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Neoproterozoic microbially-induced sedimentary structures (MISS) from Ediacaran Podillya Basin, Ukraine: mineralogical particularity and paleoenvironmental application

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Abstract. The Neoproterozoic Podillya sedimentary Basin is well known to the imprints of the Ediacaran soft-bodied fauna which were previously described by many ukrainian and foreign authors. At this period, fossil-rich siliciclastic sediments recognized as traces of early metazoans also contain evidence of significant microbiological activity. In these ediacaran sediments, many structures can be interpreted as microbially induced sedimentary structures (MISS). Their morphologies have a great similarity with modern structures observed in relation with micro-organism activity. These specific structure and surfaces and their mineral composition are the criteria used to study the bacterial structures from the ukrainian Neoproterozoic sedimentary basin. Our results demonstrate microorganisms were organized in bacterial mats whose activity was recorded in the difference of mineralogy between biological films and host rocks. On outcrop, the different type of MISS are often associated with lenticular beddings, ripples and hummocky cross structures indicative of coastal-marine conditions close to the littoral zone of the basin at this epoch. If MISS are important in the issue of paleogeographic reconstructions, they also give precious informations about early diagenetic processes, syn- and post-sedimentation. By mineralogical approach we show that during the time of development of MISS structures and the burial that followed the diagenetic processes have remained moderate. Finally, the close coexistence with ediacarian fossils suggest that such bacterial mats could be at the origin of the fossilization process of soft-bodies of enigmatic Ediacaran biota of Mohyliv-Podylska Group and their preservation until today.

Key words: Neoproterozoic, Ediacara, Vendian, MISS, bacterial activity, siliciclastic rocks

Неопротерозойські мікробактиріальні осадові структури (MISS) з Подільського басейну України: мінеральні особливості та палеокліматичне застосування

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Анотація.Неопротерозойський басейн Поділля добре відомий у світі завдяки відбиткам м'якотілої фауни едіакарського типу, які раніше були описані багатьма українськими та зарубіжними авторами. Кремнеземисті відклади неопротерозойського часу цього осадового басейну, окрім наявності макро-біоти, містять докази значної мікробіологічної активності. У цих осадових відкладеннях багато структур можуть бути інтерпретовані як бактеріальні осадові структури (MISS). Їх морфологія подібна до сучасних структур, що спостерігаються у безпосередній близькості з мікроорганізмами. Специфічна будова у поперечному розрізі, характер нашарування та мінеральний склад - ці критерії використовувалися у даній роботі для опису та аналізу бактеріальних структур з неопротерозойського осадового басейну в Україні. Наші результати показують, що макроорганізми були організовані в бактеріальних матах, активність яких була зафіксована в різниці мінерального складу між бактеріальними плівками та вміщуючими породами. На відслоненнях наявність лінзоподібних текстур, поверхневих текстур брижі та косошаруватих текстур, у комплексі з різними формами бактеріальної активності у Волино-Подільському басейні відповідає прибережно-морським умовам, близьким до прибережної зони басейну в цю епоху. Будучи важливим фактором у питанні палеогеографічних реконструкцій, MISS структури також дають цінну інформацію про діагенетичні процеси у товщі, син- та пост-седиментацію. У даній роботі демонструється метод вивчення мінерального складу бактеріальних матів для припущення

інтенсивності діагенезу під час формування MISS-структур; наявність змішаношаруватих глинистих фаз типу іллі т/смектит та іллі т/хлорит вказує, що діагенетичний вплив протягом Могилів-Подільського часу був помірним.
У даній статті описані бактеріальні структури в неопротерозойському осадовому басейні Волино-Поділля під час панування Едіакарської макро-біоти, а також охарактеризовані мінералогічні подібності та відмінності між мікробіальними матами та їх вміщуючими породами у кремнеземистих відкладах Могилів-Подільської серії.

