Ultrastructures of porostromate microproblematica from a Mulde Event (Homerian, Silurian) bioherm in Podolia, Western Ukraine

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Abstract. The Mulde Event (Homerian, Wenlock) of the Silurian is characterized by a positive $\delta^{13}C$ isotope excursion, a stepwise extinction of the hemipelagic fauna and an increase in non-skeletal deposits thought to be microbial, proliferating in shallow marine environments. There is little known about whether the proliferation of microbialites is due to reduced grazing, increased seawater saturation state or an increase in nutrient supply. We have studied a Mulde Event-associated buildup from the Muksha Formation in Bagovytsya, Podolia, Western Ukraine. This buildup differs from a typical Silurian skeletal reef in its low abundance of rugose and favositid corals. The framework of this reef is dominated by stromatoporoids, heliolitid corals and calcimicrobes, the last ones encrusting the stromatoporoids and shells and also forming oncoids. Several microproblematica are present, including *Girvanella*, *Rothpletzella* and *Hedstroemia*, along with *Ortonella*-like porostromate problematica. This study attempts to further identify the *Ortonella*-like porostromate problematica and *Hedstroemia* through SEM analyses which have revealed a recrystallized structure with microdolomite, indicating an originally high-Mg calcite composition. This suggests a red algal affinity or possibly a microbial origin. Our observations may help to constrain the environmental controls on the development of microbial- and microproblematica-dominated deposits during the Mulde Event.

Key words: microbialite, *Hedstroemia*, Silurian, calcimicrobes, reefs, carbon isotope excursion.

INTRODUCTION

A stepwise extinction during the Mulde Event in the Homerian (Wenlock, Silurian) has been suggested for hemipelagic fauna such as graptolites and conodonts (Jaeger 1991; Jeppsson 1993; Kaljo et al. 1995; Calner & Jeppsson 2003; see also a review in Cramer et al. 2012). This crisis precedes a double-peaked positive carbon isotope excursion. The post-extinction phase is in many areas associated with ecosystems dominated by calcimicrobes and microproblematica (Kõrts 1991; Calner 2005a), interpreted as resulting from impoverished ecosystem structure (Calner 2005a; Kershaw & Da Silva 2013; Jarochowska et al. 2014). Calner (2005b) compared these ecosystems to those developing in the early aftermath of extinction events due to reduced grazing. Jarochowska et al. (2014) associated them with an increase in nutrient supply which allows microbial communities to reach ecological dominance. The presence of microbialites in the early aftermath of carbon isotope excursions has been observed in other Palaeozoic events, such as near the late Silurian Lau Event (Calner 2005b), as well as other mass extinction events such as those in the End-Permian and late Devonian (Radionova

& Einasto 1986; Nose et al. 2006; Kershaw et al. 2007; Mata & Bottjer 2012 and included references). The sedimentary succession discussed in the present study is rich in microproblematica, but as their affinity is not known, we cannot be sure they represent a microbialite. A study by Jarochowska & Munnecke (2014) has shown that *Wetheredella*, an organism previously interpreted as cyanobacterium and proliferating in post-extinction intervals, shows ultrastructural features excluding such affinity. This suggests that inferences on palaeoecology based on assemblages with uncertain affinities may be biased. The goal of this study is, through ultrastructural analysis, to identify the primary $CaCO_3$ mineralogy and crystal habit of some of problematic reef builders proliferating around the Mulde Event in Baltica, and thus gain an insight into whether their calcareous walls were formed through biologically controlled precipitation or by microbial mediation.

