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Mass occurrence of benthic coccoid cyanobacteria and their role in the production of Neoproterozoic carbonates of South Africa

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ABSTRACT

The sparse Archean fossil record is based almost entirely on carbonaceous remnants of microorganisms cellularly preserved due to their early post-mortem silicification. Hitherto as an exception, sedimentary carbonate rocks from the Neoproterozoic Nauga Formation of South Africa contain calcified microbial mats composed of microbiota closely resembling modern benthic colonial cyanobacteria (Chroococcales and Pleurocapsales). Their remains, visible under the scanning electron microscope (SEM) after etching of polished rock samples, comprise capsular envelopes, mucilage sheaths, and groups of cells mineralized by calcium carbonate with an admixture of Al–K–Mg–Fe silicates. The capsular organization of the mucilaginous sheaths surrounding individual cells and cell clusters forming colonies and the mode of mineralization are the characteristic common features of the Neoproterozoic microbiota described and their modern analogues. The new findings indicate massive production of calcium carbonates by benthic coccoid cyanobacteria in the Neoproterozoic, and offer a solution to the problem of the origin of Archean carbonate platforms, stromatolites and microbial reefs.

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1. Introduction

Although it has been demonstrated that Archean sedimentary rocks contain microbial remains (e.g. Schopf et al., 2007; Glikson et al., 2008) and were formed by microbial ecosystems (microbial mats) (e.g. Hofmann et al., 1999; Tice and Lowe, 2004; Allwood et al., 2006), understanding of the genesis of such ancient rocks (3.5 Ga) and their possible relationships to modern living microbial mats and sites of carbonate rock formation, is inadequate (Grotzinger, 1989; Arp et al., 2001; Sumner and Grotzinger, 2004). The process of mineralization in microbial ecosystems in natural environments remains in general, but particularly in the Archean, one of the outstanding enigmas of carbonate rock formation, despite decades of intensive research and debate. The increasing abundance of carbonate rocks and the similarities in their chemical composition throughout Earth history have no valid explanation.

Many researchers assume that Archean seawater must have been much higher supersaturated in CaCO₃ than the present ocean,

because enzymatic biomineralization today keeps the supersaturation of calcite and aragonite at a level below which spontaneous CaCO₃ precipitation would occur. All present environments that lack enzymatically biomineralizing organisms show higher supersaturation, i.e. typically a saturation index of 0.8–1.1 while the current ocean rarely exceeds calcite Saturation Index = 0.6 (Kempe and Kazmierczak, 1990, 1994). Because CaCO₃ is relatively insoluble and alteration processes of rocks constantly introduce Ca to the ocean, Ca-bearing minerals must have precipitated from the Archean ocean non-enzymatically, i.e. under much higher supersaturation than today in the absence of biomineralization. Therefore, the search for mechanisms of the formation of Precambrian carbonates has been often centred on physicochemical models based on assumptions, such as general changes in the chemistry of seawater (e.g. Riding, 1982; Kempe and Degens, 1985; Kempe and Kazmierczak, 1990; Hardie, 1996, 2003; Hay, 1999; Sumner and Grotzinger, 2000; Loewenstein et al., 2001; Sumner, 2002; Kazmierczak et al., 2004; Kazmierczak and Kempe, 2006; Stanley, 2006) or on other mechanism delivering various solutions to the depositional sites at different times (e.g. Kempe, 1990; Kempe and Kazmierczak, 1994; Stanley and Hardie, 1998; Brennan et al., 2004).

Direct comparisons of ancient and modern sites of carbonate precipitation, on microscopic and submicroscopic level have been limited, but the few existing case studies done at this scale show

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their importance in unravelling the genesis of microbial carbonate rocks and the evolution of life (e.g. Dupraz and Visscher, 2005; Altermann et al., 2006; Benzerara et al., 2006). The preservation of (Archean) microfossils in cherts, although often unmatched in quality of details, represents only a narrow window restricted to environments of hydrothermal and diagenetic silica migration in biological, taphonomic, diagenetic and metamorphic processes. In order to overcome this preservational bias, other sedimentary rocks need to be investigated, including shales, sandstones and, foremost, microbial carbonates, as has been agreed upon during the “World Summit on Ancient Microscopic Fossils”, in August 2008, at the Center for the Study of Evolution and the Origin of Life (CSEOL), UCLA, from which the present special volume emanates.

Thus far, Archean microfossils have been reported mainly from environments subjected to early diagenetic or hydrothermal silicification, allowing for the preservation of cellular structures. Carbonate rocks are conventionally excluded as a potential source of microfossils because of the crystallization force of carbonate minerals, which is believed to be responsible for destroying prokaryotic cell-sized structures. In one reported exception, the

filaments of *Siphonophycus transvaalensis* (Klein et al., 1987) have been partly preserved in late diagenetic, euhedral dolomite crystals, in parallel with their preservation in chert. Of particular relevance to the present study, these filaments display minute needles (originally aragonite?) within the cyanobacterial sheaths that were interpreted as possible remains of cyanobacterial calcification (Wright and Altermann, 2000). Another exception is a report on production of Neoproterozoic carbonates by benthic coccoidal cyanobacteria (Kazmierczak and Altermann, 2002) which provides a basis for the new data and interpretations presented herein.

With the rapidly increasing interest in the search for extraterrestrial life, the origin of carbonate rocks on the Archean Earth gains immense importance, in the light of the unique occurrence of biological processes recorded in these carbonates, unmatched on any other extraterrestrial body. Carbonate rocks and their silicified successors are the best sites for the preservation and search for fossil remains on Earth and thus need to be found on other planets if the search for life is envisaged as a successful possibility there (Altermann, 2009).