Ключові слова: Неопротерозой, Едіакарська фауна, Венд, бактеріальні мати, осадові породи

Introduction. Microbially-induced sedimentary structures (MISS) occur in siliciclastic, shallow-marine settings throughout the geological record (Noffke, 2009). They develop during growth, metabolic activity, destruction and decay of microbial mats in siliciclastic-dominated environments (Hill et al., 2016). After Buick et al. (1981) and Noffke (2009), six criteria for biogenicity of MISS allow the exact distinction of MISS from similar but abiotic structures: a) they occur in rocks that have not undergone higher than low grade metamorphism; b) in stratigraphic section, they are located at turning points of regression-transgression; c) they appear in relation to the depositional "microbial mat facies"; d) their distribution reflects the average hydraulic pattern in a depositional area; e) the fossilized MISS shapes resemble in geometries and dimensions to modern ones; f) the MISS include microtextures that present, or were caused, or are related to ancient-biofilms and microbial mats. After Grazhdankin (2004), a biotic interaction of MISS could be decisive for distribution of Ediacaran macrobiota.

Since the mid-twentieth century, many recognized sedimentologists (Seilacher, 1946; Logan et al., 1964; Bromley, 1990) began to note that the presence of specific bacterial structures in sedimentary terrigenous rocks indicates a significant effect of biological processes during the sedimentation. Also, a detailed study of MISS-structures in terrigenous sedimentary paleo-basin could be used as an auxiliary factor for the reconstruction of paleo-conditions of sedimentary environments (Noffke, 2009; Hill et al., 2016).

Here we describe microbially induced sedimentary structures from the Volyno-Podillya sedimentary Basin. Identification of these structures is based on the six criteria for MISS biogenicity as outlined in Noffke (2009). In addition to the identification of structures, we analyzed both the mineral composition of the MISS structures and that of their host rocks in order to compare their respective mineralogical signatures. These new geological data provide important additional information on sedimentary processes and the paleo-environment during the Ediacaran period, a prelude to the "Cambrian explosion".

Geological setting. Located on the southwestern outskirts of the Ukrainian crystalline shield (Fig.1), the upper part of sedimentary basin of Podillya is stratigraphically related to the Upper Vendian - by the regional stratigraphic nomenclature, and to the Ediacaran - according to the international stratigraphic scale and confirmed by the recent results in determining the absolute age using bentonite layers from this basin (Soldatenko et al., 2019). The sedimentary cover is represented by the Upper-Ediacaran deposits, subdivided into Mohyliv-Podylska and Kanilivska Groups. In this paper, the lower term represented by the Mohyliv-Podilska Group will be considered in more detail. It is represented by siliciclastic sedimentary rocks affected by metamorphism of very low grade and presenting as such an excellent state of conservation. From bottom to top, this Group consists of three sequences of terranes (Palij, 1976, Velikanov et al., 1983) called: Mohylivska (FM), Yaryshivska (FY) and Nagoryanska (FN) Formations.

The composition of sedimentary deposits is characterized by interbedding of sandstone, siltstone and clayey facies. While MISS structures have been found in most of the Mohyliv-Podilska group, they are mostly abundant in siliciclastic deposits of the Mohylivska Formation (FM) where they overlap cyanobacterial structures very often (Fig. 2). On the other hand, it should be noted that the largest number of representatives of the Ediacaran macro-fauna in the whole Neoproterozoic basin of Volyno-Podillya (Palij, 1976) was detected precisely in the lower part of FM formation. In addition, in silty and clayey deposits (Nesterovsky et al., 2018) of the Nagoryanska Formation (FN) – also characterized by the unique presence in this basin of phosphate nodules (Velikanov et al., 1983; Nesterovsky and al., 2017) - there are also a large number of bacterial structures.

Material and Methods. To identify the bacterial MISS structures of the Volyno-Podillya Basin, we studied fifteen samples of the characteristic facies of the three main previous Formations: sandy-silts and siltstones facies (FM), sandstones and sandy siltstones (FY), claystones and clayey silts facies (FN).

