

Mineral Composition and Morphology of Dolocretes of the Devonian Burtnieki and Amata Formations, Latvia

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Abstract — Siliciclastic deposits of the Burtnieki Formation and the Amata Formation in Latvia contain carbonate inclusions in places. Morphological peculiarities and mineral composition indicate that these carbonates represent dolocretes formed during subaerial exposure events in Devonian Burtnieki and Amata times. Dolocretes show nodular and veiny structure, circumgranular cracks, and other features of brecciation, but massive dolocretes also have been found in the Amata Formation. These features indicate that the dolocretes formed under the influence of both groundwater activity and pedogenic processes. These dolocretes were formed during episodes of subaerial exposure in repeated processes of drying and wetting either due to fluctuations of the groundwater table or climate change from semi-arid to semi-humid.

Keywords — Baltic Devonian basin, clay minerals, dolomite, pedogenesis, subaerial exposure.

I. INTRODUCTION

Deposits of the Devonian are widely distributed in Latvia reaching the thickness up to 800 m [1]. Deposits of the Burtnieki Formation and the Amata Formation mainly consist of such siliciclastics as loose sandstones and clayey siltstones [2]. Deposits of the Burtnieki Formation (the Middle Devonian, Givetian) were accumulated in the tide-influenced deltaic environment [3]. The Amata Formation (the Upper Devonian, Frasnian) conforms to the transgressive cycle and these deposits were accumulated in tide-influenced estuaries [4]. Within both these siliciclastic successions dolomite inclusions are present that genetically are interpreted as dolocretes [5]–[7].

Dolocretes are carbonate crusts which predominantly consist of dolomite of groundwater or pedogenic origin. Calcretes or caliches consisting mainly of calcium carbonate minerals are better known, more often documented worldwide and more widely distributed analogues of dolocretes. However, both these types of carbonate crusts occur in near-surface settings due to influence of phreatic (groundwater calcretes and dolocretes) or vadose (pedogenic calcretes and dolocretes) waters, evaporation and accumulation of authigenic calcium carbonate in host-rocks [8]. In further diagenetic processes calcretes can preserve their initial mineral composition or alter into dolocretes. Nowadays calcretes usually form in arid to semiarid climate with mean annual precipitation less than 500–600 mm [9]. Presence of calcretes and dolocretes points to near-surface settings and probable

breaks in sedimentation and subaerial exposure during respective time; thereby they are significant indicators of palaeogeographic and palaeoclimatic conditions [8].

The aim of this paper is to establish evidences of subaerial exposure events in the Burtnieki and Amata times by studies of morphological and mineralogical features of subaerial weathering which occur in dolomite-containing siliciclastic successions. In this paper two studied successions are described in detail — the Veczemji Cliffs (the Burtnieki Formation) and the Vizulī Outcrop (the Amata Formation).

II. MATERIALS AND METHODS

During field works macro-structures, textures and bedding conditions of deposits were studied and geological sections compiled.

Deposits of the Burtnieki Formation were studied at the Veczemji Cliffs where clayey siltstones and sandstones are exposed in an outcrop belt by the Gulf of Riga. The studied object is located in the northernmost part of the outcrop belt (57°32'54" N, 24°21'58" E). Deposits of the Amata Formation were studied at the Vizulī Outcrop by the River Amata (57°13'29" N, 25°13'24" E) where the upper part of the Amata Formation in a thickness of 8 m and the overlying Pļaviņas Formation are exposed.

Mechanically resistant samples with dolomite cement and dolomite inclusions in siliciclastics were studied in polished-sections and thin-sections, as well as under scanning electron microscope (SEM). Siliciclastics surrounding dolomite inclusions were analysed using X-ray diffraction (XRD) method.

Polished-sections and thin-sections of studied deposits were produced at the Laboratory of Rocks Research, Faculty of Geography and Earth Sciences, University of Latvia. Thin-sections were analysed and photographed using microscope *Leica DM 4500P* connected to a digital camera *Leica DFC 495*. Samples of clayey deposits cemented with dolomite from the section of the Burtnieki Formation were analysed in 10 polished-sections and 6 thin-sections and samples from the succession of the Amata Formation were analysed in 11 polished-sections and 11 thin-sections.

