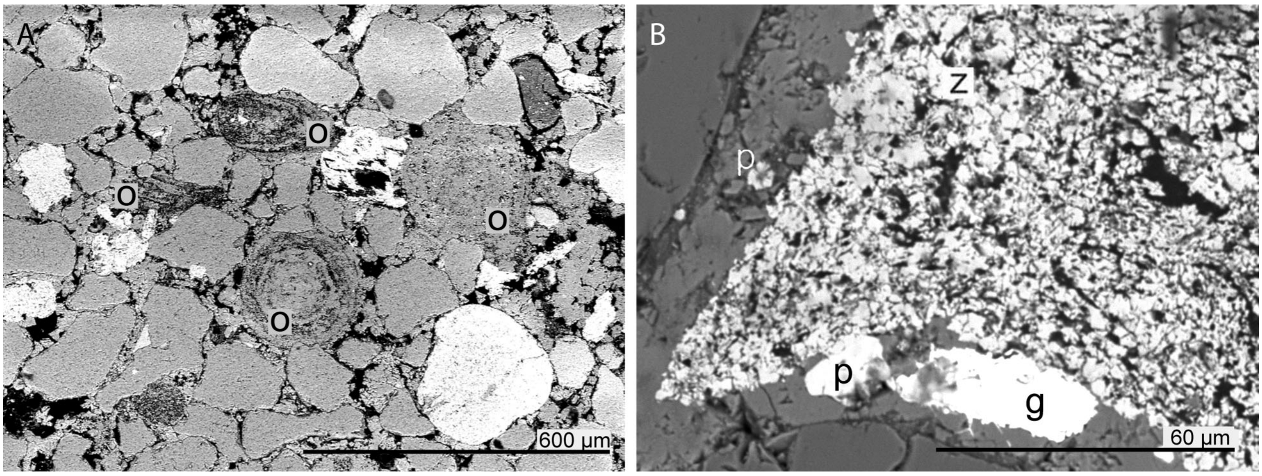


Fig. 7. Back-scattered SEM images of samples. (**A**) Fine-grained dolomite-cemented sandstone. Among detrital particles quartz grains (grey) dominate, supplemented by feldspars (white). About 10% of the rock is ooids with stratified structure (o). Cement (20%) is represented by finely crystalline (20–40 µm) dolomite. Detrital grains are often rimmed by very finely crystalline (5–10 µm) dolomite. Some grains are surrounded by C-rich coatings (black). Mehikoorma core, Pärnu Fm, GIT 550-54. (**B**) Fragment of calcite-cemented sandstone with patchy zigenite (Co–Ni sulphide) formations. Pyrite (p), galenite (g) and zigenite (z) precipitations postdate and corrode calcite cement rims. Värska-6 core, Rezekne Fm, GIT 550-209.

of the RST commonly 5–10%. Dolomite-cemented interbeds are 0.1–0.6 m thick and intercalate with claystone and/or poorly cemented siliciclastic rocks and contain clay-coated surfaces. Cementation is in many places associated with levels with phosphate and/or muddy clasts. Dolomite cement commonly occurs in 10–20% of the rocks as finely crystalline dolomite (20–60 µm), however, in the upper part of the section cement may form up to 50% as medium-crystalline dolomite with occasional zoned crystals (Fig. 5F, G).

Carbonate cementation has significantly reduced the porosity of the studied rocks (Fig. 8A). The porosity values vary from 35% to 5%. Assuming the average original porosity of sandstone to be about 40%, the maximum reduction of porosity was 35%. Purely siliciclastic rocks have a lower porosity than siliciclastic zones with a similar content of cement within the