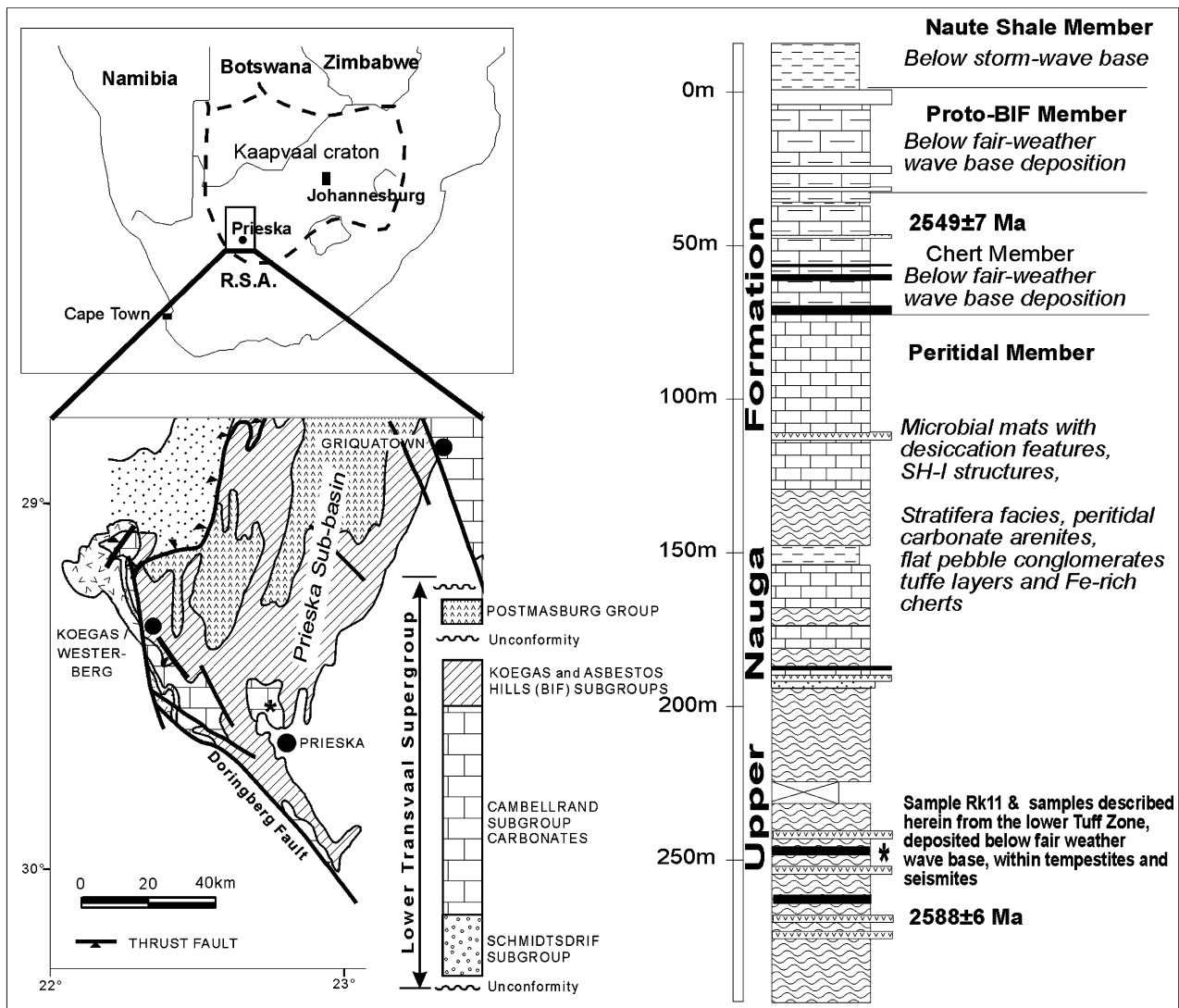


Fig. 1. Geographic and stratigraphic setting of the Neoproterozoic Nauga Formation at Prieska, South Africa and its facies relationships. The Nauga Formation is part of the Campbellrand Subgroup carbonates of the lower Transvaal Supergroup within the Griqualand West preservational basin. The geology west of the approximately N-S trending fault at Koegas, consists of Ventersdorp Supergroup lavas (>2.7 Ga) and of upper Paleoproterozoic, mainly siliciclastic rocks (dotted signature). The stratigraphic position of the samples described herein can only be regarded as approximate because thrusting obliterates their exact position, that could equally be a few tens of meters below the 2.588 Ga tuff layer.

It is generally assumed that the metabolism of the Neoproterozoic biota was essentially modern, including anaerobic fermentation, anoxygenic photosynthesis, oxygen-producing photosynthesis, and aerobic respiration in autotrophs and heterotrophs (for review, Schopf, 1992, 2004). In this contribution we report on yet another metabolic capability of Neoproterozoic microbiota, that is known from modern and Phanerozoic environments: the ability of benthic coccoid cyanobacteria resembling modern entophysalidaceans and pleurocapsaleans to mineralize (calcify) within the extracellular polymeric substances (EPS) excreted by the cells, as can many extant coccoid cyanobacteria. This mucilage may have developed either as common sheaths (glycocalyx) or as capsules surrounding individual cells or cell groups in a fashion similar to their extant counterparts, particularly under alkaline or hypersaline conditions (Stal and Reed, 1987; Decho and Herndl, 1995; Decho, 2000; Stal, 2000).

2. Geological setting

The Neoproterozoic carbonate formations underlying the banded iron formation (BIF) deposits in the Transvaal Supergroup of South Africa are still the subject of controversial facies interpretations, despite more than 30 years of sedimentological, stratigraphic and paleobiological investigations. The Ghaap Group in the Northern Cape Province of South Africa, comprises the Schmidtsdrif (2642 ± 3 Ma; Walraven and Martini, 1995) and overlying Camp-

bellrand Subgroups with a combined thickness of >3000 m (Altermann and Siegfried, 1997), deposited in the Griqualand West preservational basin of the Transvaal Supergroup. The Campbellrand platform-carbonate formations, comprising successively from the base upwards, the Monteville, Reivilo, Fairfield, Klipfontein Heuwels, Papkuil, Klippan, Kogelbeen and Gamohaam Formations, persisted from 2555 ± 19 Ma to at least 2516 ± 4 Ma (Altermann and Nelson, 1998) and comprised tidal flat and shallow marine deposits. The upper Gamohaam Formation exhibits a progressive upward increase in subtidal carbonates, as transgression extended from southwest to northeast for a distance of over 400 km across the basin. The entire carbonate succession, over 2000 m thick, comprises abundant microbialitic carbonates, including shallow water and deep water stromatolites, and ooids (Beukes, 1987).

In the south-western part of the Campbellrand Subgroup, in the Prieska area, only the Nauga Formation is present (Fig. 1) and represents the oldest part of the carbonate platform (2588 ± 6 Ma to 2549 ± 7 Ma; Altermann and Nelson, 1998). It is overlain conformably by a shale succession (Naute Shale Member) that correlates approximately in age to the Campbellrand Subgroup formations listed above. This succession can be interpreted as reflecting drowning of the Nauga carbonate platform and migration of platformal conditions towards the NE during progressive transgression. However, the carbonates of the Nauga Fm. are interpreted either as entirely basinal, deep water carbonates (Beukes, 1987) or as mainly peritidal deposits (Altermann and Herbig, 1991),

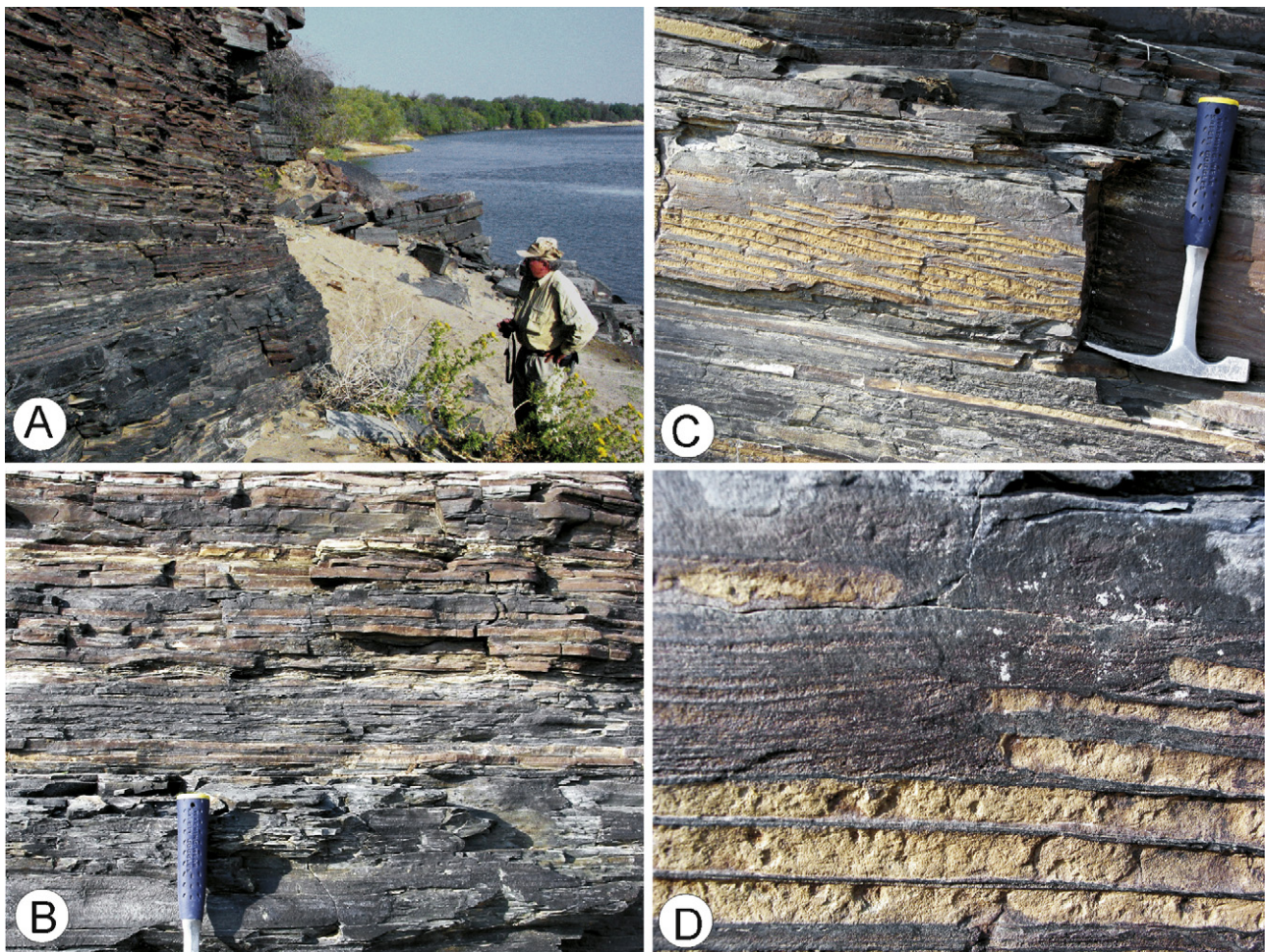


Fig. 2. Sampling site on the shore of the Orange River, near Prieska, Nauga Fm.: (A) general view, (B) part of the section showing alternating thin beds of carbonates and siliceous marls and shales, (C) imbricated carbonate flat pebbles containing the coccoid cyanobacterial mat imprints, and (D) magnification of (C), showing the fine lamination of the cross-bedded detrital carbonate sediment embedding the flat pebbles. Sample RK11 contains such flat pebbles as visible in (C) and (D) and samples SA 71 and WA07/11 are from the intercalated pelitic beds.

but becoming subtidal and passing into a shelf facies towards the top of the succession (Altermann and Nelson, 1998). The Naute Shale Member, of up to 170 m thickness and with some chert beds of great lateral continuity, is succeeded by the famous, Paleoproterozoic Transvaal or Griqualand West BIF (comp. Fig. 1) sequence, several hundred metres thick, deposited in a shelf setting, below storm wave base (Eriksson et al., 2006).

