Cyanobacterial origin and morphology of the Volkhov hardgrounds (Dapingian, Middle Ordovician) of the St. Petersburg region (Russia)

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ABSTRACT - Hardgrounds (substrate produced by synsedimentary lithification of marine sediments exposed on the sea floor) of the Volkhov Regional Stage (Middle Ordovician, Dapingian) in the east of the St. Petersburg region (Russia) are studied. Surface hardgrounds are formed due to accumulation of micrite by calcite-cyanobacterial biofilms, inferred from the presence of small irregularly round-shaped structures (diameter 1-3 cm) produced within the hardground by bubbles of gas accumulated below the seafloor, covered by microbial films or mats. SEM study of the hardgrounds supports this hypothesis and shows numerous mineralized structures reflecting biological activity of microbes. These are mainly represented by a mineralized extracellular polymeric substance coating numerous calcite grains, usually 5-15 µm thick. The composition of the calcite grains lacks significant admixture of additional elements. In the mineralized extracellular polymeric substance, the composition is considerably more complex. The predominantly cyanobacterial composition of the microbial community shows the presence of characteristic sheaths and filaments coated with an extracellular polymeric substance and forming an entangled network of filaments. The initial thin biofilms (a few mm) for hardgrounds could have been intermediate in form between cyanobacterial films and mats, thick enough to be classified as mats, despite its characteristic vertical zonation is lacking. They can be interpreted as "immature" or "incipient" mats.

INTRODUCTION

Hardgrounds are substrates produced by synsedimentary lithification of marine sediments exposed on the sea floor (Wilson & Palmer, 1992). The Ordovician hardgrounds were rapidly inhabited by diverse encrusters and burrowing organisms (Guensburg, 1992; Rozhnov & Fedorov, 2001; Rozhnov, 2002; Wright & Chems, 2016). Therefore their widespread distribution considerably influenced the number, diversity, and evolution of these faunal groups. They equally strongly influenced the processes and depth of bioturbation, and consequently the development of infauna. Hence, the study of hardgrounds and their effects on the diversity and development of marine communities are an important focus of scientific research. It has now become widely accepted that in the Ordovician, as in other so-called "calcite sea" periods, hardgrounds were formed due to the rapid precipitation of inorganic cement in the shallow-water carbonate deposits from pore solutions, which were saturated with calcium carbonate due to dissolution of aragonite shells and other skeletal remains (Wilson & Palmer, 1992; Palmer & Wilson, 2004; Vinn et al., 2015).

However, the study of the hardgrounds of the Middle Ordovician Volkov Regional Stage of the St. Petersburg area in Russia (Fig. 1) showed that microbial films largely influenced the formation of many hardgrounds. This paper further explores the hypothesis recently proposed by Rozhnov (2016).

MATERIALS AND METHODS

This paper is based on samples of hardgrounds with encrusters and burrowing traces from the eastern St. Petersburg region (Fig. 1): 1) in the section of the
Putilovskie Lomki from the Volkhov-Billingen boundary beds ("Steklo" hardground); 2) in the sections of the Putilovskie Lomki Quarry and a quarry near the village of Babino from the boundary of the Lower ("Dikari") and Middle ("Zheltifikasi") substages of the Volkhov Regional Stage ("Butok" hardground); 3) from a section of an undivided Volkhov Regional Stage in a bioherm near the village of Simonkovo on the right bank of the Volkhov River.

The surface of slabs with hardgrounds and their lateral polished surfaces were photographed using a mirror camera. Small pieces were freshly broken off, coated with gold-palladium, and examined at 20 kV on a scanning electron microscope Zeiss Evo 50 (Carl Zeiss, Germany) equipped with an Inca-450 EDX system (Oxford Instruments Analytical, UK).

THE ROLE OF MICROBIAL MATS AND FILMS IN THE DEVELOPMENT OF VARIOUS SEDIMENTARY STRUCTURES IN MARINE DEPOSITS

Microbial films and mats are widely developed on the bottom of the shelf in the photic zone in the tidal zone of modern seas. Microbial mats represent organic sheets up to several centimetres-thick, often covering large areas of the shelf and the tidal zone. This sheet is composed of entangled webs of filaments of trichome organisms submerged in mucus, with layers of minerals. Microbial mats are complex ecosystems with tightly adjusted components. They are dominated by cyanobacteria occupying the uppermost layer of the mat, 1-2 mm thick, which almost completely absorb the sunlight. Cyanobacteria of this layer are responsible for the mat structure and are the main producers of organic matter. This layer is underlain by a layer inhabited by other phototrophic bacteria, and beneath that there is a layer generally dominated by anaerobic sulphate-reducing bacteria. The layered structure of the mat with an alternation of layers with different microorganism groups is associated with geochemical barriers and mineral formation. Bacterial mats are responsible for the development of stromatolites, particularly numerous in the Precambrian. Stromatolites have a characteristic laminar structure of paired light-dark laminae, interpreted as alternating organic and mineral layers. They were usually formed in warm seas with carbonate sedimentation and with no bioturbation. Therefore at present they are usually formed in extreme environments, where metazoans can hardly survive (Rozanov, 2002).