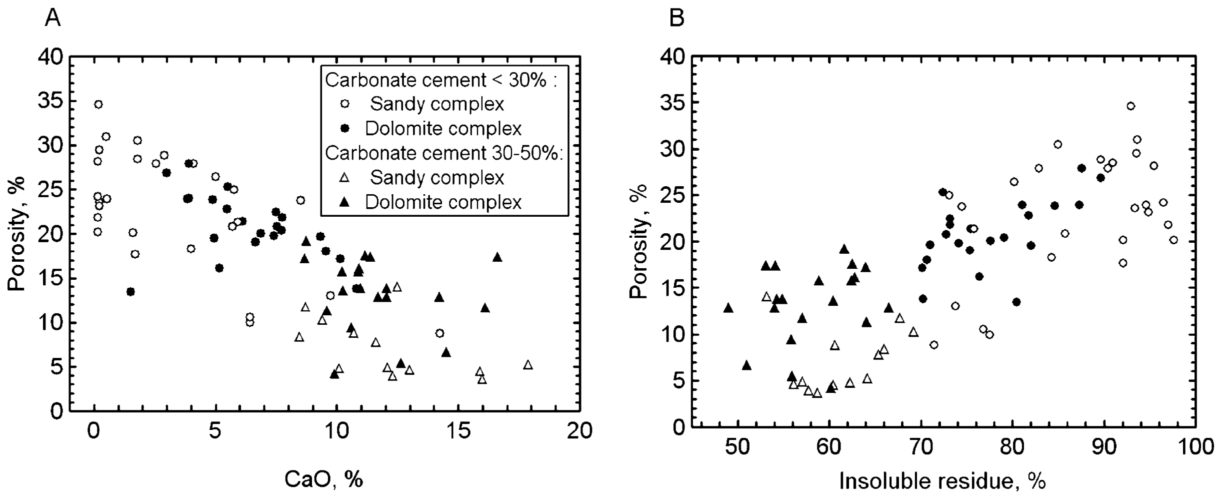


Fig. 8. (**A**) Porosity versus CaO content and (**B**) porosity versus insoluble residue content in siliciclastic rock interlayers in siliciclastic and dolomite rock types. The porosity of the rocks decreases with increasing carbonate cementation. The porosity of siliciclastic rocks is commonly lower than that of dolostones with the same insoluble residue and CaO content. The porosity of silicicilastic rocks varies in a wider range (3.6–35%) than that of dolostones (4.2–28%).

mixed siliciclastic-carbonate sequences of the Leivu and Vadja Fms (Fig. 8B), where fracturing, leaching and dissolution processes have generated secondary porosity (Kleesment & Shogenova 2005).

Concretionary cementation

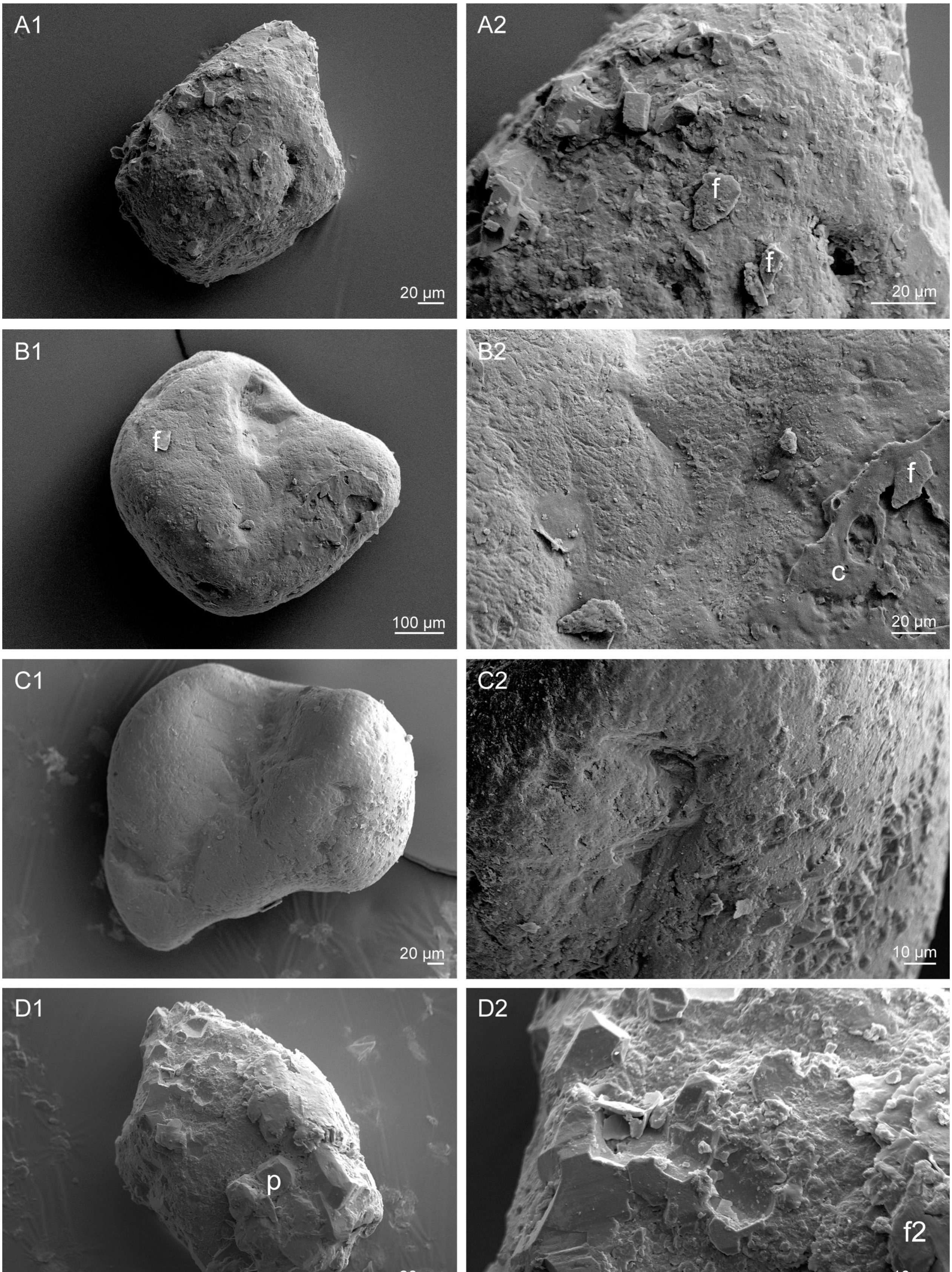
Rounded carbonate-cemented nodules, 5–10 mm in diameter and resembling dolocrete formations, are recorded in some levels of medium-cemented sandstones of the RST succession in the northern part of the Baltic basin (Figs 1, 3, 4). Concretionary structures are typically found in sandstones of the Kernave Fm, also in some levels of the Aruküla and Leivu Fms, but not in southern sections (Figs 1, 3; Kleesment 2008). In addition, carbonate-cemented spots 0.4–1 mm in diameter are present in many thin sections of clay-cemented siliciclastic rocks (Fig. 5H). Rock is grain-supported in clay-cemented areas, while carbonate-cemented spots are cement-supported and the displacement of grains is visible (Fig. 5H). However, no fracturing or grain breakage features were seen, which have been described in other studies (Khadkikar et al. 2000). Carbonate, commonly dolomite, occurs as finely to medium-crystallized subhedral grains (50–150 µm), some of which are embedded in matrix (Fig. 5H). In the studied section only dolocrete features are observed among coarse globules (5–10 mm), while both dolocrete and calcrete (Fig. 5H) formations occur in finer globules. Fossil remains, mainly dispersed fragments of fish which are common in these sediments, could have acted as nucleation centres for concretions, however, no significant correlation was found between the content of the P_2O_3 and concretionary cementation.