Micro- and nanomorphological analysis of deposits using SEM was carried out at the Faculty of Science and Technology, University of Tartu under the guidance of *Dr. geol.* I. Virčava. Two selected samples each from the successions of the Burtnieki Formation and the Amata

Formation were prepared similarly to polished sections and covered with a carbon film. Samples were analysed in SEM instrument *Zeiss EVO 15MA*. Chemical analyses in selected points under SEM were done by electron microprobe with an energy scattered detector *Oxford AZTEC X-MAX*.

XRD analysis for identification of clay minerals in siliciclastic material which surrounds dolocretes was done at the Faculty of Chemistry, University of Latvia. Samples were analysed by X-ray diffractometer *Bruker D8 DISCOVER* with $\text{CuK}\alpha$ radiation ($\lambda = 1.54060 \text{ \AA}$). Fraction $< 4 \mu\text{m}$ was used for identification of clay minerals in siliciclastics. This fraction was separated from the rest of the material by sedimentation method. Samples were prepared as air-dried oriented ones, treated in ethylene glycol atmosphere for 24 h as well as heated in $350 \text{ }^\circ\text{C}$ and $550 \text{ }^\circ\text{C}$ (2 h). Oriented and treated samples were scanned in $2.5\text{--}30^\circ 2\theta$ range with counting time of 1 s and scanning step size 0.01° . *Bruker* software *EVA* was used for processing diffractograms, identification and qualitative analysis of mineral phases. Clay minerals were identified in 3 samples from the deposits of the Burtneki Formation and in 17 samples from the deposits of the Amata Formation.

III. RESULTS AND INTERPRETATION

In both studied successions dolomite cement in siliciclastics occurred in various forms, thereby several types of dolocretes with different origin could be detected.

A. Morphology and Composition of Dolocretes of the Burtneki Formation at the Veczemji Cliffs

Approximately 1.5 m thick clayey bed crops out just above the sandy beach. This clayey bed consists of bluish clayey siltstones in its lower part (0.5–0.8 m thick) and red, mottled clayey siltstones in its upper part (up to 0.8 m thick), Fig. 1. Red clayey siltstones contain 1–15 cm large dolomite nodules [6].

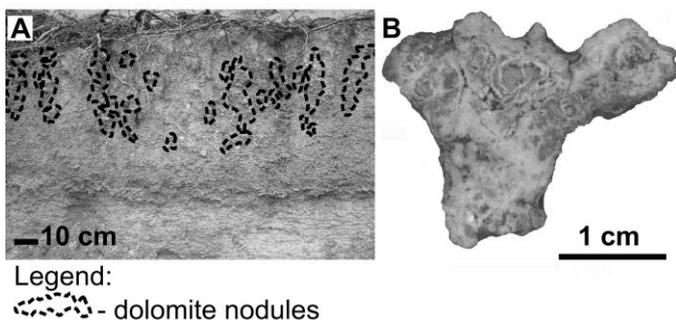


Fig. 1. Dolomite nodules in clayey deposits of the Burtneki Formation in the northern part of the Veczemji Cliffs [6]: (A) distribution of dolomite nodules in the uppermost part of the clayey bed within the red clayey siltstone; (B) V-shaped dolomite nodule oriented in its natural direction, polished section, sample VZ.3–2b.

Dolomite nodules are hard, mechanically resistant. Amount of nodules increases upwards where they have grown together forming elongated sets of dolomite. In the upper part of the bed dolomite nodules are more subvertically elongated and also V-shaped (Fig. 1). Internal structure of nodules is spotty

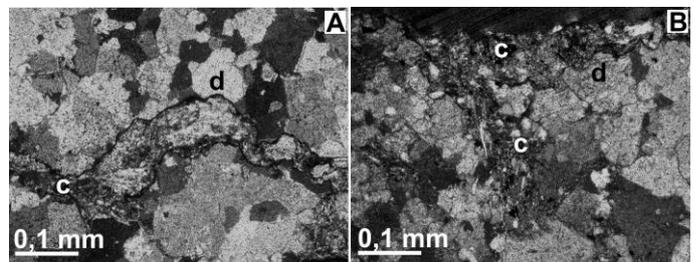
with frequent light spots of dolomite cement between a more clayey reddish material [6].