The Neoarchean carbonates of the Transvaal Supergroup are well known not only for the above controversy, but also for possible correlations to similar carbonates on the Pilbara Craton, Western Australia (Nelson et al., 1999) and their wealth of stromatolite occurrences (Eriksson and Truswell, 1974; Beukes, 1987; Altermann, 2002, 2004, 2008). These carbonates bear the best preserved and least controversial bodily preserved Archean microfossils (Lanier, 1986; Klein et al., 1987; Altermann and Schopf, 1995; Wright and Altermann, 2000). In particular, the >2588–2549 Ma (Altermann and Nelson, 1998) Nauga Formation bears the oldest morphological and geochemical evidence for cyanobacteria and their role as producers of widespread and copious, rock-forming, micritic carbonate (Kazmierczak and Altermann, 2002; Altermann and Kazmierczak, 2003; Kazmierczak et al., 2004; Altermann et al., 2006), preserved in non-silicified carbonate rocks, rich in organic matter.

This contribution presents new data on the mineralization potential of Neoarchean cyanobacteria from the Nauga Formation, found in the same and in laterally extended carbonate outcrops, as described from samples from the middle part of the Nauga Formation, at the Orange River, close to Prieska (Kazmierczak and Altermann, 2002). The sample RK11, collected by Kiefer (1995), was described as “flat pebble carbonate conglomerate, embedded in carbonate matrix, with small scale cross-bedding, and micritic, sapropel-rich intercalations” (Kazmierczak and Altermann, 2002, p. 2351) and was assigned to the stromatolitic “Peritidal Member” of the Nauga Fm. (Kiefer, 1995; Kazmierczak and Altermann, 2002). Our re-examination of the sampling site, however, calls for a reinterpretation of the facies.

The relevant outcrop is located on the Kliphuis 29 farm (topographic map of South Africa, 1:50,000, Prieska West), along the northern bank of the Orange River, at 29°36'51".110 S and 022°43'14".000 E, and stratigraphically below the “Peritidal Member” as defined by Altermann and Nelson (1998). The stratigraphic position of the extensive, vertical wall outcrop is complicated by a large thrust plane, exposed in a riverine gorge at 29°36'49".477 S and 022°43'22".786 E. This thrust plane dips at about 50° towards the WNW (285°). The thrusting is ‘top to the East’ and displaces the lower part of the Peritidal Member, including the Tuff Zone of the Nauga Fm. (Beukes, 1987), over its upper part.

The outcropping section starts with an intercalation of massive, partly graded and cross-bedded tuff and tuffite beds with some intercalated platy limestones, followed by thinly bedded dark shales. This lower part of the section is at least 50 m thick. The flat pebble carbonate conglomerate or flat pebble breccia in dark shale–marl matrix, follows on top of this zone and locally displays marked imbrication of the thin platy clasts (Fig. 2); it overlies a conspicuous ca. 80 cm thick tuff bed. The thin platy carbonate beds display no stromatolitic laminations and no fenestral structures, otherwise very common in the Nauga Formation. Thin tuff beds are intercalated with the platy limestones. The intercalation displays slump structures, hummocky cross-beds in tuffites and flat pebble clasts in carbonates. The intercalated calcareous shales are partly very dark and rich in organic matter. Some 3 m above the distinct flat pebble conglomeratic clast layer, V-shaped cracks filled with brown-weathering dolomitic, Fe-rich carbonate are abundant in platy, thinly bedded to laminated carbonates. These cracks somewhat resemble molar tooth structures in vertical section (Bishop and Sumner, 2006) but are laminated themselves, with lamination

not matching that of the host beds, as the laminae are finer in the crack-filling brown carbonate. The laminae of the V-shaped crack infill material are concave downwards, forming small saucer shaped sagging structures. The V-shaped cracks are regularly spaced, at about 10–20 cm distance in vertical view. In a plan view, parallel to bedding, they display a regular pattern of polygonal to lenticular shapes of some 20–30 cm width, but often also connected to each other by a thin veneer of the brown weathering Fe-rich dolomitic carbonate, as in the cracks themselves. Above this cracked interval, a 40 cm thick graded tuff layer displays climbing ripple trains and cross-bedding, indicating transport direction towards the west. Above this conspicuous tuff bed, the intercalation of rippled and graded tuffs and platy limestones and marls continues for another few tens of metres.

In contrast to the earlier assignment of this outcrop section to the “Peritidal Member” of the Nauga Fm. (Kiefer, 1995; Kazmierczak and Altermann, 2002), this facies should rather be interpreted as deep subtidal, reflecting below-fair-weather-wave base deposition, in a restricted, rapidly subsiding and filled basin, under the influence of relatively proximal lapilli, accretionary lapilli and ash tuff volcanic input (Altermann, 1996); additionally, seismic activity is documented by the V-shaped cracks formed in the semi-consolidated limestones. This interpretation is consistent with tempestitic deposition and hummocky structures (Dumas and Arnott, 2006) in tuffs and tuffites. Thus the samples described by Kazmierczak and Altermann (2002) and the new samples collected for this study, should be considered to reflect accumulation of organic-rich calcareous shales, flat pebble breccias, conglomerates and platy carbonates in a subtidal rather than a peritidal setting, probably below fair weather but above the storm wave base. An interval of intertidal to supratidal carbonates with desiccation features and birds eye structures follows on top of this subtidal

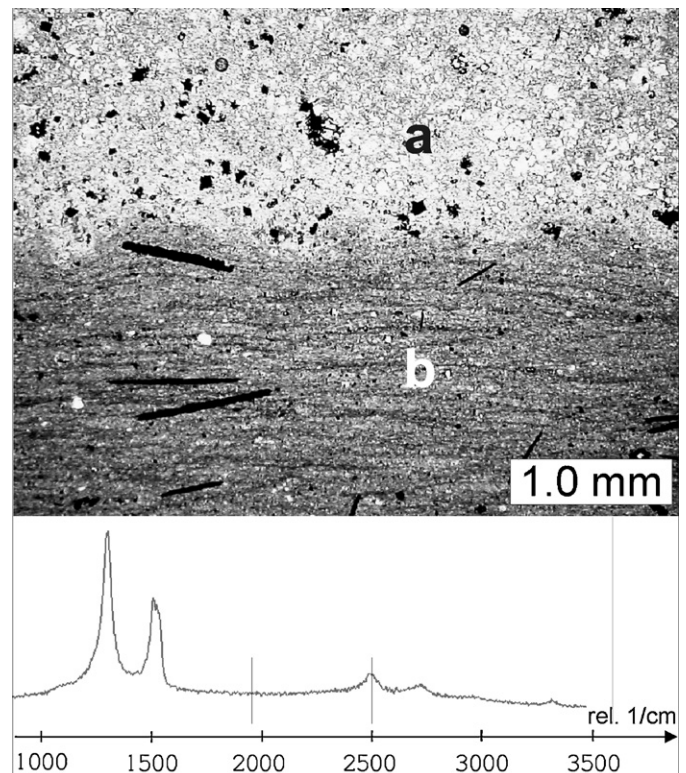


Fig. 3. Example of first-order and corresponding second-order regions of Raman spectra from calcareous siltite and shale underlying the studied limestone clast. Photo: transmitted light microscopy image of the area in which the Raman spectra were measured on sample RK11.