Displacement, deformation and surface textures of quartz grains

Displacement of clastic grains is common in the studied thin sections. The relation between the displacement of clastic grains and carbonate cementation is well evident in the concretionary-cemented rocks (Fig. 5H). Grain breakage is observed in the areas where carbonate cement is present in more than 30% of the rock. A few cases of in situ fracturing were recognized in rocks of the Pärnu, Vadja and Leivu Fms with the cement content of at least 30–40% (Fig. 5E). Undulous extinction of quartz grains occurs in both clay- and carbonate-cemented rocks. Usually deformed grains form 10–20% of the rock, but account for 20–30% in carbonate-cemented siliciclastic rocks of the Rezekne, Pärnu, Vadja and Leivu Fms, in one case also in the Aruküla Fm. The increased deformation of quartz grains is more frequent in carbonate-cemented rocks, where cement forms more than 20% and the rock and the cement are comparatively coarse-grained (Fig. 5A, B, G; Fig. 6A1, B1). No connection between undulous quartz grains with burial depth was recorded and the occurrence of undulous quartz is thus assigned to changes in the sediment source area rather than to diagenetic alteration.

The studied rocks contain numerous quartz grains with corroded outlines (Figs 5, 6). However, in many cases it is difficult to recognize whether corrosion took place during cementation or transport and deposition. The comparison of surface features revealed that many textures, such as V-shaped pits and linear grooves (Fig. 9A–C), are morphologically similar in loose and dolomite-cemented rocks (Kleesment 2009). Quartz grains of the studied dolomite-cemented sandstones have also syntaxial quartz overgrowths (Fig. 9C, D). The recorded syntaxial quartz overgrowths are euhedral (Fig. 9C2, D2), indicating the simultaneous etching-precipitation process in marine environment, which was post-dated by rapid carbonate cementation of rocks. Quartz grains are typically covered by C-rich adhering particles-clusters (45–55% C), which are sometimes covered by Fe-rich rims and patches (Fig. 9B2). Fe-rich rims are covered by carbonate cement and postdate C-rich particles (Fig. 9B2). Also, rare authigenic pyrite crystals occur on quartz grains (Fig. 9D1). Weakly cemented sandstones lack such features (Kleesment 2009).