According to structure of the dolomite-containing succession, the distribution of dolomite nodules and internal morphology of dolomite nodules, the layer of dolomite nodules within the clayey siltstones corresponds to pedogenic nodular dolocretes [6], [10]–[12].

According to data obtained from the analysis of thin-sections of dolomite nodules, two types of cracks can be distinguished:

- desiccation cracks filled with coarse crystalline dolomite in fine to medium crystalline dolomite matrix,
- desiccation cracks filled with clayey material in fine to medium crystalline dolomite matrix [6].

Cracks filled with dolomite cement were up to 1 cm long and up to 1 mm wide. The widening of these cracks was also stimulated by growing of dolomite crystals within them in addition to drying.



Legend: d - dolomite, c - silty material (quartz, feldspar, mica, illite)

Fig. 2. Cracks in dolomite nodules; the Burtneki Formation at the Veczemji Cliffs, thin-sections, sample VZ.1–2; (A) cracks filled with clayey, silty and sandy material in matrix of medium crystalline dolomite; (B) pocket-like cavity near the nodule surface filled with siliciclastics.

Crystallization of carbonates took place not only within desiccation cracks, but throughout the whole nodules; this explained the high mechanical resistance and spotty structure of nodules. Dolomite crystals grown in fine-grained siliciclastic matrix often were well-shaped, even euhedral.

Cracks filled with clayey material (Fig. 2) in places reached width up to 1 mm. However, as a result of branching, these cracks became narrower forming a dense net with long, narrow and even filament-like branches, up to 0.01 mm wide. Boundaries between surrounding dolomite and cracks filled with clayey silt were sharp, evidencing that the clayey material was washed into desiccation cracks that had already developed. Textures similar to karst cavities on the surface of dolomite nodules also provide evidence of illuvial processes (Fig. 2). These karst-like pockets were filled with clayey silty material with well-expressed subvertically oriented micas that were seen in microscope.

As could be recognized in SEM microphotographs, also a lot of small (just 10–100 μm wide) filament-like cracks occurred inside dolomite nodules. These narrow cracks in dolomite matrix, as well as pores between dolomite crystals, were filled with strongly weathered material composed of feldspar grains, micas, and illite.

Features of weathered material were also found in clayey material which surrounded the dolomite nodules. According to XRD data, clay minerals were mainly represented by illite. Illite presumably is detritic by origin and this mineral was accumulated in sedimentary processes together with the rest of siliciclastic material such as quartz grains, weathered feldspars, and micas [2]. Chlorite was also abundant in clayey material. Formation of chlorite in soils is promoted by leaching and decarbonatization processes. Likely, that in studied deposits chlorite was accumulated within illuvial horizon as a result of soil processes [14]. However, chlorite can be also accumulated as debris of igneous-metamorphic weathering crust material [14]. Small amounts of kaolinite can be recognized in places in studied deposits as well.

B. Morphology and Composition of Dolocretes of the Amata Formation at the Vizuli Outcrop

Deposits of the Amata Formation in this outcrop consisted of alternation of fine-grained sandstones and clayey siltstones. The succession in the lower part is sandier, while in the upper part it contained more clayey interlayers (Fig. 3).