The bulk and clay fraction of MISS-structures and of host deposits were determined by X-ray diffraction in laboratory of University of Poitiers. The bulk analysis was carried out on the material previously crushed and sieved at 50 μm and mounted in randomly ordered powder mode in order to characterize the reflections (hkl) of the minerals.

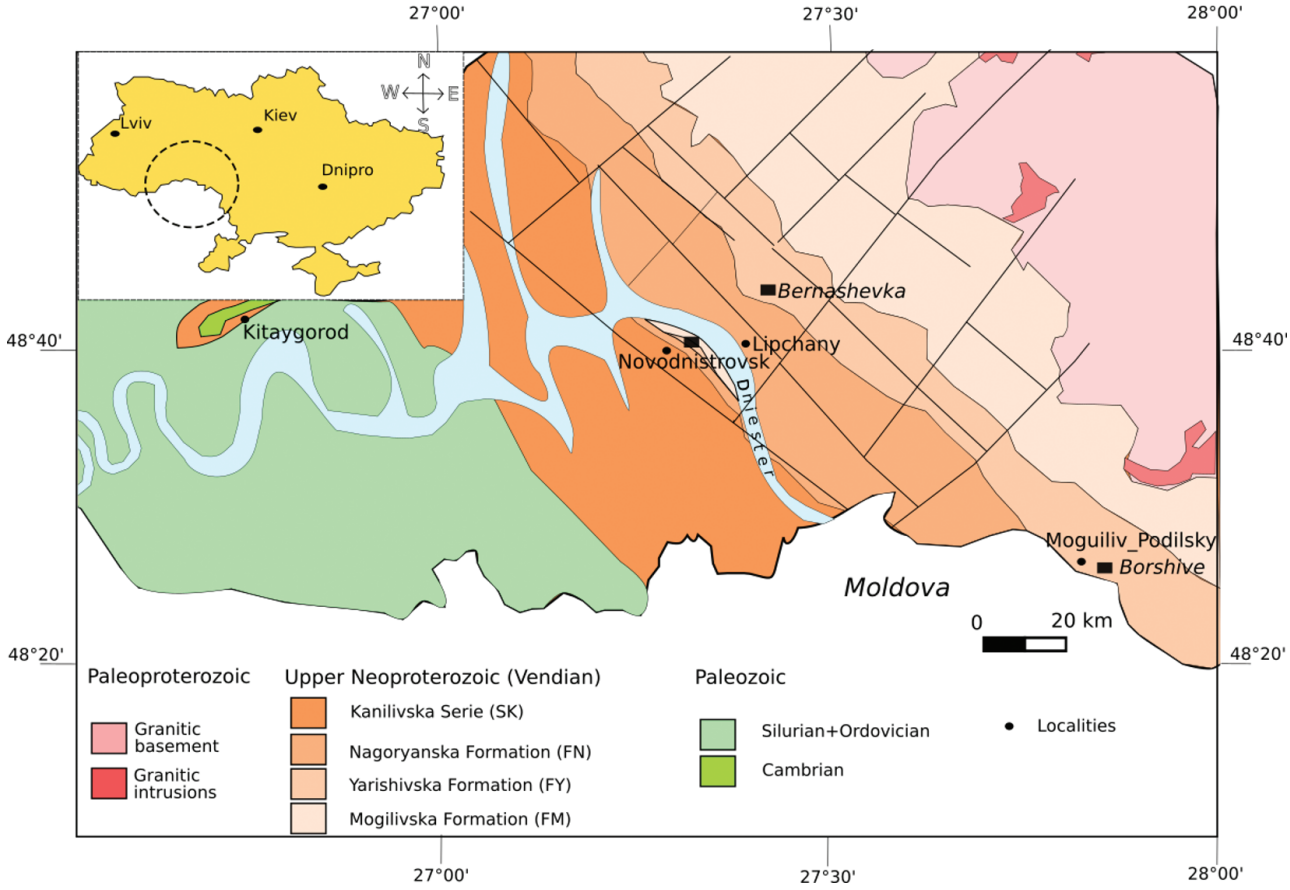

Fig. 1. Synthetic geological map showing the Paleozoic-Precambrian sedimentary cover and the Ukrainian Crystalline Shield.