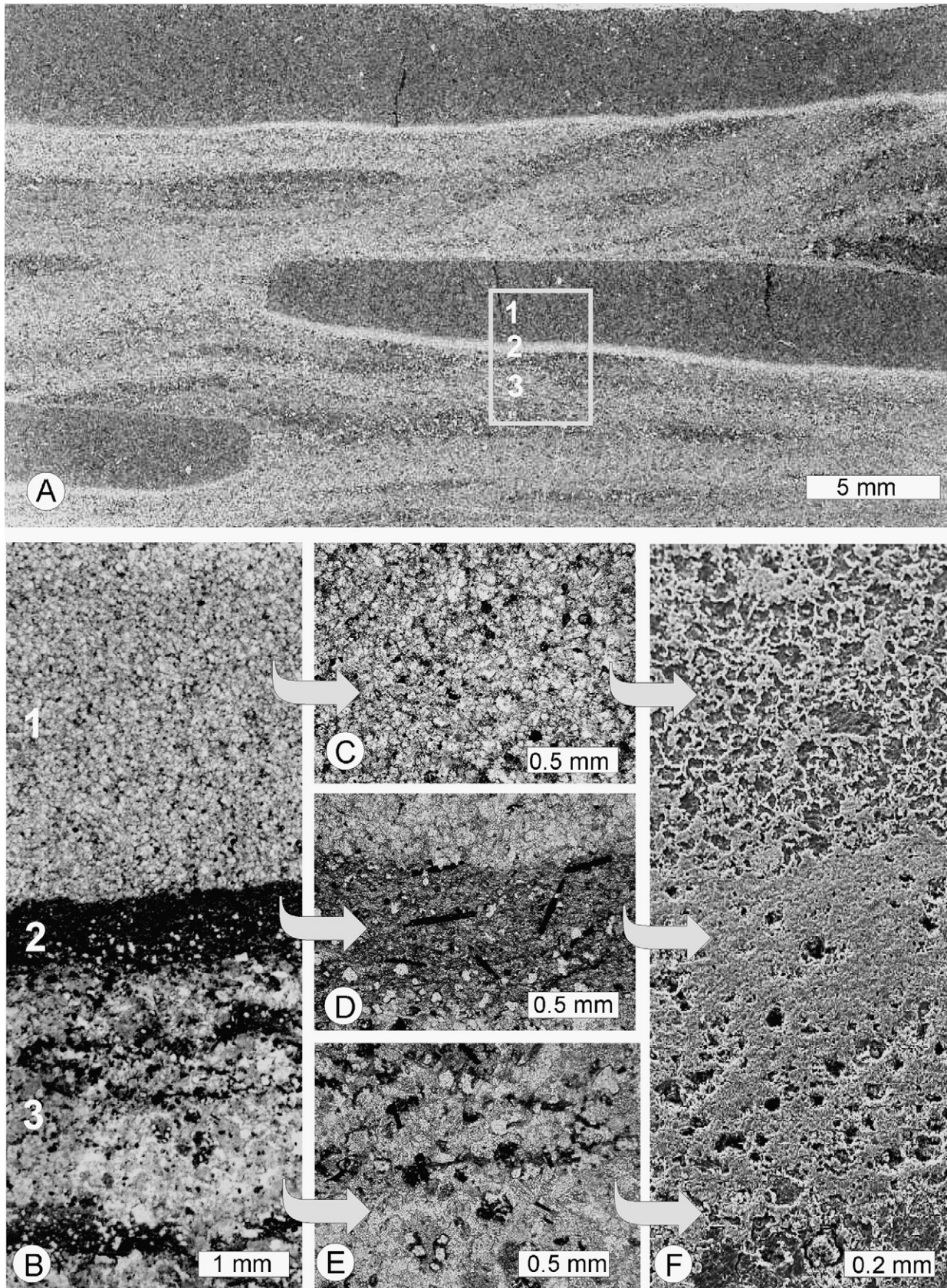


Fig. 4. (A) Reflected light photograph (vertical section) showing carbonate flat pebbles in cross-bedded carbonate siltite. Numbers in the frame indicate three types of sediments comprising the rock. (B) Magnification of the frame in (A), in petrographic thin section (transmitted light photograph) showing microbial carbonate (1), siliceous marl–shale (2) rich in organic matter and stilpnomelane blades [visible in (D)], and carbonate siltite (3). (C–E) Display magnified fragments of the three sediment layers shown in (A) and (B). (F) SEM image of formic acid-etched fragment of the same sample area, showing the same three sediment layers; note the cobweb-like etching pattern of the layer, representing mineralized microbial (cyanobacterial) mat.

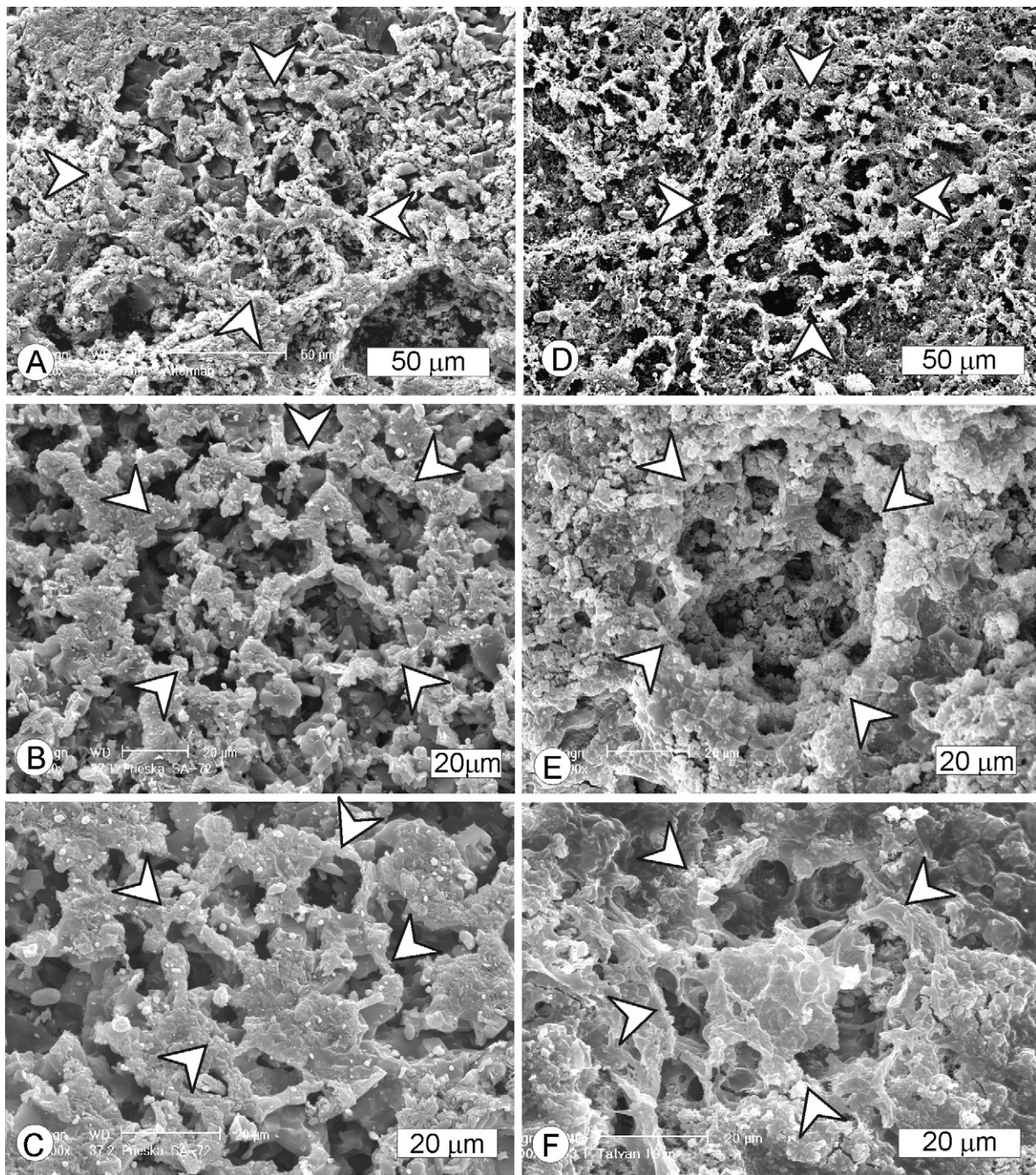


Fig. 5. (A–C) SEM images (etched limestone platelets) showing sub-circular aggregates of coccoid cyanobacteria (the periphery of which is denoted by arrow in each part of the figure) from the Neoproterozoic Nauga Formation, with common mucilage sheaths mineralized by calcium carbonate and authigenic silicates. (D–F) Similarly mineralized common mucilage sheaths of modern colonial coccoid cyanobacteria from Lake Van, Turkey.

succession and the former became drowned at the transition to the sedimentation of the Naute Shale Member of the Nauga Formation. The stratigraphic and inferred facies relationships of the sampling site are summarized in Fig. 1.