GEOLOGICAL SETTING

The samples were collected from the Bagovytsya section (48°36′21.00″N; 26°43′45.50″E), a Homerian

(Wenlock, Silurian) succession exposed in a tributary in the valley of the Dniester River in Podolia, Ukraine (Fig. 1; Jarochowska et al. 2014). The outcrop is exposed in a narrow vertical trench and the geometry of the bioherm is not entirely visible. This succession was deposited on a vast carbonate ramp, which was located in the southernmost part of the Baltic Basin on the southern rim of the Baltica palaeocontinent (Cocks & Torsvik 2005). The carbon isotope record, revealing the Mulde excursion, was published from this locality by Kaljo et al. (2007). A recent study by Jarochowska et al. (2014) provided a detailed sedimentological analysis across the stratigraphic range of this excursion (Fig. 2A).

METHODS

Our samples were collected along a well-exposed, vertical section but with limited lateral extension. For each sample, the way up and metres above a marker boundary were noted. The samples were imbedded with resin for stabilization and cut perpendicular to the bedding. The samples were then polished to better observe the main components. After scanning the polished slabs, samples were selected for thin section production, and after completion were scanned at high resolution for documentation. Some thin sections were etched with 1N HCl for 30 s, sputter-coated in gold and examined using scanning electron microscopy (TESCAN Vega\\xmu). Finally, energy-dispersive X-ray spectroscopy (EDX) analyses were made using the same scanning electron microscope. Each EDX analysis used a time of measurement of 30 s with 5 iterations.