The mineralogy of the fine fraction was previously separated by sedimentation after dispersion and then centrifugation at 20°C and 1000 s/min during 120 s using a centrifuge JOUAN GR 422. After drying, 15 mg of clay diluted in 1.5 mL of osmosed water and then deposited on a glass slide to study the position of the reflections (00*l*) during the treatments (drying, glycolage) described by Brindley & Brown (1980) et Moore & Reynolds (1989). The X-ray diffractogramme were obtained using a Bruker D8 advance A25 diffractometer, equipped with a copper source (($\lambda_{CuK\alpha}$ = 1.5418 Å) and controlled by the software Diffract Suite© v11.0.8 (2009). Its optical system consists of an anti-divergence slot of 0.11 °2θ, an anti-diffusion slit of 0.11 ° 2θ, two Soller slits and a Kβ filter of nickel. The analytical conditions are 40 kV and 40 mA; acquisition parameters are 1s for a step of 0,025 °2θ for angular ranges of 2-65 °2θ and 2-30 °2θ, in powder and oriented respectively.

Results.

1. Basic characteristics of the bacterial structures from the Neoproterozoic Volyno-Podilsky Basin. Proofs of microbial activity in the Vendian sedimentary rocks of the Volyno-Podillya Basin are found in all terrigenous sediments, starting from the FM and FY Formations in coarse and medium grained deposits of sandstones and sandy siltstone. MISS structures are often associated with imprints of the Ediacaran macrofauna, but very often they can completely form they own surface structures (Fig. 3). In the upper FN Formation, the imprints of typical Ediacaran macrofossils practically disappear, while the presence of microbial structures becomes dominant. By instance, browned silty claystones of this Formation are often covered with a thin microbial layer, which partly determines the wave-like surface of deposits (Fig. 3A, B). Sometimes microbial structures are characterized by brown and greenish-brown shades in layering, and black spots on this surface (Fig. 3C); in other cases, these bacterial structures are characterized by repeating ornaments on the surface of sediments (Fig. 3D). In the vertical section, the microbial mats correspond to thin clayey layers; these layers are most often represented as separate fragments of clay sedimentary material preserved in the sandy siltstone (Fig. 3E, F).

2. Mineral composition of bacterial mats and their host rocks. Five samples from FM, FY, FN Formations were selected for detailed study of the mineral composition of bacterial mats and host rocks (Fig. 4).

The mineral composition of sedimentary deposits containing MISS structures is characterized by the presence of quartz, feldspars and mica minerals; as