3. Materials and methods

The samples analyzed here have been extracted from: (i) imbricated flat pebble carbonate clasts embedded in fine carbonate–siltite and shale-to-marl matrix (Figs. 2 and 3), dis-

playing small-scale cross-bedding structures (samples WA07/11, SA71 and RK11) and (ii) thin beds of similar fine grained carbonates, interlayered with siliceous, organic matter-rich marl and shale (sample SA72). The microfossils were found in micritic carbonate (Mg-calcite), in the immediate vicinity of the siliceous, organic-rich shale–marl laminae interleaving the carbonate thin beds and flat pebbles.

The biostructures are observable in SEM images of the SA71, SA72 and RK11 carbonate samples as characteristic patterns, made visible by etching polished rock platelets for 5–10 s with 5% formic acid, and/or 3% hydrochloric acid, rinsed subsequently with dis-

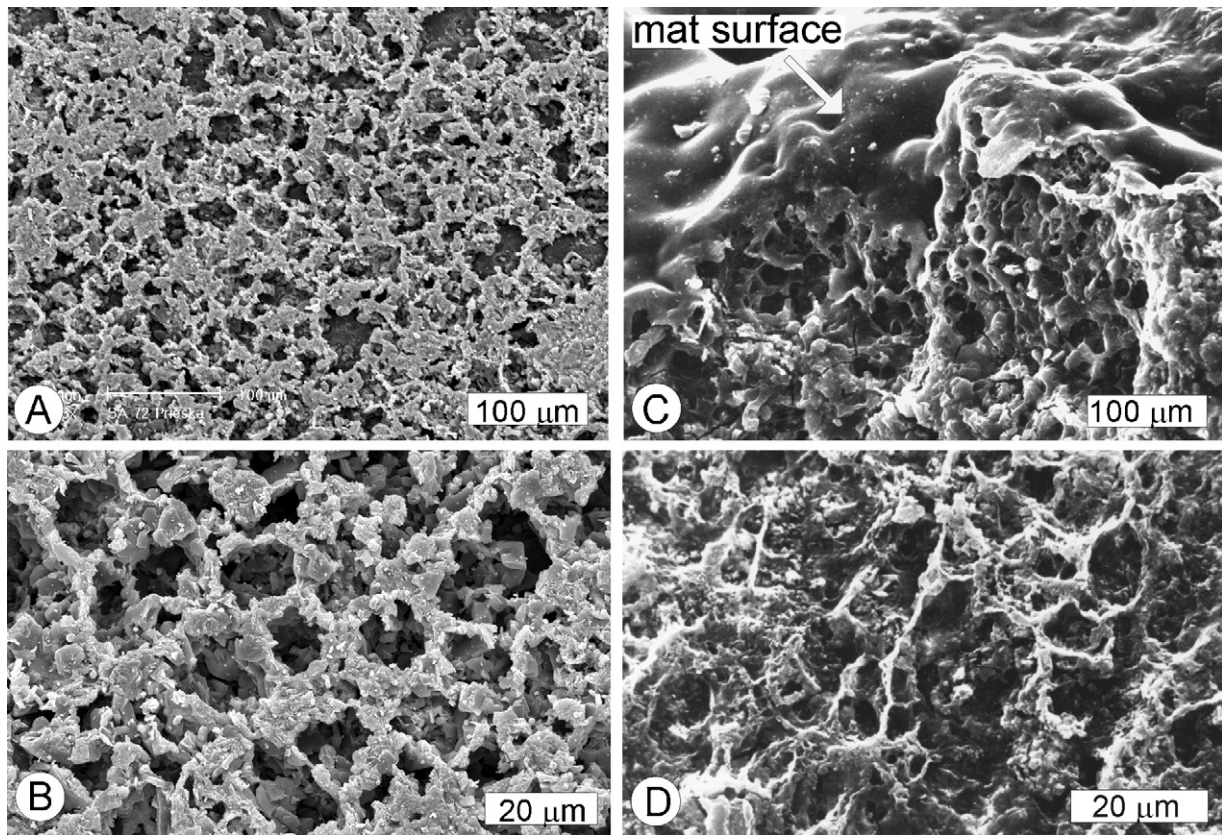


Fig. 6. Comparison of Neoproterozoic (Nauga Fm.) and modern (Lake Van, Turkey) *in situ* mineralized common sheaths (glycocalyx) and capsules of coccoid cyanobacterial aggregates. (A and B) SEM images of an etched fragment of Neoproterozoic carbonate flat pebble showing web-like pattern comprised of calcium carbonate-filled pits surrounded by walls composed of a mixture of calcium carbonate and authigenic silicates. (C) SEM image of an oblique cross-section of mineralized capsular mucilage sheaths of modern colonial coccoid cyanobacterial mat from Lake Van. (D) SEM image of etched section of deeper part of the above Lake Van mat, showing remnants of capsular mucilage sheaths, similar to those shown in (B).

tilled water and sputtered with platinum. This etching technique for identification of remains of cyanobacterial sheaths and capsules has proved effective for samples of calcified modern and Phanerozoic-aged cyanobacterial mats (Horodyski and Vonder Haar, 1975; Kempe and Kazmierczak, 1993; Kazmierczak et al., 1996) and has also been applied in our previous report on the RK11 sample (Kazmierczak and Altermann, 2002).

The modern samples used for comparison in this study, derive from calcareous microbialites collected in 1989 during a German-Turkish Geological Expedition to Lake Van (Kempe et al., 1991). The samples illustrated in Figs. 5–8 and 10 were taken from Tatvan Bay (near Tatvan harbor), at water depths 16–19 m, whereas the mat shown in Fig. 9 has been collected in Pore Bay (southwestern part of Lake Van), at 1 m water depth.

The scanning electron microscopic examination involved a Philips XL 20 instrument, equipped with an EDX dual-window (UTW/Open) microprobe equipped with an ECON detector Model Econ-6 (Institute of Paleobiology, PAS, Warsaw), and a Zeiss DSM 960A equipped with EDS detector Bruker axs (LMU University, Munich).

Raman measurements were done using a confocal microscope alpha 300 R (WITec, Jungingen, Germany) with a piezo scan stage (100 μm \times 100 μm \times 20 μm , PI, Germany). The system is equipped with a 100 \times microscope lens for measuring in air, with a working distance of 0.26 mm and a numerical aperture NA = 0.90 (Nikon, Düsseldorf, Germany). The depth of focus was about 1 μm . Raman spectra were collected from individual carbonaceous grains on polished rock plates under 100 \times magnification. For each sample, several spectra were collected. The measurements were performed by focusing the laser beam on the OM beneath the surface.

Two peaks characteristic of carbonaceous matter were observed in the first order region of the studied samples (Fig. 3). The usual D1 band occurred at 1350 cm^{-1} and the G band appeared near 1600 cm^{-1} . The D1 band is markedly larger and more intense than the G band. On the G band shoulder, an additional D2 band is slightly marked. Its intensity decreases with increasing degree of organization of CM. The second-order (2500–3000 cm^{-1}) spectra of carbonaceous matter show two distinct, but not extensive bands. The S1 band ($\sim 2700 \text{ cm}^{-1}$) is slightly higher than S2 ($\sim 2900 \text{ cm}^{-1}$). The D peak position and shape as well as the relative peak intensities suggest that the samples have been altered to lower greenschist metamorphic facies or slightly above it. This is consistent with the regional “very low grade” metamorphism for the overlying BIF (Miyano and Beukes, 1984) and with illite crystallinity measurements ($<350^\circ$) on the Naute Shale Member, stratigraphically above the microfossiliferous layer sampled herein, and below the BIF (Altermann, 1997); this is also consistent with temperatures of above 250 $^\circ$, inferred from fluid inclusions in quartz from the Ghaap Plateau carbonates (Altermann and Wotherspoon, 1995).