Fig. 9. SEM microphotographs of quartz grains from dolomite-cemented siliciclastic rocks. (**A1**) Subrounded grain with abundant adhering particles and linear grooves on the surface. Põlva core, Pärnu Fm. (**A2**) Enlarged detail of the same grain. Adhering particles (f) determined with the EDS analyser contain 22% Fe, 12% Si, 9% Al and 9% Mg. (**B1**) Subrounded grain with some irregular and V-shaped abrasion features and a Fe-rich adhering particle (f). Kihnu core, Pärnu Fm. (**B2**) Enlarged detail of the same grain. Cement remnants (c) determined with the EDS analyser contain 55% C and adhering particles (f) contain 24% Fe, 14% Si, 5% K and 4% Mg. (**C1**) Subrounded grain with V-shaped and linear abrasion grooves. Uulu core, Pärnu Fm. (**C2**) Enlarged detail of the same grain with fresh syntaxial quartz crystals on the surface. (**D1**) Subangular grain with complicated surface texture. Pyrite cluster on the surface (p) contains 33.5% S, 29% Fe and 29% C with supplement of As (1.9%) and Si (0.6%). Remte core, Leivu Fm. (**D2**) Enlarged detail of the same grain with fresh syntaxial quartz crystals in the upper part and C-rich adhering particles (f1, f2). Particle f1 is composed of 54% C, 22% Si and 21% O, with supplement of K (1.3%) and Na (<1%); f2 is composed of 79% C, 9.8% S and 6.1% Fe.


A1
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Carbon and oxygen isotopic composition

The carbon and oxygen isotopic composition ($\delta^{13}C$ and $\delta^{18}O$) of dolomite-cemented siliciclastic rocks and early diagenetic aphano- to finely crystalline dolostones was studied. The measured $\delta^{13}C$ values of the dolostones range from –2.95‰ to +3.37‰. The $\delta^{18}O$ composition of dolostone samples varies from –3.98‰ to +0.11‰. Most of the dolostones have $\delta^{13}C$ values between +3.3‰ and –1.6‰. The values of $\delta^{13}C$ and $\delta^{18}O$ of dolomite-cemented siliciclastic rocks of the Vadja, Leivu and Kernave Fms are usually lower, from +2‰ to –2‰ and from –1‰ to –6‰, respectively. Dolomite-cemented siliciclastic rocks have more negative $\delta^{13}C$ and $\delta^{18}O$ values than dolostones, however, the range of the values of the former rocks of the Vadja, Leivu and Kernave Fms shows an overlap with the areas of dolostones. Stable isotope values of dolomite-cemented siliciclastic rocks are close to those of dolostones of the Leivu Fm in the Mehikoorma core and of the Leivu and Kernave Fms in the Värska core, while in the southern area (Valga and Tsiistre cores), and in the Vadja Fm and the basal part of the Leivu Fm in the Mehikoorma core the dolomite-siliciclastic rocks are characterized by decreased isotope values (Fig. 10, Table 1). Dolomite-cemented interlayers of the Pärnu Fm show variable values of $\delta^{13}C$ and $\delta^{18}O$, ranging from –4‰ to –7.45‰ and from –2.6‰ to –5.6‰, respectively. The $\delta^{13}C$ and $\delta^{18}O$ values of calcite-cemented sandstone are –1.35‰ and –6.4‰, respectively, whereas the oxygen isotope value is significantly lower than for dolomite-cemented siliciclastic rocks in the Narva Regional Stage (Fig. 10, Table 1).

DISCUSSION

Our results show that the formation of diagenetic carbonate cements in the studied siliciclastic and mixed siliciclastic-carbonate rock sequences spans the entire range of the diagenetic history. Although the timing and duration of each diagenetic event is difficult to determine, some assessment of paragenesis of the observed processes is possible based on textural relationships of various diagenetic precipitates in the studied rocks (Fig. 11).

The spatial distribution of carbonate-cemented beds in the studied sections is the most frequent at the level of the MFS and/or above it within the RST sediments (Fig. 3). The prolonged residence of the sediments close to the seafloor due to low sedimentation rates along the MFS typically results in the formation of microcrystalline Mg-calcite or dolomite cementation zones (carbonate hardground-firmgounds) (see also Al-Ramadan et al. 2005; Van den Bril & Swennen 2009; Morad et al. 2010). This concurs with the microcrystalline character of the dolomite zones in the upper part of the TST, along the MFS and in the lower part of RST sediments. Similarly, the formation of early diagenetic concretionary, clotted, patchy dolomite (or calcite) cementation has been discussed in the context with very low accumulation rates, or during breaks in the sedimentation (Rogers & Reed 1926; Seilacher 2001; Taylor et al. 2004; Sinha et al. 2006; Taylor & Machent 2010). These concretionary structures have been interpreted as calcretes and dolocretes, which were typically formed in arid to semi-arid conditions with near-surface temperatures 25–35 °C through the influence of groundwater