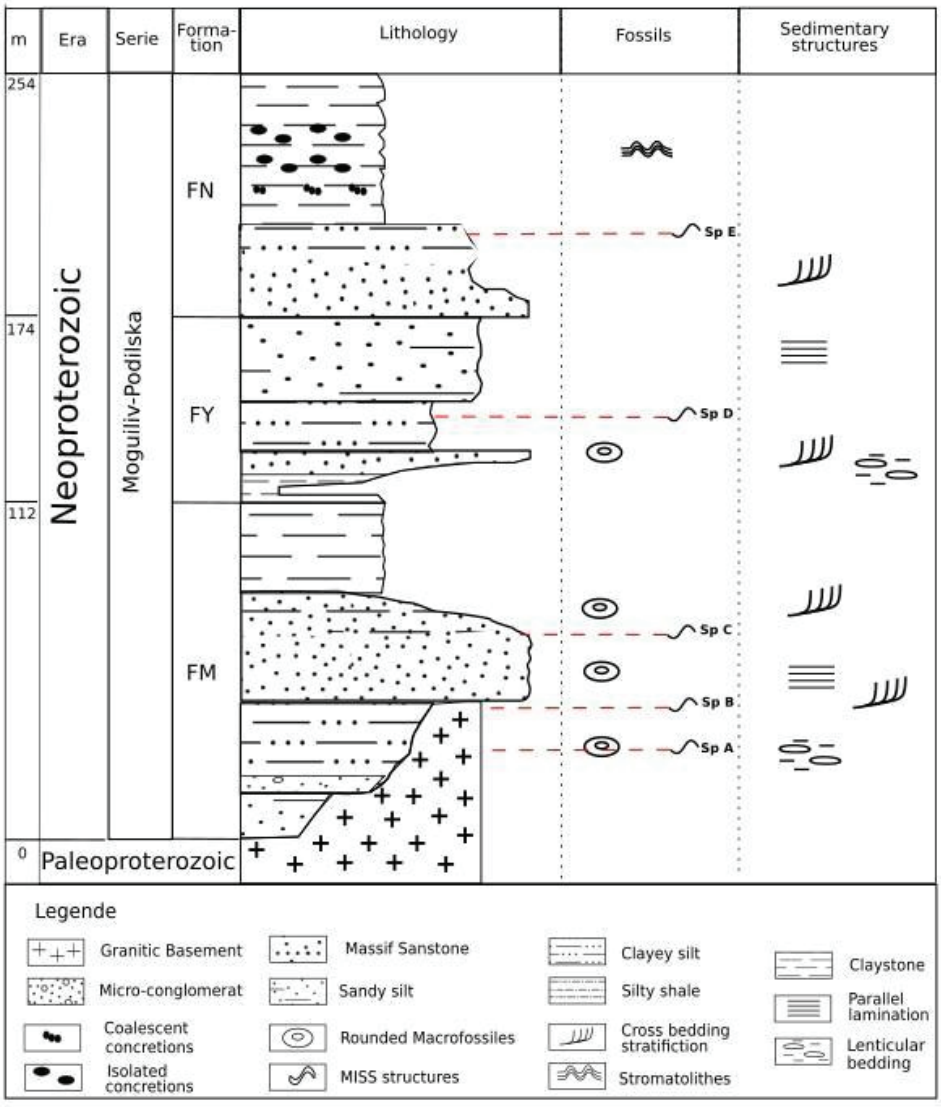

Fig. 2. Stratigraphic column (after Velikanov et al., 1983, Bratslavsky et al., 2008) showing the lithological succession in the Moguiliv-Podilska Neoproterozoic Series of Southern Podolya basin, and detailed locations of sampling for this work (Sp A - Sp E).

for clay minerals, the main representatives are illite, chlorite, illite/smectite mixed-layer and sometimes kaolinite, which can be a secondary product of weathering of feldspars. The mineral composition of the MISS structures from those rocks is identical to the qualitative index, however, the peaks of the clay components become much more intense; in addition, mixed-layers become dominant, as indicated by more intense and broad peaks on diffractograms (Fig. 5).

MISS structures in sediments from the FM Formation appear in the form of thin clayey films covering the surface of siliciclastic rocks (Fig. 4A), sometimes coinciding with "wrinkled" surfaces (Fig. 4B, C). For this Formation, sandy siltstone and medium-grained sandstones are gray, greenish with blue shades. The main mineral phases of bacterial structures in these sediments are chlorite (peaks 14.20 Å and 7.08 Å), biotite and illite with a high degree of crystallization, which indicates an acute form of peak at 10,0 Å, as well as a mixed-layer illite/smectite (10.50 Å) (Fig. 5A, B, C). A characteristic feature from FM Formation in two cases - host rocks and their MISS structures - is the presence of a specific mixed-layered phase of illite/chlorite (11.70-12.00 Å and 8.37 Å); in this case, this rare mineral phase is associated with sandy-siltstone, which includes the largest number of imprints of the Ediacaran fossils in the Volyno-Podillya Basin. Finally, other mixed-layer of illite/chlorite-type is almost equal to the percentage of each clay component.