Biofilms developing as thin layers on the substrate surface and coating particles within sediments are
similar to microbial mats. The microbial films are mainly composed of cyanobacteria. They are considerably thinner than mats and have no vertical lamination. Growing microbial films coat grains of sediment and excrete microbial extracellular polymeric substances (EPS), which hold the sediment and the biofilm together. As a result of this cohesive effect, the sediment is stabilized preserving the texture of the sandy surface, e.g., ripple marks that remain for a long time after the flow of water is settled. Later, due to the presence of this cohesive substance the ripple patterns may remain in fossil state. Microbial films and connected microbiially induced sedimentary structures are characteristic of cold-water seas with predominantly siliciclastic sedimentation (Noffke, 2010).

The extracellular polymeric substances (EPS) represent a complex high-molecular-weight polysaccharide matrix, which can include proteins and peptides, other organic compounds, and also inorganic compounds, such as sulphates and phosphates. It forms a matrix around the microbial cells, integrating the bacterial mat into a single structure. The EPS serves as a template for carbonate nucleation and a key component of organomineralisation along with the alkalinity engine (see Dupraz et al., 2009 for review). This facilitated quick mineralization of the EPS by precipitating carbonate. This process can be active (biologically induced) or passive (biologically influenced). During active carbonate precipitation, the degradation of the labile fraction of the EPS matrix can liberate calcium bound to the polymers, and can also increase the alkalinity. The simultaneous increase in the calcium concentration and the alkalinity results in biologically-induced mineralization, which is important in the formation of marine stromatolites.

Passive mineralization is associated with biological influence and occurs when all functional groups of polymers are occupied with bound cations, and a combination of alkaline conditions and the presence of free Ca$^{2+}$ ions can lead to nucleation of calcium carbonate on the EPS matrix. This process can be important for formation of minerals mediated by non-living organic substrate when the precipitation is no longer inhibited by formerly living EPS. All these processes can occur very rapidly, hence well-preserved mineralized sheaths of filaments and the EPS structures retaining pores and channels can frequently be observed microscopically (Konhauser & Riding, 2012).

Stromatolites produced by microbial mats are formed in warm basins with well-developed carbonate precipitation and sedimentation. Microbial films and sedimentary structures induced by them are characteristic of cold-water seas with mainly siliciclastic sedimentation (Noffke, 2010). The Ordovician Baltic Basin was cold during Volkhov time, but with carbonate sedimentation (Dronov & Rozhnov, 2007). The resulting microbially induced sedimentary structures had specific features, primarily observed in characters of hardgrounds.

HARDGROUNDS IN THE MIDDLE ORDOVICIAN OF THE ST. PETERSBURG REGION AND THEIR FEATURES

Hardgrounds of the Volkhov Regional Stage in the eastern St. Petersburg region (Fig. 1) are unusual in that they were densely populated by attached and burrowing organisms (Figs 2-3). These are primarily burrows of...
Trypanites, attached bryozoans Dianulites and various holdfasts of crinoids and other stalked echinoderms (Fig. 2). They are widespread in the section of the Volkhov Regional Stage of the St. Petersburg region and northern Estonia and are represented by two types. Hardgrounds of the first type do not exactly fit its definition, as they were not synsedimentary but were formed within the sediment slightly later. They became hardgrounds after the overlying layer of soft substrate was eroded and the hard substrate lithified within the sediment as a result of calcite precipitation from pore solutions was exposed on the seafloor. These hardgrounds have calcite detritus of varying size and origin. This type of hardground is not discussed further in this paper, because its formation was not directly associated with the surface cyanobacterial films and mats.

The second type is not connected with the erosion and was formed immediately on the substrate surface synchronously with the sedimentation. It can be subdivided into two subtypes. The first subtype marks
a sedimentary gap and is traced over areas of hundreds of kilometres. A good example is the surface of the hardground referred to as “Steklo” by quarry workers (Fig. 3). This surface coincides with the Billingen-Volkhov boundary. The second subtype is found in bioherms of uncertain origin, and in surrounding facies. These bioherms crop out in quarries and cliffs along the Ladoga glist. They take the shape of low, rounded humps, with clay covered by micrite limestones with hardground surfaces, bearing numerous attachment structures of bryozoans and echinoderms (Fig. 2), for example a bioherm hardground near the village of Simonkovo on the right bank of the Volkhov River.