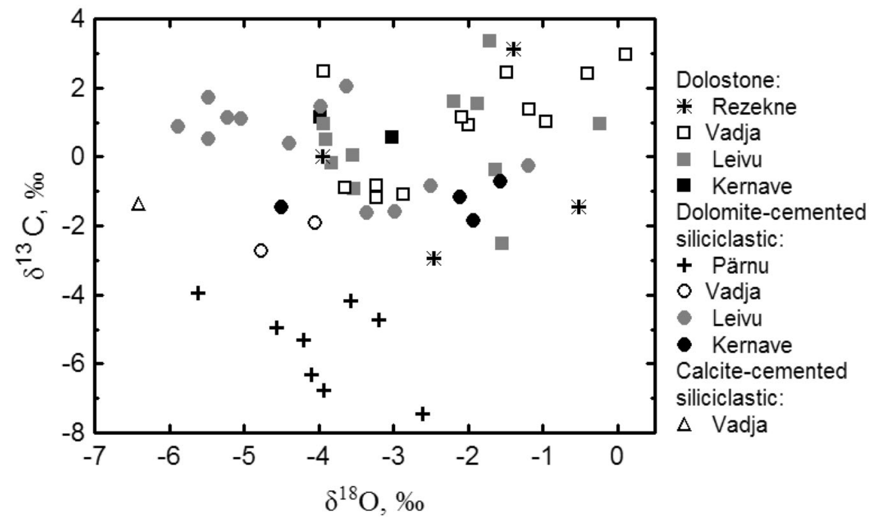

Fig. 10. Stable $\delta^{13}C$ and $\delta^{18}O$ isotopic composition of basin dolostones and dolomite-cemented siliciclastic rocks. Isotope values of dolostones are somewhat higher or overlap with values of dolomite-cemented rocks of the Vadja, Leivu and Kernave Fms. The $\delta^{13}C$ values of dolomite-cemented siliciclastic rocks of the Pärnu Fm are lower than those of the other studied rocks. The $\delta^{18}O$ value of calcite-cemented rock is lower than those of the other studied samples.

Table 1. Carbon and oxygen isotope data of the studied samples

Formation	Sample	Depth, m	$\delta^{18}O$, ‰	$\delta^{13}C$, ‰
		Dolostones		
Leivu	Tsiistre	358.0	−0.24	0.95
Leivu	Tsiistre	360.5	−3.83	−0.17
Leivu	Tsiistre	362.8	−3.90	0.50
Leivu	Tsiistre	368.8	−2.19	1.60
Vadja	Tsiistre	401.5	0.11	2.97
Vadja	Tsiistre	403.6	−0.95	1.01
Vadja	Tsiistre	408.7	−3.23	−0.83
Rezekne	Tsiistre	463.0	−0.51	−1.47
Leivu	Häädemeeste	57.9	−1.87	1.53
Leivu	Häädemeeste	66.6	−1.64	−0.39
Leivu	Häädemeeste	74.0	−1.55	−2.52
Kernave	Mehikoorma	149.2	−3.02	0.58
Leivu	Mehikoorma	176.5	−3.54	0.04
Leivu	Mehikoorma	177.6	−3.52	−0.93
Leivu	Mehikoorma	180.0	−3.93	2.47
Vadja	Mehikoorma	184.1	−3.93	2.47
Vadja	Mehikoorma	188.1	−2.00	0.93
Vadja	Mehikoorma	188.5	−0.40	2.42
Vadja	Mehikoorma	190.6	−3.65	−0.91
Vadja	Mehikoorma	192.4	−1.48	2.46
Rezekne	Mehikoorma	227.9	−1.38	3.12
Rezekne	Mehikoorma	228.2	−2.45	−2.95
Rezekne	Mehikoorma	245.4	−3.94	0.01
Kernave	Valga	156.0	−3.98	1.15
Leivu	Valga	175.4	−3.93	0.96
Leivu	Valga	212.0	−1.71	3.37
Vadja	Valga	218.3	−1.18	1.37
Vadja	Valga	229.4	−2.09	1.14
Vadja	Värska-6	204.6	−3.23	−1.19
Vadja	Värska-6	243.9	−2.87	−1.10
	Dolomite-cemented siliciclastics of the Narva RS			
Leivu	Tsiistre	377.5	−4.39	0.39
Vadja	Tsiistre	415.6	−4.76	−2.73
Leivu	Mehikoorma	164.1	−2.98	−1.60
Leivu	Mehikoorma	166.8	−1.19	−0.25
Leivu	Mehikoorma	174.9	−3.97	1.46
Leivu	Mehikoorma	175.1	−3.62	2.05
Leivu	Mehikoorma	182.0	−3.36	−1.61
Vadja	Mehikoorma	198.9	−4.05	−1.92
Kernave	Valga	146.0	−4.49	−1.47
Leivu	Valga	174.4	−5.48	0.50
Leivu	Valga	187.1	−5.47	1.72
Leivu	Valga	190.4	−5.88	0.86
Leivu	Valga	192.6	−5.22	1.13
Leivu	Valga	195.5	−5.03	1.09
Kernave	Värska-6	183.5	−1.92	−1.86
Kernave	Värska-6	189.0	−2.10	−1.16
Kernave	Värska-6	190.3	−1.56	−0.71
Leivu	Värska-6	224.8	−2.49	−0.83
	Dolomite-cemented siliciclastics of the Pärnu Fm			
Pärnu	Mehikoorma	203.7	−3.19	−4.75
Pärnu	Mehikoorma	209.5	−3.56	−4.20
Pärnu	Tartu	140.0	−4.20	−5.33
Pärnu	Värska-6	267.5	−4.56	−4.98
Pärnu	Taagepera	220.0	−3.92	−6.77
Pärnu	Taagepera	230.0	−4.09	−6.33
Pärnu	Ruhnu	110.0	−2.60	−7.45
Pärnu	Võru	308.5	−5.61	−3.96
	Calcite-cemented sandstone			
Vadja	Värska-6	252.0	−6.40	−1.35