BIOHERM MICROFACIES

Several microfacies were identified through this 1.9 m thick bioherm (Figs 2B, 3). The bioherm can be subdivided into three main microfacies. The lowermost part, up to approximately 0.45 m, is the early bioherm facies developed as a crinoidal-oncoidal packstone. The oncoids, as large as 2 cm, typically have a bryozoan, stromatoporoid or brachiopod shell fragment as nucleus, encrusted with *Girvanella* and *Rothpletzella*. Other major reef components, such as corals (rugose, heliolitid) and stromatoporoids, are already present, although not abundant. These stromatoporoids have two main morphologies, domical (Fig. 3D) and laminar (Fig. 3E). A few *Ortonella*-like porostromate problematica were also present early in the reef core. They are unattached, bulbous tubular organisms (Fig. 3D), approximately 1–3 mm in diameter with erect tubules approximately 50–100 μm in diameter. The next section is the reef core facies, which shows unusual characteristics. A calcimicrobial (*Hedstroemia*, *Girvanella* and *Rothpletzella*)
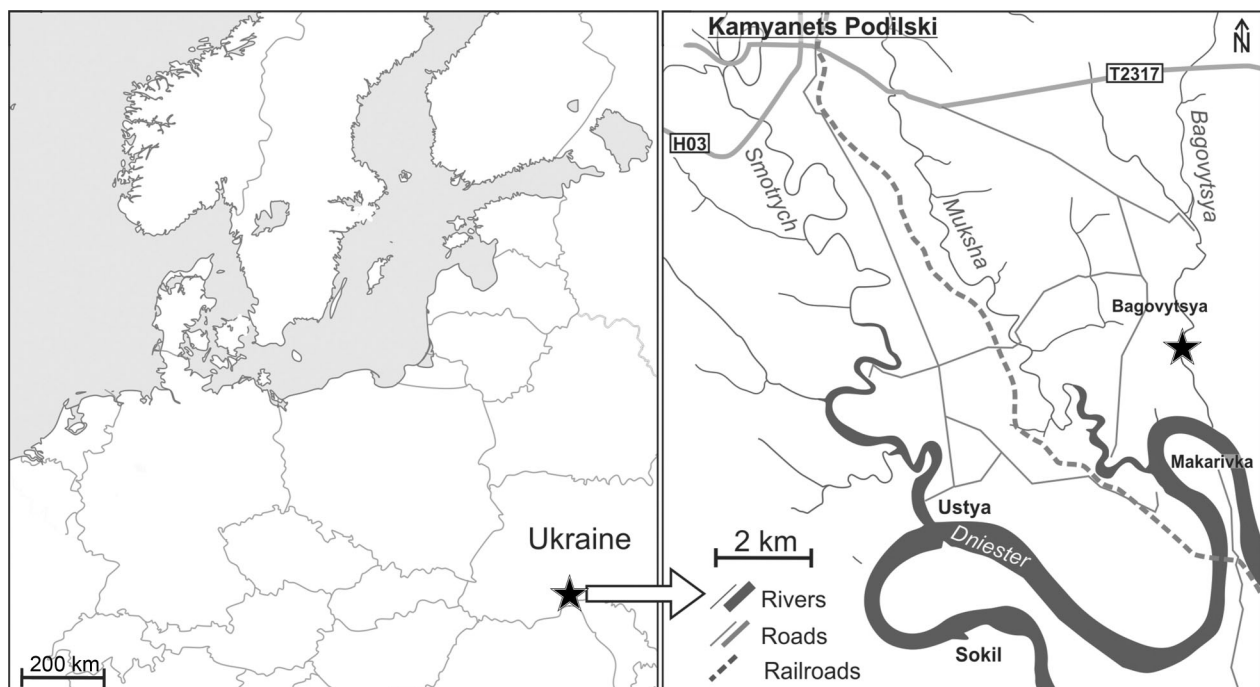
Fig. 1. Overview map showing location of the study area in Ukraine (modified from Jarochowska et al. 2014). The locality is shown with a black star.
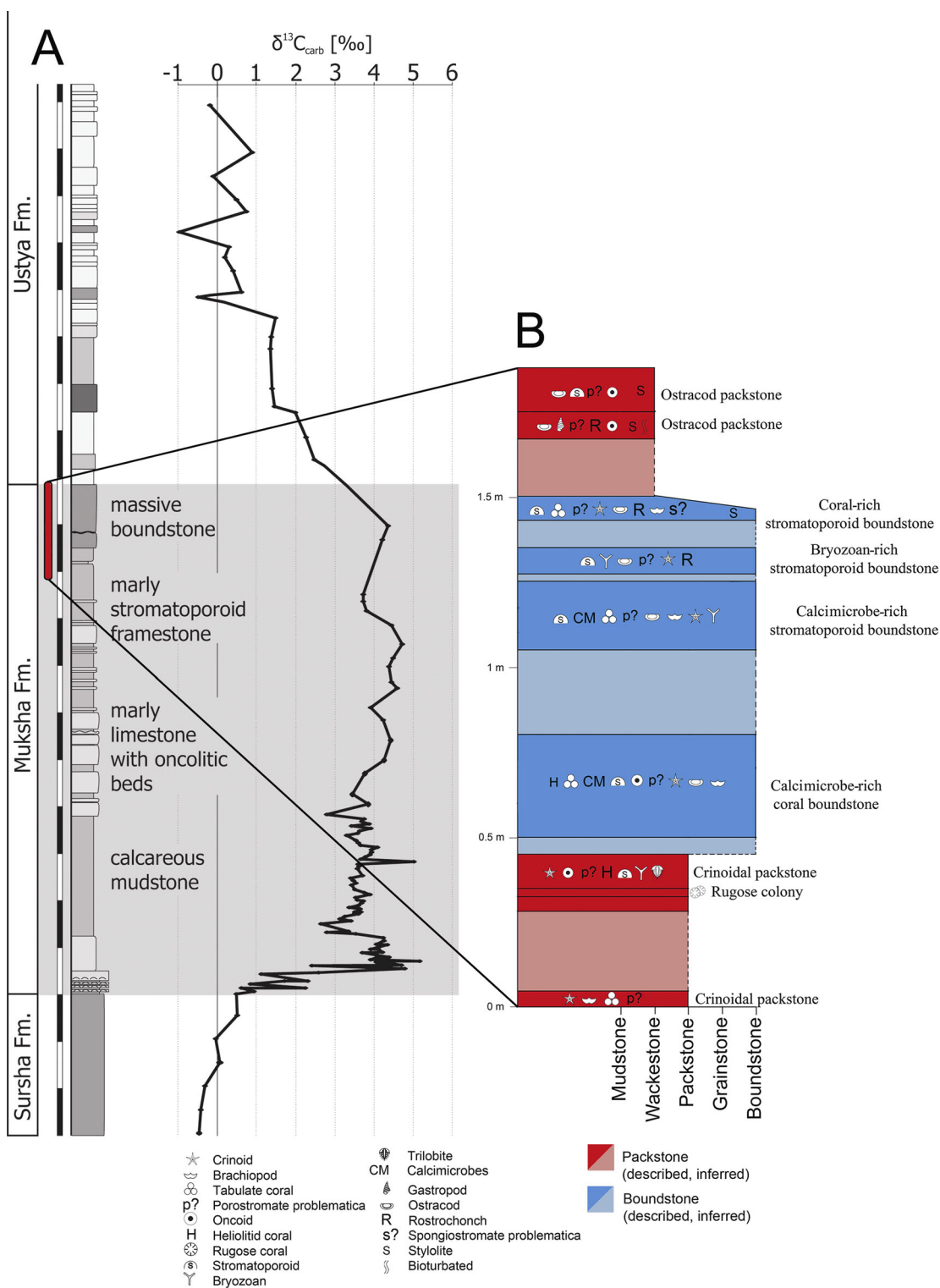
Fig. 2. A, stratigraphic column of the Muksha Formation (highlighted in grey) showing the elevated δ¹³C values (V-PDB) in this interval. The red bar shows an approximate range of the interval in this study (for detailed lithological description see Jarochowska et al. 2014). Scale is in metres. **B**, lithological column based on the description of polished slabs and thin sections. Inferred sections are due to lack of thin sections.