In the FY and FN Formations MISS structures are traced in the form of brown surface films on siltstone deposits of greenish-brown color. By opposite, for the FY Formation, the layering patterns are more typical (Fig. 4D), whereas in the FN Formation bacterial structures manifest themselves as scaly plating, slightly bubbly on their surface (Fig. 4E). If the mineral content of the host rock and MISS structures

Fig. 3. Vendian deposits from sedimentary Formations of Volyno-Podillya basin showing MISS structures on their surfaces: A, B, C - siltstones from FN Formation (48°53', 27°48'); D - sandy silts from FM Formation (48°40', 28°00') ; E, F - vertical section of silty sandstones from FM Formation (48°59', 27°46') whose contain clayey microbial micro-layer.

is compared, in the case of the Sp D, the peaks of chlorite (14.30 Å), mica (10.00 Å) and kaolinite (7.15 Å) are present in both samples, while feldsapths, K as Ca,Na-rich (6.49 Å and 6.38 Å), are completely absent in the mineral composition of the bacterial mat (Fig. 5D). Concerning the illite/smectite mixed

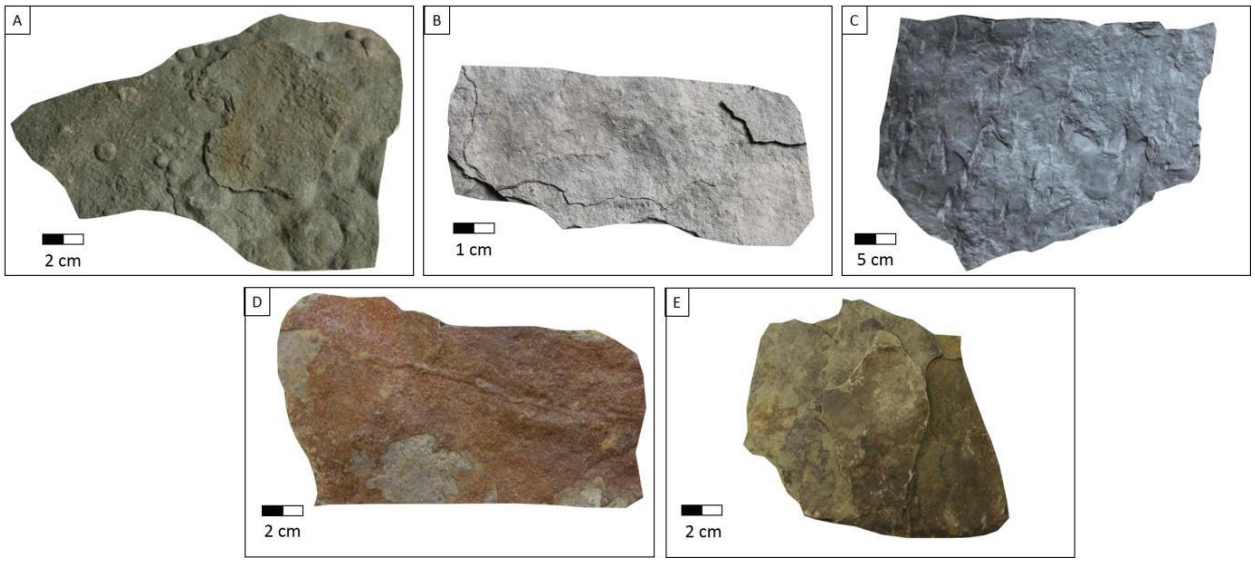

Fig. 4. Samples from Ediacaran deposits selected for mineralogical analysis from sedimentary Podillya basin with MISS structures on their surfaces: A, B, C - sandy silts from FM Formation (48°59', 27°46'); D - siltstone from FY Formation (48°46', 27°78'); E - clayey silts from FN Formation (48°53', 27°48').