These bioherm humps were first studied and described by Vishnyakov & Hecker (1937), and in the last decade have been studied by A.Yu. Ivantsov, A.V. Dronov and in particular detail by P.V. Fedorov (see Dronov & Ivantsov, 1994; Fedorov, 1996, 2000, 2002; Fedorov & Dronov, 1998). These authors suggested that these bioherms were formed by colonies of demersal sessile filtrators, e.g., brachiopods (Dronov & Ivantsov, 1994) or sponges (Fedorov, 2002). Fedorov (2002) discussed in great detail all hypotheses of the possible origin of these bioherms. He considered them as metabolic products of sponges, whose spicules are occasionally present in the clay. He also criticized the theory that they were produced by bacterial mats, since the deposits contained no stromatolites - the products of their metabolism.

The hardgrounds of the second type were produced by slow carbonate precipitation of carbonate cement from the pore water, the material for which came from the dissolving aragonite of mollusc shells (Wilson & Palmer, 1992; Palmer & Wilson, 2004). Traces of this dissolution can indeed be observed in the section of the Regional Stage on the originally aragonite shells of cephalopods. The possibility of purely chemogenic precipitation of calcite from the pore water, and more so from the marine water at the water-sediment boundary in cold seas, is doubtful because of temperatures unsuitable for this precipitation. Therefore, cementation of the surface hardground could not have happened without the microbial component. A microbial origin of the hardgrounds of the second type is suggested by small, diameter 1-3 cm, often irregularly round-shaped structures in the hardground of the first type, e.g., on the “Steklo” (Fig. 3), and also on the hardgrounds of the bed nicknamed “Butok” by the quarry workers. If the edges of the round-shaped structures in the “Steklo” hardground were smoothened by a small erosion, the window edges on the “Butok” hardground near a bioherm from a quarry near the village of Babino were raised upwards (Fig. 4). It can be suggested, therefore, that these windows were caused by the tearing of the thin mat by bubbles of gas, accumulating beneath the film of the mineralizing mat. The formation of such hardgrounds and development of such “windows” could happen when the bottom was covered by bacterial films or bacterial mats. This hypothesis of the cyanobacterial origin of hardgrounds can be tested by SEM observations of the bacterial traces in the hardgrounds.

SEM-EDX STUDIES OF HARDGROUNDS

SEM-EDX study of hardgrounds revealed numerous mineralized formations, the origin of which is associated with microbial activity, primarily of the mineralized EPS coating small calcite grains usually 5-15 micron in size (Fig. 5). The composition of the mineralized EPS is considerably more complex. Apart from calcium, carbon, and oxygen, here there is significant admixture of silicon, aluminium, iron, magnesium, potassium, and titanium (Fig. 5). These data suggest that calcite grains, after having reached the seafloor, were immediately encrusted with cyanobacterial films that excreted the EPS, which amalgamated them into an integrated substance. The EPS absorbed many elements from the environment, primarily calcium, magnesium, iron, silicon, which, as the organics degraded, formed the first complex organomineral compounds, and were later completely mineralized, by cementing calcite grains into hardground. The predominantly cyanobacterial composition of the microbial communities shows the presence of characteristic sheaths of filaments surrounded by EPS (Fig. 6) or forming an entangled web of filaments.
Apart from the sheaths, filaments, and EPS, there are also mineralized remains of other bacteria, e.g., coccoid colonies and sheaths of elongated forms.

**DISCUSSION**

The micritic size of calcite bioclasts coated by calcite carbonate cement, with a considerable admixture of many elements and lacking microlamination and vertical biogeochemical zones in the examined hardgrounds, suggests that they were produced by metabolic activity of extremely thin cyanobacterial mats or extremely thick cyanobacterial films. The depth of the solidifying biofilm on the seafloor surface is estimated to be close to the first millimetres by the thickness of the raise edges of the windows ripping through its surface. This suggests the intermediate state of these formations between the bacterial films and mats, with a thickness sufficient to call them mats, but without vertical zonation always found in mats. These formations are probably “immature” or “incipient” mats. Bacteria excreted the EPS, which trapped the precipitating small calcite grains and more rarely larger bioclasts. In places, chemogenic calcite in shape of small crystals precipitated in the cavities of the former cyanobacterial mat, but their role in the hardground formation is not significant (Fig. 7). A small amount of chemogenous carbonates in the hardground cement was associated with the cold temperatures of the basin in the Volkhovian time (Dronov & Rozhnov, 2007), which prevented precipitation of chemogenous carbonates from sea water in substantial quantities. In warm carbonate seas with a large proportion of peloid material were probably formed on the slopes of this clay core around sponge colonies. An increased sedimentation rate in places led to the decline of the microbial community resulting in the patchy distribution of the hardgrounds around mounds and their alternation by the EPS. The bioclasts were primarily produced by echinoderms and bryozoans which abundantly inhabited the hardgrounds of shallow-water mounds.