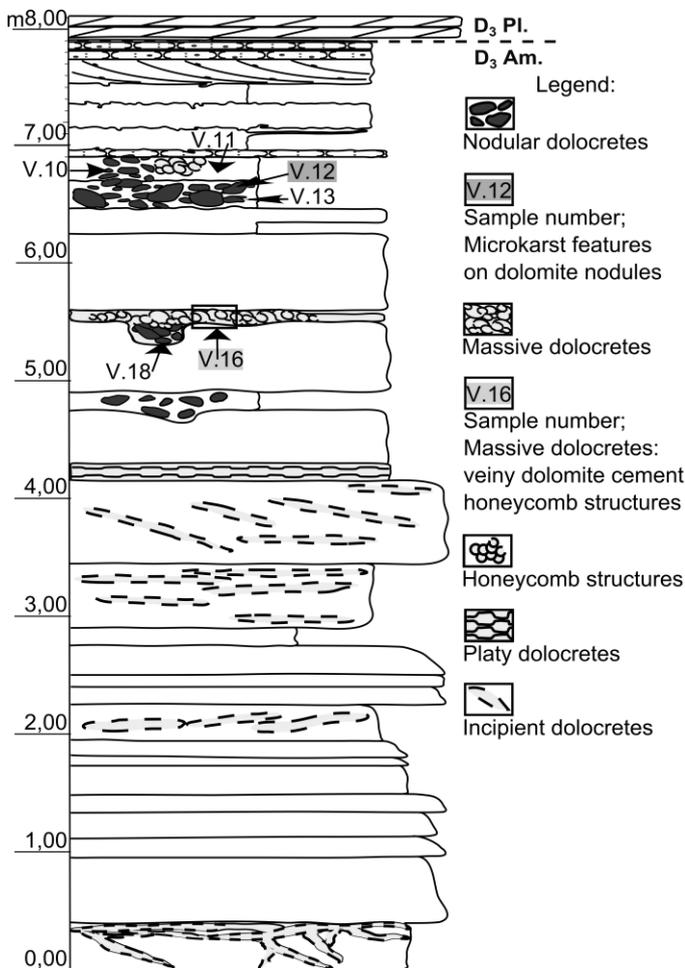


Fig. 3. Generalised geological section of deposits of the Amata Formation and the Płaviņas Formation at the Vizuli Outcrop.

Loose sandstone in the lower 4 m interval of the studied section contains irregularly distributed inclusions of dolomite cement which gave evidence of incipient formations of

dolocretes. These formations mostly were weakly cemented and in places contained such primary sedimentary structures as current ripples.

About 4 m below the boundary of the Amata Formation and the Płaviņas Formation the horizon of platy dolocretes occurred (Fig. 3). In this horizon dolomite cement was distributed in subvertical and subhorizontal belts 1–2 cm wide. Dolomite belts formed dense rectangular net made of 1 × 2 cm large subhorizontally elongated cells with sandy material inside. These platy dolocretes supposedly were formed due to fluctuations of groundwater table both in phreatic and capillary fringe zone, near the vadose zone under the influence of laminar groundwater flows and subvertically percolating waters [8].

Upwards in the succession lie horizons of massive dolocretes and nodular dolocretes (Fig. 3). These horizons show features characteristic of pedogenic dolocretes. Massive dolocretes 2.5 m below the boundary of the Amata Formation and Płaviņas Formation had veiny structure, besides incipient fine lamination structures and honeycomb structures occurred on the surface of the horizon (Fig. 3). Both of them are characteristic of the upper part of profiles of pedogenic dolocretes [8], [9], [11], [12]. Nodular dolocretes consisted of veiny dolomite nodules distributed in clayey siltstones. Roundish honeycomb structures and rare microkarst features (Fig. 3) were recognized in nodular dolocretes 1.5 m below the boundary of the Amata Formation and the Płaviņas Formation.

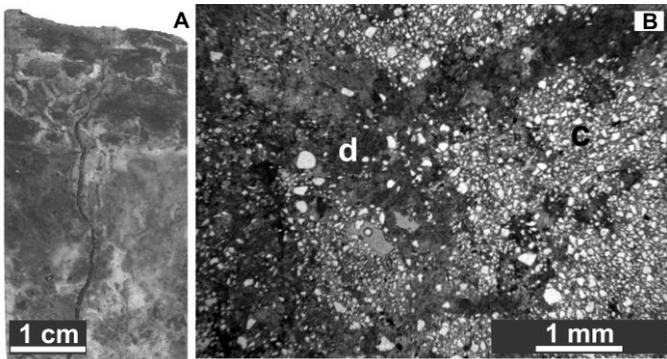
Mineral composition and microstructural features that gave evidence of subaerial weathering during the Burtneiki and Amata times were found in both studied sections at the Veczemji Cliffs and at the Vizuli Outcrop.