4. Observations and comparison

Under the petrographic optical microscope, in thin section, the samples display coarse sparitic texture within the flat pebble carbonate clasts (Fig. 4C). The clasts are underlain by an approximately 1 mm thick lamina of dark, silicified shale to marl, displaying blades of stilpnomelane, grains of carbonate and some silt-size detrital quartz grains (Fig. 4D). The organic matter in these laminae is very fine grained, finely dispersed and appears as granular and short,

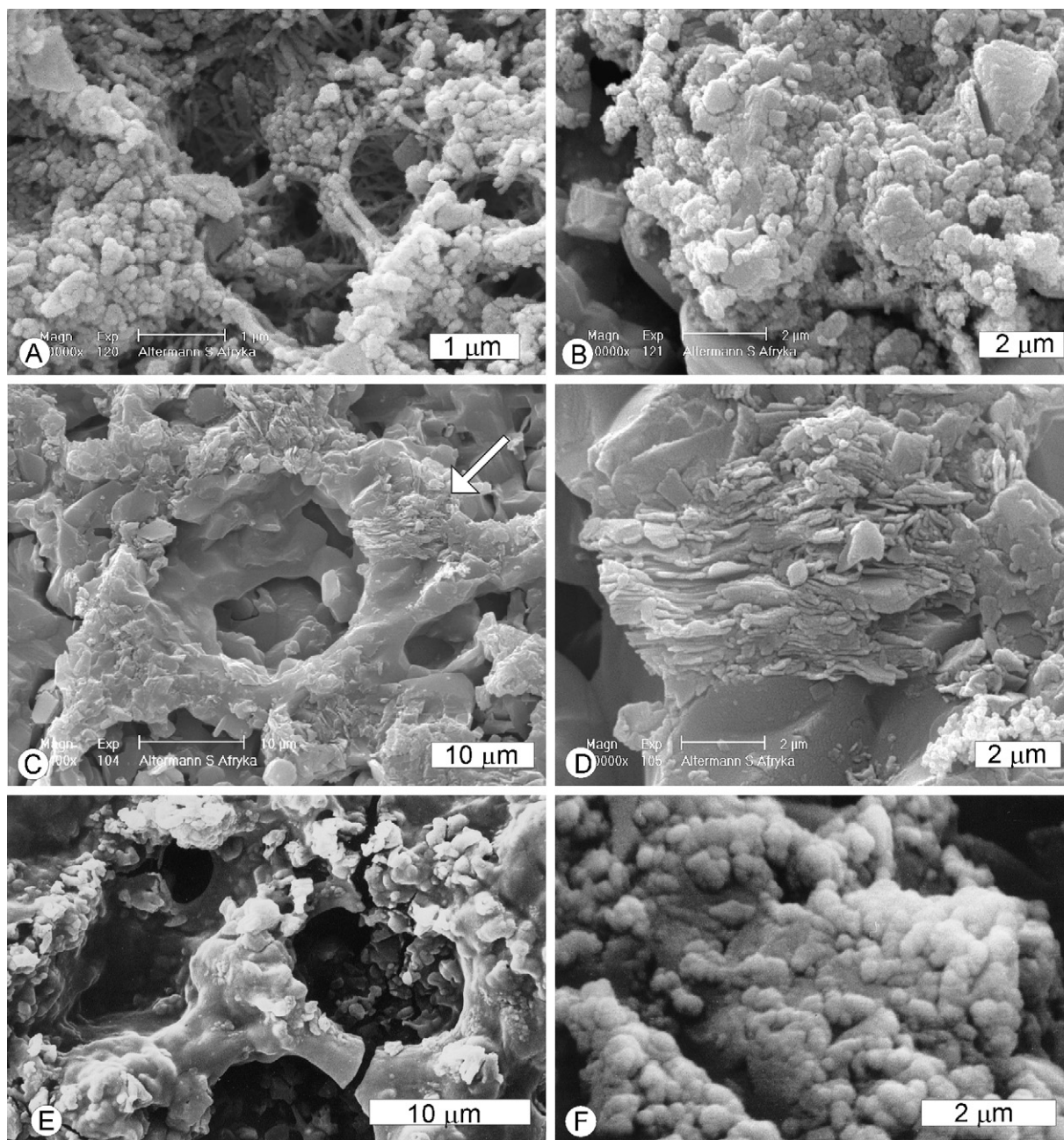


Fig. 7. Comparison of structure of Al–Fe silicate mineralized common sheaths of Neoproterozoic (Nauga Fm.) and modern (Lake Van) coccoid cyanobacteria. (A and B) Neoproterozoic microgranular silicate. (C and D) Neoproterozoic layered silicate (phyllosilicate). (D) is an enlargement of (C), as pointed out by the arrow. (E and F) Mixture of microgranular aragonite and silicate precipitated in mucilage sheath of modern Lake Van mat. All photographs are SEM images.

irregular string-like particles, optically hardly resolvable, because of poor light transparency of these dark laminae. Compaction is visible in the laminae and throughout the matrix. The fine grained carbonate–siltite matrix displays micro-scaled cross-bedding. It is also rich in organic carbon, which is in parts concentrated along grain boundaries and micro-stylolites, but mainly dispersed and less abundant than in the laminae directly underlying the clasts. The matrix also contains fewer clay minerals (Fig. 4E). Silicification is concentrated in nests, is not pervasive and is somewhat weaker than in the siliceous shale–marl laminae. In both, dark shale–marl and in the carbonate–siltite matrix, haematite and goethite after haematite and Fe-carbonate, as indicated by petrographic investigations, are present in irregular patches, nests, and build reddish and brown rims around and within ghosts of idiomorphic dolomite crystals. In some of these dolomite crystal ghosts and in the shaly

silicified matrix, red and brown haematite–goethite and probably carbon-containing (dark) silicified globules of 2–5 μm diameter are visible in thin section. They match in size the globular structures shown in Fig. 10 (comp. below) but are less sharply defined in the surrounding rock matrix.

In SEM, the etched platelets of the Nauga Fm. carbonates show two types of characteristic structures. One of these patterns resembles a web-like structure with meshes of various sizes. This web-like pattern is visible as a system composed of often sub-spherical pits and walls. The system is not regular and is visible almost throughout the whole etched surface of the sample (Figs. 5 and 6). The walls of the pits have different thicknesses. The thicker walls are on average 3–5 μm thick and the thinnest are 1–2 μm . The average diameter of the pits ranges between 15 and 35 μm (with the smallest attaining 3–10 μm in diameter). The thicker walls enclose the largest pits,

which in turn may in some cases enclose a system of thin-walled smaller pits.

The walls have mostly micro-granular structure but in places mineral groups of stacked micro-plates occur, verifying the presence of phyllosilicates (Fig. 7C and D), as visible also in thin section. The results of EDX analyses indicate that the walls of the pits are formed of calcium carbonate with high admixtures of silicates (mostly Al–Fe silicates with some Mg and K) and dolomite, whereas the material filling the pits is almost pure calcium carbonate (Fig. 8).

Similar web-like patterns occur commonly in modern coccoid cyanobacterial mats and are connected with their selective degradation. Observations on decaying colonies of modern *Entophysalis* (Horodyski and Vonder Haar, 1975) and *Pleurocapsa* (Krumbein and Swart, 1983; Kempe and Kazmierczak, 1993; Kazmierczak et al., 1996; Kazmierczak and Kempe, 2004) have shown that degradation of these colonial cyanobacteria is similarly selective. The intracellular material and the relatively thin inner sheaths that enclose single cells and small groups of cells decompose first. The relatively thick sheaths that enclose larger groups of cells or form the outer sheath of a colony are much more resistant to biodegradation and decomposition and thus, often remain as the only traces of the primary colonial organization in subfossil and fossil coc-

coid cyanobacteria (Horodyski and Vonder Haar, 1975; Horodyski, 1980; Kempe and Kazmierczak, 1993). This can be seen in Fig. 9, where a vertical profile of a coccoid cyanobacterial mat is shown, and increasing degradation downwards in the mat is discernible. Morphological forms resulting from preservation of only the more durable, thicker outer sheaths, resemble such web-like structure as described above (Fig. 9A). It is important to note, that the size range of these structures corresponds well with the diameter range of *Eoentophysalis* sp. as measured under the optical microscope in chert samples from the same stratigraphic unit (Campbellrand Subgroup—see Altermann and Schopf, 1995) as that of the current samples. Moreover, preservation of such sub-globular structures, resembling a cobweb of comparable size in microdigitate, partly silicified carbonate stromatolites from the Campbellrand Subgroup, has been shown by Kazmierczak et al. (2004), (their Fig. 6.4–10) and compared to almost identical modern occurrences.