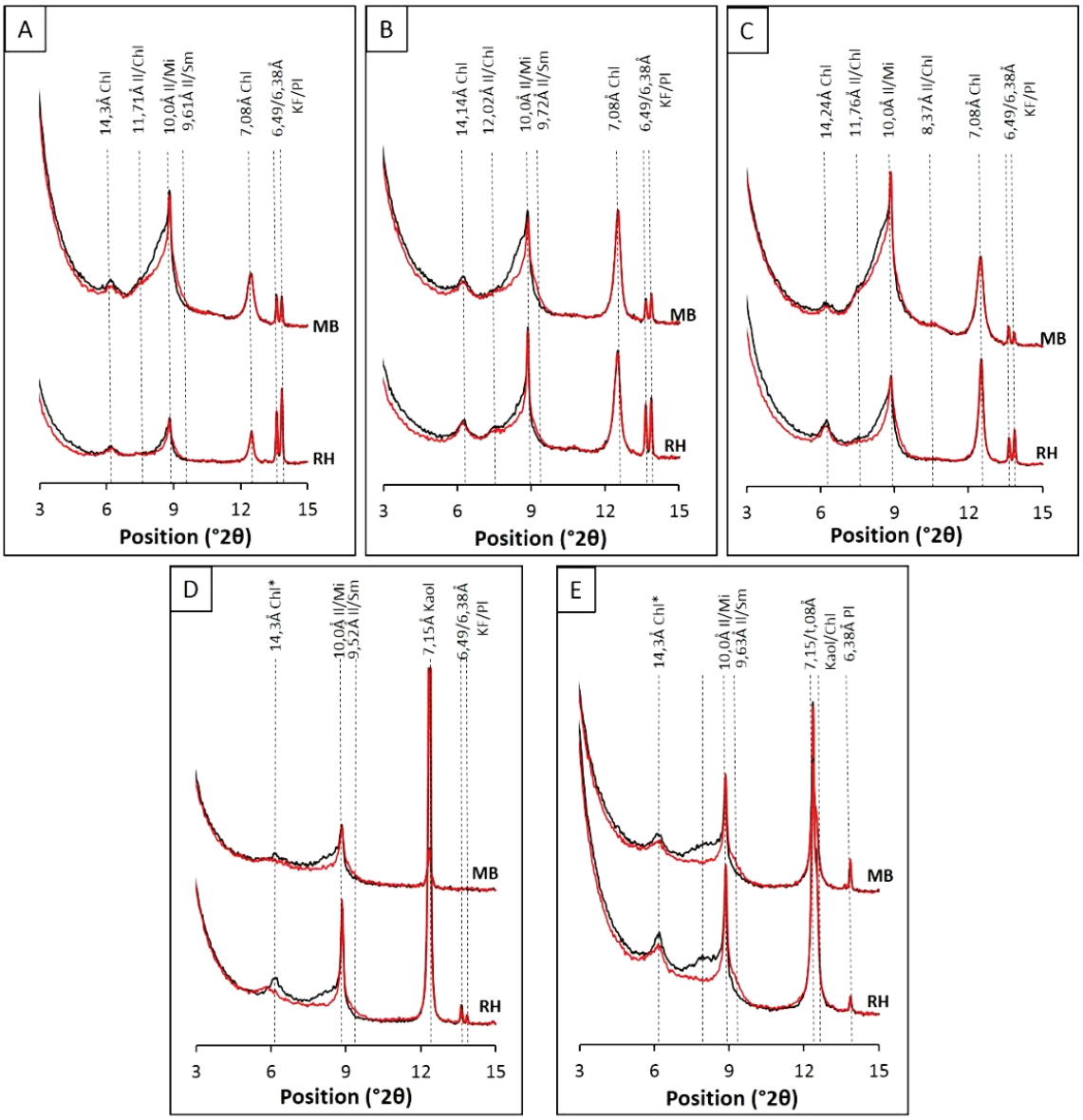

Fig. 5. Diffractogram patterns of bulk sample (oriented preparation) in air dried (black) and ethylene glycol solvated treatment (red) of: A) Sp A from FM Formation; B) Sp B from FM Formation; C) Sp C from FM Formation; D) Sp D from FY Formation; E) Sp E from FN Formation. Identified minerals: (KF) K-feldspar; (I/C) illite/chlorite mixed-layer; (Chl) chlorite; (I/S) illite/smectite mixed-layer; (K) kaolinite; (M) mica; (P) plagioclase.

layer, it is present in samples of the host rocks, and in samples of bacterial mats from the FY and FN Formations (Fig. 5D, E).