Massive dolocretes 2.5 m below the boundary of the Amata Formation and the Płaviņas Formation had a well-expressed veiny structure throughout the whole horizon (Fig. 4). Dolomite veins are densely distributed within clayey fine-grained sandstone in the lower part of the horizon and within siltstones in the upper part of the horizon. This kind of dolomite cement was the reason of the high mechanical resistance of massive dolocretes.

Dolomite cement is distributed in a form of branched veins. Separate dolomite veins are elongated and sets of them form subvertical belts (Fig. 4). Formation of veiny structure takes place due to solution, recurrent precipitation and recementation of mineral material [9]–[11], [15]. Migration of carbonate solutions could be possible due to the infiltration of meteoric waters and their downward movements. Another possibility is upward percolation of waters from phreatic zone within capillary fringe zone.

Elongated dolomite veins which in the upper part of the horizon branched subvertically gave evidence of upward movements of carbonate solutions and their percolation through to the capillary fringe zone. However, presence of thin subhorizontal belt (0.5 cm thick) with features of initial fine-laminar structure in the uppermost part of the horizon as well as honeycomb structure on the surface of the horizon indicated vadose zone settings for development of massive dolocretes.

Honeycomb structure appeared as roundish 1–2 mm wide dolomite veins with 0.5–1 cm wide deepening filled with clays. Both fine-laminar and honeycomb features characteristically form in vadose zone within pedogenic calcrete horizon [8], [9], [11], [13].



Legend: d - dolomite,
c - silty material (quartz, feldspar, mica, illite)

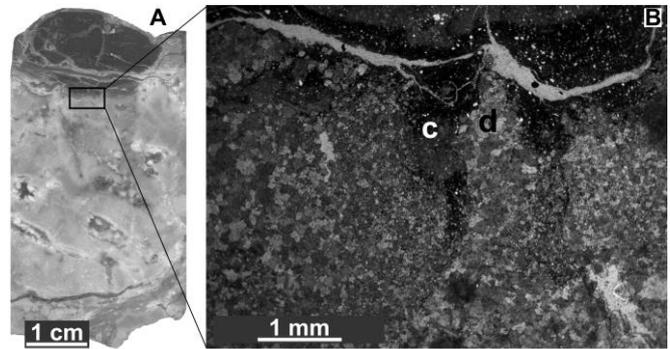
Fig. 4. Structure of the massive dolocrete horizon, sample V.16: (A) linear, radial and circumgranular cracks filled with dolomite cement, polished section, dolomite veins are subvertical in the middle to the upper part of horizon and branched in the upper part of horizon; (B) radially branched cracks filled with medium-crystalline dolomite in siliciclastic deposits with dolomite cement, thin-section, plane-polarised light.

As it is well seen in the thin-sections, the siliciclastic deposits were crossed by medium-crystalline dolomite veins. These veins of dolomite were irregular, radially branched, as well as circumgranular (Fig. 4). Radial veins point to migration of carbonate solutions in radially developed desiccation cracks [8], [11]. Circumgranular cracks are characteristic of calcretes and dolocretes that have pedogenic origin and of well-developed soil profiles [11], [16].

Horizon of nodular dolocretes lay in clayey siltstones 1.5 m below the boundary of the Amata Formation and the Pļaviņas Formation. Matrix of dolomite nodules there consisted of very fine-grained sandstones and siltstones cemented with dolomite. Dolomite nodules were crossed by irregular net of dolomite veins thereby having a veiny structure (Fig. 5). Micro-karst features on the surface of the dolomite nodules were recognized in thin-sections. Roundish honeycomb structures on the surface of the same nodular horizon (Fig. 3) were found during the field works. These structures indicate subaerial exposure during formation of the nodular horizon [8], [9], [11], [13], [17].

In the uppermost part of a dolomite nodule (sample V.12), which is included in clayey host, a deep filled with red clays was present (Fig. 5). In thin-section it was recognized that downwards from clay-dolomite boundary dolomite was notched and elongated micro-karst pockets with steep edges were present. Micro-karst pockets in dolomite were approximately 0.5–1 mm wide and 1–2 mm deep. These structures are filled with clayey material. Close to the edges of the karst pockets as well as below them dolomite was micro-crystalline, but downwards its crystal size increased to fine-crystalline. Supposedly, this change of crystal-size was related to dolomite recrystallization processes during later diagenetic

stages: in places where dolomite was purer recrystallization developed more intensively, while near the karst pockets clay admixture confined the processes of recrystallization of dolomite.