The other characteristic structure, next to the cobweb-like structure, is represented by spherical bodies, 3–5 µm in diameter, that have been identified inside many of the pits (Fig. 10). Most of them are distributed loosely within the walled depressions, but some closely adhere to each other, giving an impression of dividing (cyano-)bacterial cells. A comparison with living cells of the coc-

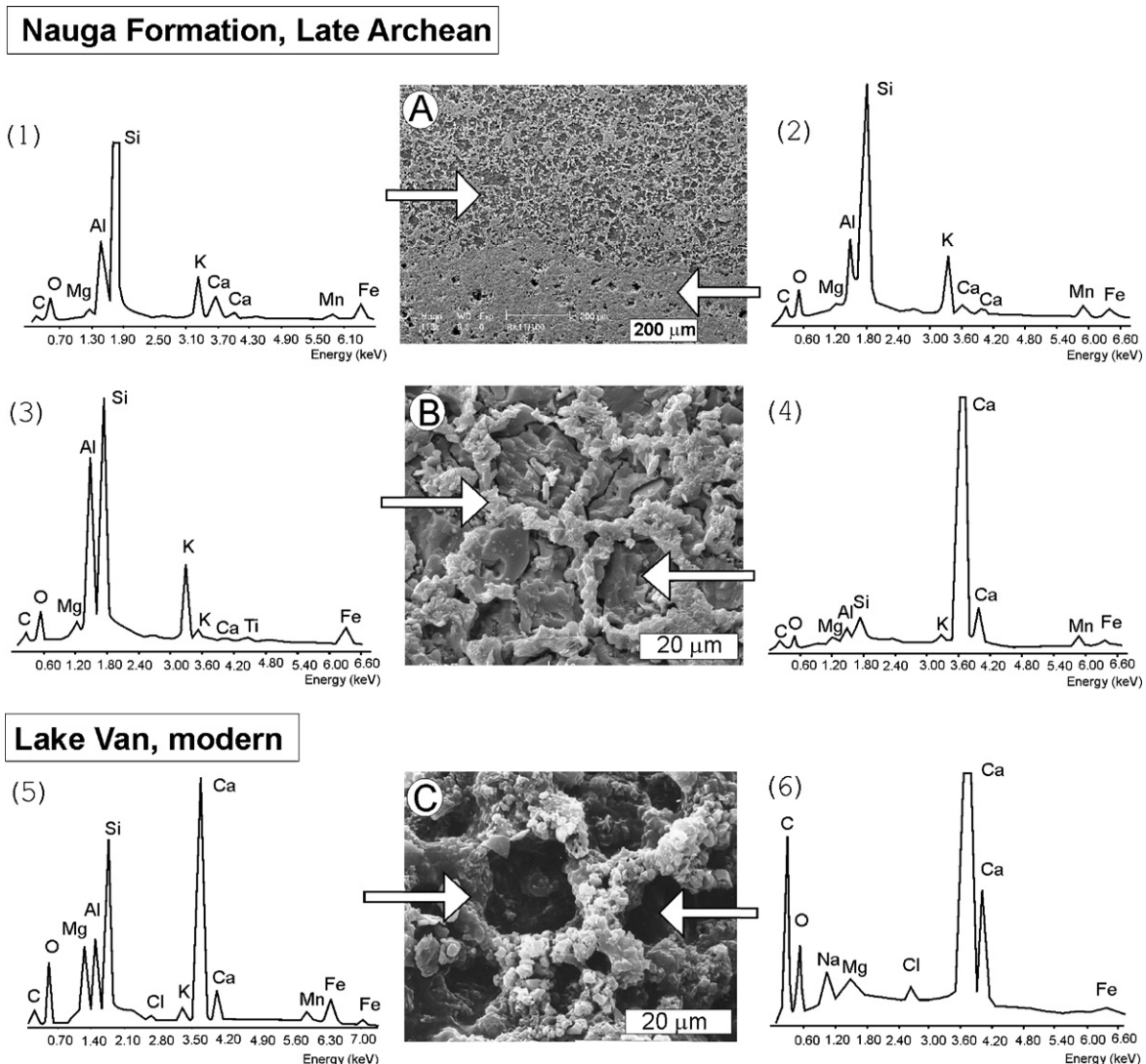


Fig. 8. Comparison of EDX spectra of mineralized coccoid cyanobacterial mats from the Neoproterozoic Nauga Formation (A and B) and the modern cyanobacterial mats from Lake Van, Turkey (C). Frame analyses from the carbonate mineralized Archean mat (1) and underlying silicified marl and shale (2); spot analyses of the pit wall (mineralized common mucilage sheath) (3) and pit-filling (4). Similar analyses of the pit wall (5) and pit-filling (6) from Lake Van. A, B and C are SEM images of etched rock platelets.

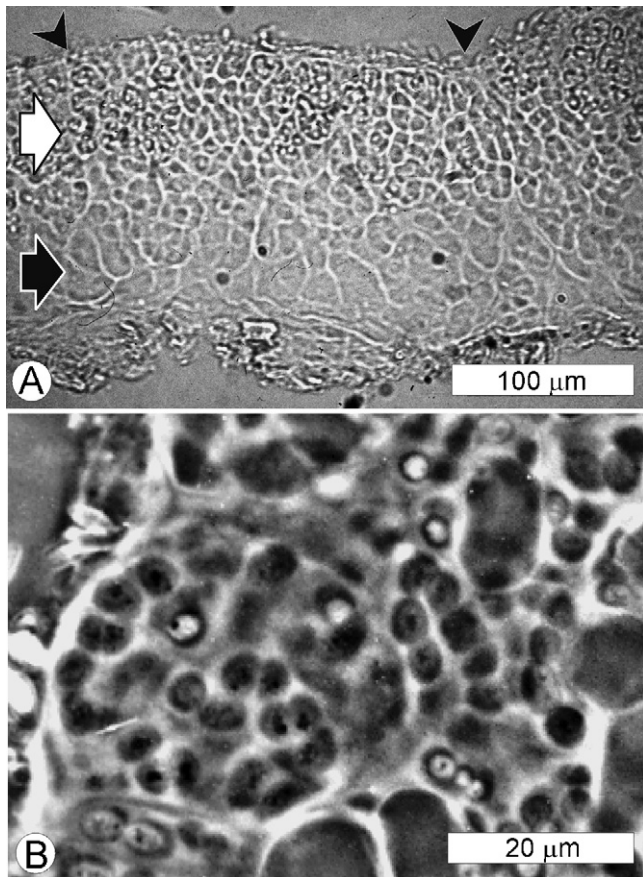


Fig. 9. (A) Vertical section (transmitted light) of modern coccoid cyanobacterial mat from Lake Van (Turkey) showing living cell aggregates (white arrow) close to the mat surface (black arrow heads), and degraded zone of the mat, in which only thicker mucilage sheaths surrounding groups of cells are preserved (black arrow). (B) Magnified fragment of the living mat showing aggregates of cells embedded in common mucilage sheaths of various thicknesses.

coid cyanobacteria, forming mats participating in the formation of the huge Lake Van microbialites, and with coccoid cyanobacterial cells from the Silurian cherts from the Sudeten Mountains in Poland (Kremer, 2006) suggests a great similarity, if not an almost identical character (Fig. 10E and F, respectively). The shape, size and location of these globular bodies inside the pits leaves little doubt that they represent *bona fide* mineralized remains of the cyanobacterial cells that originally formed the microbialites.

EDX spectra of the spherical bodies (Fig. 10) indicate that, as in the case of modern bacterial cells, they have been mineralized by Al–K–Fe silicates with an admixture of Fe oxides (Tazaki, 1997). It has been shown that bacterial surfaces are good sorption interfaces for Al–K–Fe silicate ions (Urrutia and Beveridge, 1994; Tazaki, 1997). Especially Fe is known to be adsorbed on the surface of modern bacteria, e.g. in metal-polluted waters. Such silicates begin to form as poorly ordered phases but over time, became crystalline. A similar, but very weak signal was obtained from the fragment of silicified mucilage partly covering the spheroid cells, in the centre of the capsule shown in Fig. 10C. In contrast, much stronger Al, K, Mg (and Fe) peaks within the wall of the capsule containing these cells signal the presence of phyllosilicates in the capsular wall remains, as discussed above (comp. Fig. 8).

The very good preservation of these coccoids has triggered the suspicion that they might represent post-depositional bacterial contaminants to the rock. However, on closer examination, this objection can be discarded. The singular coccoid cells occur exclusively in the etched molds of colonial imprints, between the walls

of the cobweb-like structure described above, which is also typical for the occurrence in the Lake Van microbialites (Kempe et al., 1991; Kazmierczak et al., 2004; López-García et al., 2005; Kempe and Kazmierczak, 2007) and Phanerozoic silicified cyanobacterial mats (Kremer, 2006). Similar occurrence of coccoid cells surrounded by mucilage, in modern environments, has been shown by Horodyski (1980). A post-depositional contamination should rather affect the whole rock and be especially visible on the less etched walls of the web structure.