1 mm
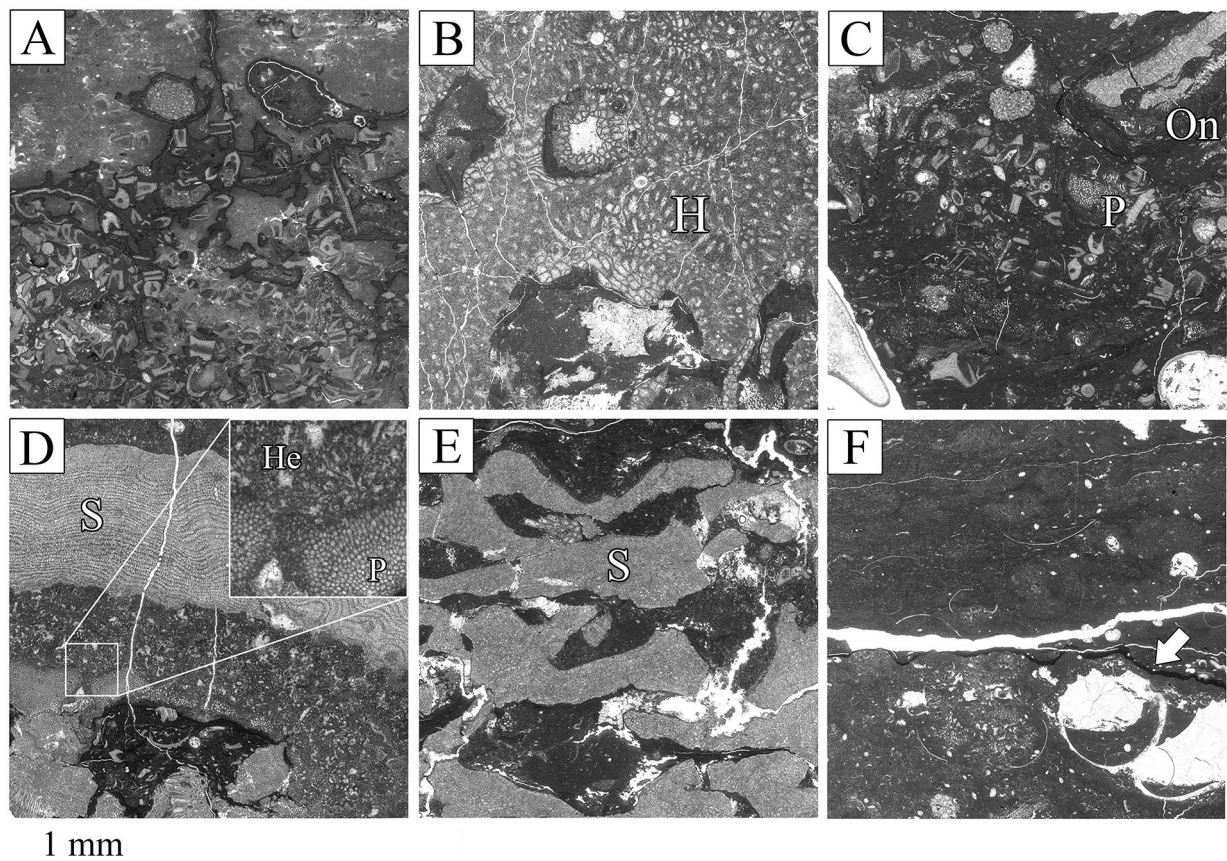
Fig. 3. A, (0.1 m) early bioherm; crinoidal packstone with bryozoans, dark areas enriched in crinoids are clay seams produced by dissolution, exhibiting a lower degree of cementation than the surrounding limestones; the dark colour is partially an artifact due to the resin penetrating into these areas during imbedding. **B**, (0.4 m) bioherm; heliolitid coral (H) boundstone. **C**, (0.75 m) bioherm; calcimicrobe (*Girvanella*, *Rothpletzella*) rich stromatoporoid boundstone with oncoids (On), porostromate problematicum (P) and brachiopods. **D**, (1.2 m) bioherm; calcimicrobe (He, *Hedstroemia*) stromatoporoid (S) boundstone with porostromate problematicum (P). **E**, (1.3 m) bioherm; stromatoporoid (S) boundstone with bryozoan. **F**, (1.7 m) late bioherm; ostracod wackestone with gastropod shells and stylolite (arrow).