Legend:
d - dolomite, c - clayey material (quartz, mica, illite)

Fig. 5. Microkarst features on the surface of dolomite nodule, sample V.12: (A) polished-section of the dolomite nodule with pocket-like depression filled with clays; (B) karsted area in thin-section — microkarst pockets (dark parts) filled with clays in the dolomite matrix.

Karsted surface of dolomite nodules gave evidence of subaerial exposure of horizon of nodular dolocretes and influence of meteoric waters on deposits [17]. Downwards-circulating waters in vadose zone favoured dissolution of dolomite cement, leaching of siliciclastic material in dissolved cavities and recrystallization of carbonate minerals.

Dolomite solution features also occurred elsewhere in the section of the Vizuļi Outcrop. It was recognized in SEM microphotographs that cavities filled with detritic material in places had developed in massive dolocretes due to solution of dolomite.

Similarly to the deposits of the Burtņieki Formation at the Veczemji Cliffs illite also was the dominant clay mineral in siliciclastic deposits with dolomite inclusions of the Amata Formation at the Vizuļi Outcrop (Fig. 6).

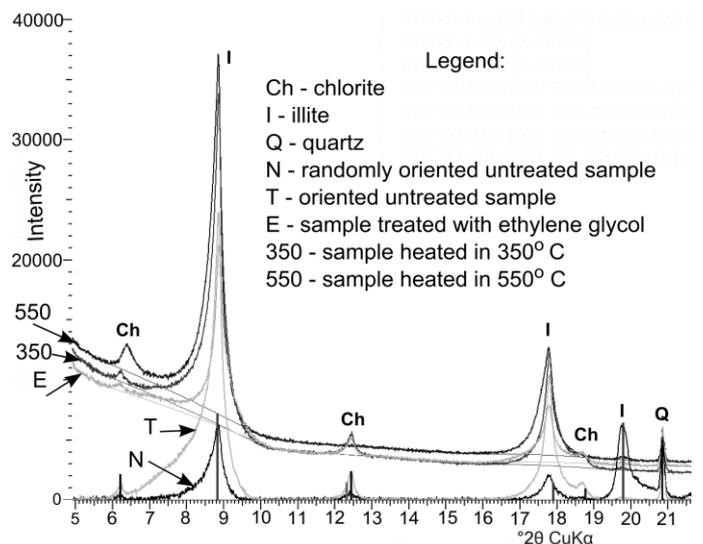


Fig. 6. Composition of clay minerals within clayey matrix in nodular dolocretes at the Vizuļi Outcrop, the Amata Formation, fraction < 4 μm, sample V.11.

Chlorite was recognised in small amount — less than in clays of the Burtnieki Formation at the Veczemji Cliffs, and traces of mixed-layer illite-smectite and kaolinite also could be identified in places. Often monomineral illite represented clay fraction in siliciclastics of the Amata Formation. Such a clay mineral composition according to XRD data was characteristic of the whole succession of the Amata Formation at the Vizūļi Outcrop and it also does not change near dolocretes. Even in nodular dolocrete horizon where karst features were identified, illite with a small amount of chlorite admixture was found in the clayey material which filled the karst pockets.

Origin of illite and chlorite in deposits of the Amata Formation can be explained by weathering of igneous and metamorphic rocks [14] at the provenance. These clay minerals were accumulated during sedimentation as fine detritus.

IV. CONCLUSION

Recurrent drying and wetting processes took place during subaerial exposure episodes when the pedogenic nodular dolocretes formed in the Veczemji Cliffs area during the Burtnieki time. It was indicated by relations of dolomite cement and siliciclastic material in dolomite nodules such as dolomite crystals grown in the clayey matrix, and terrigenous material washed in the cracks of the dolomite nodules. These relationships pointed either to semiarid or subhumid climate or development of dolocretes in fluctuating water table settings. Such changing climatic, hydrologic or hydrogeologic conditions favoured *in situ* weathering of clayey host deposits and siliciclastics, formation of cracks in the dolomite nodules as well as washing-in of weathered material into these cracks.