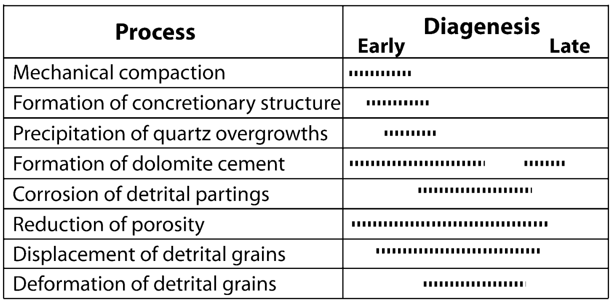

Fig. 11. Proposed paragenetic sequence of major cementation-related diagenetic processes in the studied section.

in increasingly episodic depositional conditions with frequent shoreline shifts accompanied by repeated alternation of subaerial and shallow-marine conditions (Tanner 2000; Seilacher 2001; El-ghali et al. 2006; Schmid et al. 2006; Sinha et al. 2006; Stinkulis 2008). Variation in the mineralogical composition of calcrete and dolocrete profiles is mainly attributed to differences in the chemical composition of groundwater and its flow pattern (Khalaf 2007). The concretionary cementation in the studied sections occurs with few exceptions, only in the RST – in the Kernave Fm and in the lower part of the Aruküla Fm (Figs 1, 3), which were deposited in shallow-marine delta front to tidal flat environments (Tänavsuu-Milkeviciene & Plink-Björklund 2009). Probably, at the time of deposition marine conditions were repeatedly interrupted by short subaerial periods. Levels with concretionary structures mark, then, the positions of subaerial exposure surfaces and dolomitization processes are in this case connected with early phases of diagenesis (Fig. 11; see also Taylor & Gawthorpe 2003; Sinha et al. 2006; Zamanzadeh et al. 2009; Kadir et al. 2010; Taylor & Machent 2010).

The spatial distribution of layered dolomite-cemented zones within the investigated Middle Devonian siliciclastic sequence is connected with the RST and the initial phase of the TST, with deposits of the initial phase of transgression (Rezekne and Pärnu Fms) and shallow-marine carbonate-siliciclastic sequence of the Leivu and Kernave Fms (Fig. 3). Typically the diagenetic alterations in the TST are mainly associated with post-sedimentary processes, while the influence of sedimentation has been minor (Fig. 11). The near-surface early diagenetic alteration was controlled by depositional facies/rock composition, climate and mainly by relative changes in sea level (Morad et al. 2000; Ketzer et al. 2003).

The different origin of the cementation is evident form the wide variation in stable isotope composition data and indicates that the examined section has a multistage cementation history. The position of the