In the deposits of whole FM Formation, it should be noted that the shift of the position of the major peak for illite/smectite mixed-layer after ethylene glycol solvation (Fig. 5A, B, C) indicates higher smectite content in the interstratification. On the contrary, the illite/smectite mixed layers of samples from FY and FN Formations show a less significant swelling effect (Fig. 5D, E) indicative of their more illitic character. Finally, the other mixed-layer of illite/chlorite-type, which was characteristic for FM Formation, is no longer present either in the rocks or in the levels of bacterial mats in the deposits of FY and FN Formations (Fig. 5D, E).

MISS structures - mineralogical particularity and paleoenvironmental application. The presence of MISS structures in the siliciclastic sediments of the Volyno-Podillya Basin serves as a reliable criterion for the conditions of sedimentation during the Late Neoproterozoic time. Together with the appearance of numerous sedimentary structures in all Formations of the Mohyliv-Podilsky Group (ripples, HCS), bacterial MISS structures reflect moderately deep basin with an active hydrodynamic regime that corresponds to the coastal-marine conditions of the littoral zone. For assumptions about the depth of this paleobasin, it should be taken into account that bacterial structures could dominate at depths that are within the reach of the photic zone. More generally, the presence of Ediacaran fauna in the basin, and their association

with bacterial structures in particular (Nesterovsky et al., 2018) are also additional indicators of moderate depths and reach of the photic zone.

An important role of bacterial mats could be to facilitate the preservation of external morphological features of macrobiota (Aubineau et al., 2018). Most likely, MISS structures have become a kind of elastic interlayer, composed of clay material. Proceeding from the fact that the sedimentary conditions during the prosperity of the Ediacaran fauna were mostly active and the nature of the sediments was from medium to coarse-grained, the clayey characteristic of bacterial mats became the most suitable for preserving the soft-bodied fauna (Samanta et al., 2015). In the other hand, thanks to the presence of the bacterial mats the process of "biostabilisation" of the siliciclastic rock also took place (Kovalchuk et al., 2017).

Also, bacterial mats can be used as an additional criterion for moderate impact of diagenesis. The mixed layer illite/chlorite was detected in the sediments of that section, which corresponds to the maximum amount of the Ediacaran biota in the Podillya basin. According to Ahn et al. (1988), such a rather rare clay phase as illite/chlorite mixed layer is very sensitive to temperature changes and high pressure actions. Lee and Peacor (1985) also found that the chemical difference between these two phyllosilicates, respectively di- and trioctahedral, would result in a significant mis-fitting at the interface. Therefore, the illite/chlorite mixed layer is structurally unstable, and consequently, it can be saved exclusively in rocks that have undergone the minimal transformations after sedimentation.

Conclusion. MISS structures are of a great importance to determine the state of the bottom environment from the Neoproterozoic sedimentary Podillya basin. There, such structures were distributed in different parts of the littoral zone and at present they characterize the facial conditions of sedimentation.

A good preservation of Ediacaran macrobiota in Podillya basin is mainly due to the dispersed (clayey) substrate composition formed during the development of MISS structures, in combination with their sandy-silty overlapping deposits.

Sediments, in which bacterial structures were buried, did not undergo significant post-sedimentary changes. It is characterized by the presence of illite-smectite and illite-chlorite mixed-layer components in the matrix of these structures.

The study of substrate from the accumulation of microbial mats in conjunction with geological features of coastal-marine lithogenesis (ripples, HCS) provides new opportunities for paleogeographic reconstruction of the basin, in which the first soft-bodied multicellular organisms appeared.

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