coral boundstone dominates the lowermost part of this facies, with heliolitids and favositids as the main constructors and calcimicrobes as the binders. This is followed upwards by a series of stromatoporoid boundstones with varying fauna, such as crinoid and brachiopods, and a gradual decline in *Girvanella*, *Rothpletzella* and *Hedstroemia* until they are absent at approximately 1.25 m. The late bioherm facies, starting at approximately 1.5 m, is an ostracod thrombolitic wackestone in which ostracods dominate with some stromatoporoid and porostromate problematica.

ULTRAFACIES AND ULTRASTRUCTURES

The *Ortonella*-like porostromate problematica, found throughout the entire 1.9 m thick succession, and

Hedstroemia, found mainly in the bioherm facies, were observed under SEM for documentation of ultrastructures (Fig. 4) using three thin sections. Both *Hedstroemia* and the porostromate problematica have been partially recrystallized. Despite recrystallization, tubule walls are differentiable from the surrounding matrix and from the sparitic cement filling the inside of the tubules (Fig. 4B, E) by the crystal size, although much less visible in *Hedstroemia* (Fig. 4H). The cement crystals within the tubule are coarser while the crystals of the wall are finer (up to 30 μm). There does not seem to be any crystal order in the wall but the crystal size is uniform (Fig. 4C). *Hedstroemia* has branching clusters of tubules rather than erect tubules but they are much harder to differentiate against the surrounding matrix. The wall areas contain subhedral rhombohedral crystals approximately 5–10 μm in size (Fig. 4C, F, I). In the
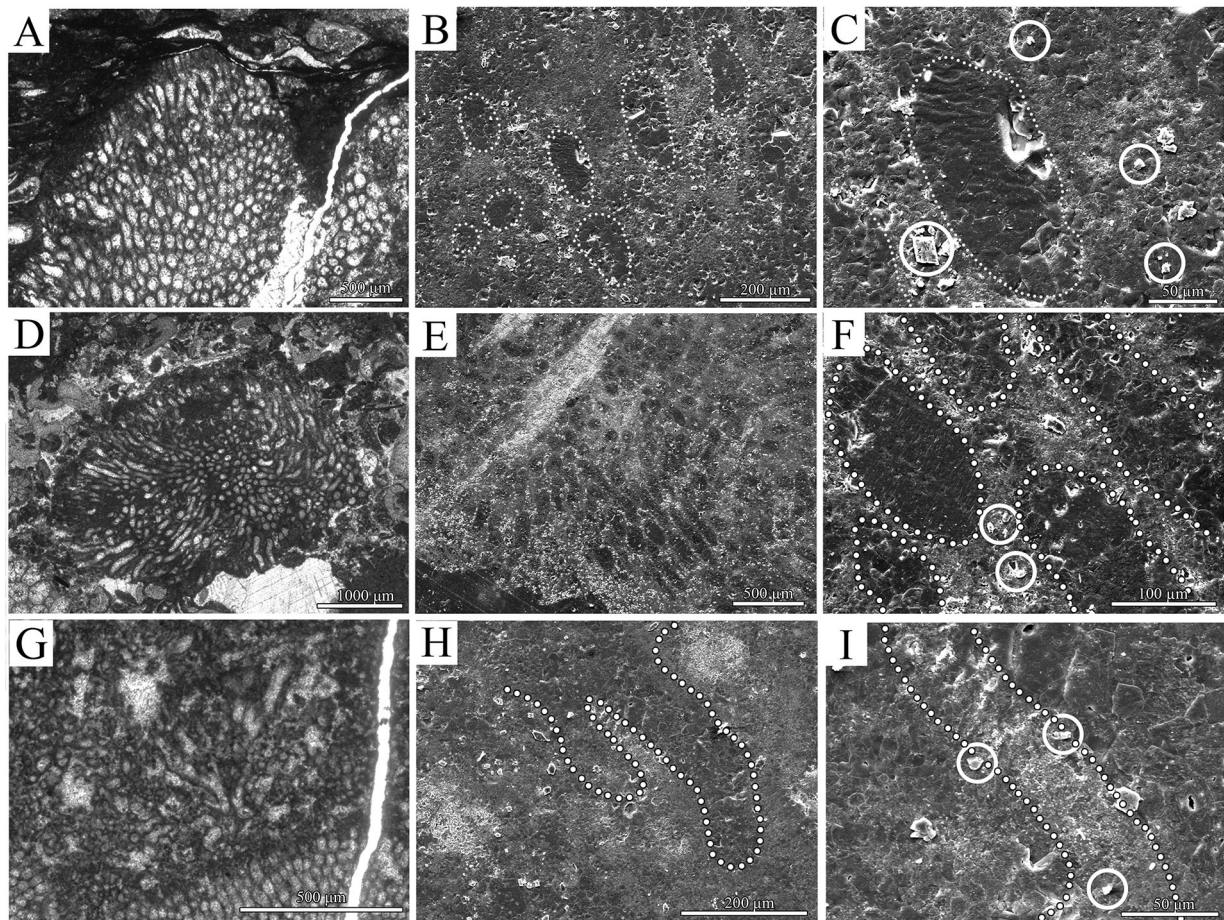
Fig. 4. Comparison of thin section photomicrographs and equivalent SEM photomicrographs. **A**, thin section photomicrograph of a porostromate problematicum at 1.3 m in the section. **B**, SEM photograph of the porostromate problematicum in Fig. 4A outlining the tubules from the walls with a dotted line. **C**, closer SEM photograph of the porostromate problematicum in 4A outlining the tubules from the walls with a dotted line and possible microdolomite circled. **D**, thin section photomicrograph of a porostromate problematicum at 0.65 m in the section. **E**, SEM photograph of the porostromate problematicum in 4D showing many tubules. **F**, closer SEM photograph of the porostromate problematicum in 4D outlining the tubules from the walls with a dotted line and possible microdolomite circled. **G**, thin section photomicrograph of microproblematicum *Hedstroemia* at 1.3 m in the section. **H**, SEM photograph of the *Hedstroemia* in 4G outlining the tubules with a dotted line. **I**, closer SEM photograph of the *Hedstroemia* in 4G outlining the tubules with a dotted line and possible microdolomite circled.