Dolocretes of the Amata Formation at the Vizūļi Outcrop were polygenetic, because they formed both in groundwater and in vadose zone settings. The lower part of the studied succession deposits contained incipient and groundwater dolocretes, but the upper part had distinct features of subaerial exposure. These subaerial exposure features were identified in two levels of the section — in the massive dolocretes 2.5 m below the boundary of the Amata Formation and the Pļaviņas Formation and in nodular dolocretes 1.5 m below this boundary. Desiccation cracks filled with dolomite cement and dolomite dissolution structures filled with weathered fine-grained terrigenous material gave evidence that pedogenic dolocretes of the Amata Formation also were formed during repeated drying and wetting processes. These processes took place during subaerial exposure times in changing semiarid or subhumid climate or in fluctuating groundwater table settings. Homogeneous composition of clay minerals in siliciclastics throughout the whole succession of dolocretes pointed to relatively small duration of the subaerial exposure episodes.

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Daiga Pipira, Juris Kostjukovs, Ģirts Stinkulis. Devona Burtņieku un Amatas svītas dolokrētu minerālais sastāvs un morfoloģija Latvijā.

Latvijā plaši sastopamie devona Burtņieku un Amatas svītas klastiskie nogulumi (smilšakmeņi, aleirolīti un māli) daudzviet satur dolomīta ieslēgumus. Šo dolomīta veidojumu izplatība ģeoloģiskajā griezumā, morfoloģiskās īpatnības un minerālais sastāvs norāda, ka tie ir dolokrēti, kas veidojušies virszemei tuvos apstākļos subaerālās atsegšanās epizodēs Burtņieku un Amatas laikposmos. Mālainas Burtņieku svītas slāņkopas augšējo daļu Veczemju klintīs veido pedogēnas izcelsmes brekčijveida dolokrētu horizonts: mālainajos nogulumos izplatītas iegarenas un V-veida dolomīta konkrēcijas ar dzīslainu iekšējo uzbūvi, radiālām un riņķveida žūšanas plaisām, kas aizpildītas ar rupjkristāliska dolomīta cementu vai plaisās ieskalotu aleirītiski mālainu dēdējummateriālu. Amatas svītas smilšaini mālainajos nogulumos Vizuļu iezī vairākos līmeņos izplatīti dažādi dolomīta veidojumi — plātņainie, masīvie un brekčijveida dolokrēti. Amatas slāņkopas apakšējā daļā iegulošie dolomīta veidojumi atbilst gruntsūdens dolokrētiem: dolomīta veidojumi ir vāji vai vidēji konsolidēti, tajos saglabājušās klastisko nogulumu primārās sedimentācijas tekstūras, kā arī dolomīta cements izplatīts plātņu veidā. Virzienā uz Amatas slāņkopas augšu dolomīta veidojumi iegūst arī pedogēnas izcelsmes dolokrētiem raksturīgās pazīmes: masīvo dolokrētu horizontā nogulumiem ir dzīslveida uzbūve, riņķveida žūšanas plaisas, sākotnējo sīkslāņoto tekstūru pazīmes, kā arī šūnveida dolomīta tekstūras; brekčijveida dolokrētu horizontos sastopamas šūnveida dolomīta tekstūras mālainajos nogulumos, dolomīta konkrēcijas ir ar dzīslveida iekšējo uzbūvi, kā arī mikrokarsta pazīmēm uz konkrēciju virsmas. Šo pazīmju kopums Amatas svītas slāņkopā norāda uz dolokrētu veidošanos gan gruntsūdens, gan aerācijas zonā. Burtņieku un Amatas svītas dolokrēti veidojušies subaerālās atsegšanās epizodēs atkārtotu žūšanas un samirkšanas procesu ietekmē mainīgos semiarīda un subhumīda klimata apstākļos vai arī mainīga gruntsūdens līmeņa režīmā.