$\delta^{13}C$ and $\delta^{18}O$ values in Fig. 10 reflects differences in fluid–rock interaction and introduction of multiple chemically distinct fluids at different times throughout the diagenetic history (Wright at al. 2000). Dolomite-cemented siliciclastic rocks show a trend towards more negative values of $\delta^{13}C$ and $\delta^{18}O$ compared to early diagenetic normal marine dolostones (Fig. 10). Using $\delta^{18}O$ values of these fine crystalline dolomite cements varying between –1‰ and –6‰ (average –3.78‰), the $^{16/18}O$ fractionation for the dolomite-water system ($10^3 \ln\alpha_{\text{dolomite-water}} = 2.78 \times 10^6\ T^{-2} + 0.91$, Land 1985) and assuming equatorial surface temperatures (of 20–30 °C), we get that the dolomites would have been precipitated in equilibrium with pore water with $\delta^{18}O$ values from –1.3‰ to –8.5‰ V-SMOW. The estimated Middle to Late Devonian oxygen isotopic composition of seawater during this time period without any significant continental ice sheets was –1‰ V-SMOW (e.g. Joachimski et al. 2004). This suggests that dolomite in the studied cemented rocks precipitated form marine and mixed marine-meteoric pore waters. Part of the siliciclastic interlayers were cemented during early diagenesis penecontemporaneously with the formation of early diagenetic dolostones using up the seawater just below the sea floor before lithification of deposits. The cemented interlayers belonging to the TST in the Mehikoorma core (Leivu Fm) and Värska core (Leivu and Kernave Fms) yielded the $\delta^{18}O$ values which overlap with the isotopic range of the interbedded early diagenetic dolostones and reflect a typical Devonian seawater source (Qing 1998). However, interlayers of siliciclastic rocks that accumulated at the same time in shallow sea in the southern area (Valga and Tsiistre cores), as well as siliciclastic rocks of the Vadja Fm and the basal part of the Leivu Fm of the Mehikoorma core exhibit lower $\delta^{18}O$ values (Fig. 10, Table 1) and bear signatures of mixed marine-meteoric pore water. Nevertheless, in both cases the $\delta^{13}C$ values of dolomite (–2.7‰ to 2.1‰, average –0.3‰) suggest that dissolved carbon was derived mainly from marine water. In contrast, significantly lower $\delta^{13}C$ values (–3.96‰ to –7.45‰, average –5.47‰) of dolomite-cemented interlayers of the Pärnu Fm (Fig. 10, Table 1) suggest input of reduced carbon, probably from oxidation of organic matter from the pedogenic zone (Staddon 2004), whereas the estimated $\delta^{18}O$ composition of diagenetic fluids indicates mixed marine-meteoric to meteoric (–2.9‰ to –8.1‰ V-SMOW) origin of pore water. It could be suggested that meteoric fluids entered the relatively coarse-grained estuarine sandstones of the Rezekne and Pärnu Fms (Tovmasyan et al. 2008) during low-stands by remobilizing dolomite from dolomitic interlayers that occur in the same section. Unsaturated meteoric fluids, infiltrating through soil profiles and enriched with respect to organic dissolved carbon, gained Ca, Mg and additional bicarbonate as a result of dolomite dissolution. The mixing of these fresh waters with marine pore water in the estuarine sandstones would have favoured dolomite precipitation (Hardie 1987; Morad et al. 1992; Immenhauser et al. 2003).

Though mostly no cathodoluminescence zonation was observed within the spar cement which is dull luminescent (Fig. 6A2), referring to early diagenetic origin of cementation, in some cases the dolomite-cemented rocks of the Vadja and Leivu Fms revealed a somewhat increased content of Mn in dolomite, indicating that in these levels cementation of siliciclastic layers presumably progressed during burial diagenesis under the impact of evolved pore waters. Carbonate cementation started at grain contacts with grain-rimming cement and continued with pore space filling cementation.

Dolomite cementation was accompanied by displacement and deformation of detrital grains. Quartz grains became deformed in cement-supported and coarse-grained layers (Fig. 5A, B, G), being occasionally also fractured and cracked (Fig. 5E). The fracturing and displacement of quartz grains in carbonate-cemented siliciclastic rocks has been described in many places (Becker & Day 1916; Dapples 1971; Watts 1978; Buczynski & Chafetz 1987; Braithwaite 1989), among others also in the Old Red Sandstone of Scotland (Saigal & Walton 1988). Carbonate cement in siliciclastic rocks may fill intergranular pores without modification in the arrangement of the detrital grain framework and the shape of such grains, or cause expansion of the intergranular space and consequent rearrangement in the packing of detrital grains. Simultaneously some corrosion of detrital partings occurred (Fig. 5A, B, E, G; Fig. 6A, C). The etching and corroding of quartz grains by carbonate-bearing waters during carbonate cementation has been described by several researchers since the beginning of the 20th century (Hatch et al. 1938; Weedman et al. 1992; El-ghali et al. 2006; Estupiñan et al. 2007). The studied rocks contain numerous quartz grains with a corroded outline (Figs 5, 6). The comparison of surface features has revealed that many textures, such as V-shaped pits and linear grooves (Fig. 9A–C), are morphologically similar in loose and dolomite-cemented rocks (Kleesment 2009). Clear corrosion features have been recorded in iron-oxide cemented sandstones of the Burtnieki Fm (Shogenova et al. 2009) and in the matrix-supported sandstones of the Pärnu and Leivu Fms (Tamme 1964), and also in Cambrian sandstones (Pirrus 2002).