porostromate problematica, eight crystals were tested with EDX and they all showed elevated magnesium content, indicating that they were formed by micro-dolomite. The average weight percentages in these crystals are 8% Mg, 25% C, 55% O, 11% Ca and less than 1% Al and Si (all weight per cent). For comparison, the average of the background values, tested at three sites, was 23% C, 53% O and 25% Ca. For *Hedstroemia*, microdolomite was present although less abundant. Of the 23 crystals tested, eight contained Mg. In these eight crystals, the average weight percentages were 9% Mg, 25% C, 52% O, 13% Ca and less than 1% Si. The average of the background values was not recorded for *Hedstroemia*.

DISCUSSION AND CONCLUSIONS

The primary ultrastructures of both problematica were obliterated by recrystallization, but the growth habit and chemical composition of the recrystallized structures provided an insight into the original mineralogy. As shown by previous studies (Lohmann & Meyers 1977), microdolomite inclusions result from the redistribution of Mg ions during recrystallization and therefore the association with microdolomite inclusions suggests that high-Mg calcite, not low-Mg calcite or aragonite, was their original mineralogy, although the lower abundance of microdolomite in *Hedstroemia* suggests that high-Mg calcite may have formed only an admixture. Primarily

high-Mg calcite mineralogy is characteristic of red algae (Oti & Muller 1985), indicating a possible non-microbial affinity in both cases of microproblematica. In contrast, the walls show microcrystalline and unordered crystals. This indicates a microbial origin as it suggests that calcite was precipitated extracellularly without enzymatic control over the crystal structure (Munnecke et al. 2010; Westphal et al. 2010) and would suggest a prokaryotic affinity. Wray (1977) suggested that *Ortonella* and similar forms, such as *Hedstroemia*, are cyanobacteria. Riding (1991) also considered *Ortonella* a cyanobacterium but mentioned that many have compared *Hedstroemia* to codiacean green algae because of the size of their tubules. Jarochowska et al. (2014) suggested that the proliferation of calcifying bacteria during the Mulde Event might be a response to increased sea-water alkalinity, which would facilitate biologically mediated precipitation of calcium carbonate (see also Riding & Liang 2005) characteristic of prokaryotic calcifying organisms. As biologically mediated precipitation does not allow the organism to impose the $CaCO_3$ polymorph being precipitated, low-Mg calcite mineralogy would be expected in the Silurian calcite sea (Sandberg 1983). However, epeiric, restricted up-ramp settings of Podolia or Gotland may have well-developed shallow waters on the platform with salinities elevated due to increased evaporation. Such settings would not be representative for the ocean seawater Mg/Ca ratio, therefore the primary mineralogy of the studied problematica may reflect bacterial biologically mediated precipitation in saline waters. In addition, scarce bio-marker evidence currently available indicates that a shift to bacteria-dominated communities during the Mulde Event was not limited to up-ramp settings, but occurred equally in open-shelf settings (Porębska et al. 2004). What is more, altered community structure is also visible in the composition of the skeletal reef builders in the studied buildup, characterized by the lack of rugose corals and the abundance of heliolitid corals.

In conclusion, we have managed to limit the possibilities as to the original affinity of *Hedstroemia* and *Ortonella*-like porostromate problematicum. The high-Mg calcite composition suggests a red algal affinity, yet the unordered microcrystalline structure of the walls does not exclude a microbial origin, suggesting also the possibility that the primary metastable mineralogy reflected precipitation in waters with elevated alkalinity.

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