Environmental conditions that need to be met for such a large area of the sea substrate to be covered by incipient mats include: sufficient illumination, a prolonged period of calm environment, and the absence of strong bioturbation. Hence, it is possible that the development of large cyanobacterial mats on the seafloor occurred as the sea level increased, to levels below storm wave base but still shallow enough to allow sufficient illumination, e.g., 30-40 m. It is also possible that during epochs of widespread distribution of bacterial mats in a basin, long episodes of stagnation resulting from mixing of seawater were also possible. The presence of such incipient mats would preclude settlement of many benthiic animals. These episodes, apparently, were very short, possibly a few years or less. This was sufficient time for thin layers of high EPS-substrate to settle over large areas of seafloor and rapidly mineralize to form a hardground. The demise of the microbial community of these incipient mats could result from a fall in sea level and the onset of a high-energy environment. The so formed hardground was colonized by burrowing organisms *Trypanites*, bryozoans, and stalked echinoderms. The presence of small irregularly round-shaped structures, sometimes with raised edges, in the studied hardgrounds suggests the possible accumulation of gas beneath the solidifying hardground. This hypothesis can profoundly change our understanding of biota beneath hardgrounds and its early diagenesis.

The formation of bacterial mats of bioherms occurred in the similar way. This supports Fedorov’s (1996, 2000, 2002) hypothesis that the clay core of the mound was formed by the deposition of fine sediment around sponge colonies. Microbial mats trapping and consolidating small calcite particles and sometimes large quantities of peloid material were probably formed on the slopes of this clay core around sponge colonies. An increased sedimentation rate in places led to the decline of the microbial community resulting in the patchy distribution of the hardgrounds around mounds and their alternation...
with soft substrates. This resulted in mosaic pattern of faunal communities abundantly colonizing hardgrounds left behind by declined microbial mats and avoiding live mats where their larvae could not survive. The settlements of echinoderms and bryozoans supplied abundant calcite detritus, partly reworked in the high-energy environments near the bioherm mounds. These tiny calcite bioclasts rapidly accumulated on the surface of the biofilms on the bioherm and over large areas of the seafloor around it.

CONCLUSIONS

The micritic composition of calcite grains and their spatial arrangement in the carbonate cement with considerable admixture of many elements in a thin surface layer of hardgrounds, the presence of many mineralized bacterial remains and traces suggest a leading role of the cyanobacterial mats in the formation and consolidation of the Middle Ordovician hardgrounds in the eastern Baltic Paleobasin. It was probably a specific kind of thin bacterial mats, which produced deposits lacking noticeable vertical zonation or microlamination. These mats and resulting hardgrounds could only develop in cold seas with carbonate sedimentation. In warm carbonate seas, with a large input of chemogenous carbonate precipitation, this niche was occupied by stromatolites, whereas cold seas with siliciclastic sedimentation supported formation of various microbially-influenced sedimentary structures.

The development of microbial mats over large areas of the seafloor of the Middle Ordovician Baltic Paleobasin and formation of the associated hardgrounds probably occurred at depth of 30-40 m in a low-energy environment. These mats were formed very rapidly and were probably not long-lived, perhaps lasting no more than a few years. Their mineralization and decline were followed by the development of hardgrounds, which were rapidly colonized by stalked echinoderms, bryozoans and burrowing organisms.

The development of hardgrounds on and around bioherm mounds occurred in the shallower water and was mosaic due to the live cyanobacterial mats alternating with mineralized mats and replacing them with hardground. Organisms inhabiting the bioherm hardground supplied carbonate detritus, including that of micritic size, over large areas of the seafloor surrounding the bioherm mounds.

It is possible that gas accumulated beneath bacterial mats, with bubbles in places rippling through the cyanobacterial mat forming small irregularly-shaped structures. Therefore, hardgrounds were not only biotopes for a unique community of attached and burrowing animals and plants but also an important, albeit poorly studied, factor in the development of biota beneath the mats, certainly contributing to the early diagenesis of the sediment. The study of the infaunal traces and of the entire biota of the sediment beneath the hardgrounds warrants further paleoichnological research.

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