In places syntaxial quartz overgrowths appeared during the early phase of carbonate cementation (Fig. 9C, D). However, the exact mechanism of overgrowth formation remains unclear – whether they formed during or after carbonate cement precipitation

(Mørk & Moen 2007). The most likely source of authigenic quartz crystals determined in this study (Fig. 9C, D) is local release of silica from the dissolution of smectite and precipitation of illite at temperatures of 60–100 °C, as suggested by Thyberg et al. (2009). Illitic clays predominate in the observed section (Kuršs 1975) and samples with authigenic quartz overgrowths are rich in illite. The formation of illite in the slowly subsiding Baltic Cambrian basin at shallow burial depths is described by Kirsimäe et al. (1999). Usually such overgrowths are connected with silicate cementation and their coexistence with carbonate cement is explained by their reworking from previously quartz-cemented sandstone. It is thought that carbonate cement postdates the overgrowths (Pitman et al. 1997; Al-Ramadan et al. 2005; Van den Bril & Swennen 2009), however, the etching that developed due to chemical solution activity of seawater under alkaline conditions is also known (Cherian et al. 2004). Rarely quartz overgrowths formed concurrently with burial carbonate cementation (El-ghali et al. 2006), which has obviously been the case in the studied rocks.

CONCLUSIONS

1. This research allowed us to interpret the paragenetic sequence of dolomite cementation and associated processes in Devonian siliciclastic rocks in the northern part of the Baltic basin from early to late stages of diagenesis.
2. Concretionary cementation has proceeded in periods of sedimentary breaks during post-depositional subaerial exposure with significant meteoric water migration. The distribution of concretionary structures in the studied sections gives evidence of the uplift of the northern region, causing erosional unconformities in the mentioned strata.
3. Stable isotope data suggest the marine and/or mixed marine-meteoric origin of diagenetic fluids. The marine origin of fluids is interpreted in the diagenetic alteration of siliciclastic interlayers in the Leivu and Kernave sequences that were cemented penecontemporaneously with early diagenetic dolomitization of carbonate rocks. The siliciclastic interlayers of the Vadja Fm and partly of the Leivu Fm were cemented somewhat later with dolomite precipitated from mixed marine-meteoric pore water. Carbon isotopic values suggest mainly carbon derived from marine sources.
4. The significantly negative $\delta^{13}C$ values of dolomite-cemented siliciclastic rocks of the Pärnu Fm suggest carbon input from oxidation of organic materials. The cementation of these interlayers has probably proceeded at a later stage of diagenesis in conditions of mixing marine-meteoric pore waters enriched in carbon from the pedogenic zone.

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Diageneesiprotsesside seostatus settetingimuste ja stratigraafiaga Balti basseini põhjaosas

Anne Kleesment, Kalle Kirsimäe, Tõnu Martma, Alla Shogenova,
Kristjan Urtson ja Kazbulat Shogenov

Kasutades geokeemilisi ja hapniku ning süsiniku isotoopkoosseisu andmeid ja uuringuid optilises, skaneerivas ning katoodluminestsentsmikroskoobis, tehti kindlaks karbonaatse tsementatsiooni diageneetiliste ilmingute olemus Põhja-Balti basseini Devoni purdsetetes. Valdavalt on tegemist dolomiitse tsemendiga, kaltsiitset tsementi esineb harva. Dolomiitse tsemendiga tasemed on esindatud nii plaatjate kihtide, läätsede kui ka konkretsiooniliste vormidena. Tsementeerunud vahekihid esinevad sagedamini tasemetes, mis esindavad läbilõikes transgressiooni maksimumi ja regressiivse staadiumi setteid. Konkretsioonilise tsementatsiooni teke on tõenäoliselt seotud Devoni-aegsete settekatkestustega. Süsinik- ja hapnikisotoopide andmete alusel võib eraldada diageneetiliste lahuste päritolu. Kui Leivu ja Kernave settekompleksides toimus purdsetete tsementatsiooniprotsess osaliselt üheaegselt diageneetiliste dolokivide tekkega merevee mõjutusel, siis Vadja ning mõnede Leivu kihistu tsementeeritud vahekihtide teke on olnud hilisem ja dolomiitse komponendi moodustumine on siin seotud merelis-mageveeliste poorilahuste mõjuga. Süsinikisotoobi negatiivsed väärtused Pärnu kihistu tsementeerunud vahekihtides viitavad orgaanilise materjali oksüdatsiooni mõjule.