Possible post-depositional bacterial contamination can be also excluded, because where silicification of the shale and marl in the same samples (RK11; WA07/11; SA72) is sufficient, such spheres in larger capsular bodies are also visible in thin section within the rock, sometimes affected by early compaction (Fig. 10D lower globules and covering dark laminae). There, the spheres appear red to brown, showing transformation of haematite towards goethite, as can also be observed for comparison in the Silurian sample (Fig. 10F) and as was described by Altermann and Schopf (1995) from the Neoproterozoic Campbellrand Subgroup. Additionally, the above-discussed abundant occurrences of microfossils of entophysalidacean affinity in the rocks of the Campbellrand Subgroup and stratigraphic equivalents in South Africa (e.g. Lanier, 1986; Altermann and Schopf, 1995; Kazmierczak et al., 2004), strengthen our interpretation.

Concerning the taxonomic position of the cyanobacterial remains studied here, the bio-structures visible in the SEM images are essentially similar to capsules and common mucilage sheaths of modern benthic cyanobacteria. They are traditionally classified within the order Chroococcales, as members of the family Entophysalidaceae (exemplified by genera: *Entophysalis*, *Cyanosarcina*, *Pseudocapsa*, *Paracapsa*, *Lithocapsa*, and *Chlorogloea*), or within the order Pleurocapsales (exemplified by genera: *Pleurocapsa*, *Chroococciopsis*, *Xenococcus*, and *Chroococcopsis*) (Komárek and Anagnostidis, 1999; Silva and Pienaar, 2000). According to the new taxonomic system (Boone and Castenholz, 2001) these cyanobacteria belong to Subsections I and II. The characteristic feature of all these cyanobacteria is the capsular organization of their mucilaginous sheaths surrounding individual cells and cell clusters forming colonies. Such cyanobacterial mat organization is exemplified in Figs. 5–9. The relatively thin inner sheaths enclose single cells and small groups of cells whereas thicker sheaths enclose larger groups of cells or constitute the outer sheath (capsule) of a colony (Figs. 5 and 9). In the older zones of such a biofilm the small cells are usually strongly degraded (Fig. 9A, black arrow) and only the thicker mucilage sheaths are easily visible.

5. Discussion

The new findings on Neoproterozoic microbiota reported here represent, in our opinion, benthic colonial coccoid cyanobacteria preserved as the remains of mineralized capsules, sheaths and cellular remains. Their exceptional preservation in carbonate rocks appears to be dependent on the unusual environment of deposition, weak silicification and the presence of finely distributed organic matter in the samples, that combined to prevent coarse and thorough recrystallization.

In the case of the Nauga Formation cyanobacteria, the process of early *post-mortem* mineralization was most probably associated with the action of heterotrophic bacteria upon the dead cyanobacterial biomass. The lytic action of the heterotrophic bacteria might have led, similarly as in recent mats, to liberation of Ca and Mg cations stored (complexed) in the cyanobacterial EPS and glycolyx during the cyanobacterial lifetime (cf. Geesey and Jang, 1989; Decho, 2000; Stal, 2000; Paerl et al., 2001; Köhl et al., 2003; Kremer et al., 2008). This, in turn, might have enhanced precipitation of

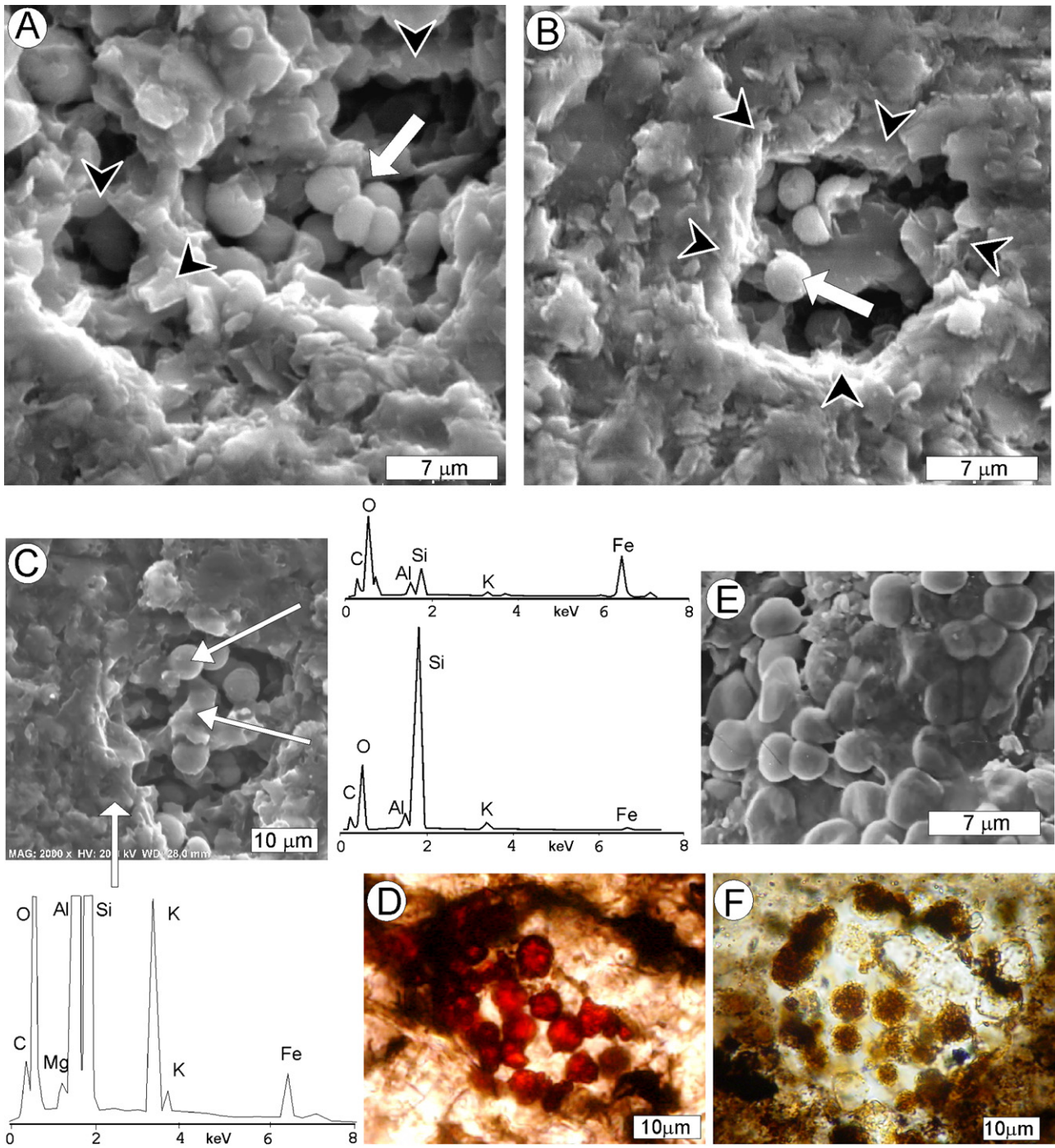


Fig. 10. SEM images of etched Neoproterozoic calcareous, silicified shale (Nauga Fm.) with spherical bodies inside mineralized sheaths (A–C) reminiscent of cyanobacterial cells, compared with a group of modern non-mineralized coccoid cyanobacterial cells from Lake Van microbialites (E). (D) Neoproterozoic aggregate of coccoid cyanobacterial (Sample WA07/11 from the same outcrop as RK11) and (F) similar cells in Silurian chert from the Sudetes region, Poland (Kremer, 2006). D and F are transmitted light photographs of a petrographic thin section, demonstrating that the microfossils are embedded in the rock matrix and thus clearly indigenous to the rock (Buick, 1991). White arrows in (A and B) point to the spherical bodies, black arrows point to the mineralized walls of the etch moulds. The three EDX spectra show elemental composition of the Neoproterozoic spherical bodies and the mineralized mucilage sheath measured on the Archean sample shown in (C). The measured spots are pointed out by arrows. Differences between coccoid cells, wall structure and mucilage remnants (middle arrow) are apparent. As described in the text, the wall elemental composition displays distinct Al, K and less distinct Mg and Fe peaks, signalling the presence of phyllosilicates (comp. Fig. 8). The strong Fe signal from the spherical cell-like bodies may indicate the presence of Fe-hydroxides, known to be adsorbed on the surface of modern bacteria in metal-polluted waters. Such Fe-hydroxides are turned to haematite during metamorphism and back to hydroxides during weathering. Red haematite is visible in thin section (D), where the spheres appear reddish-brown, decomposition of haematite to goethite and limonite can be observed, as in the Silurian sample (F).

carbonate minerals within the extracellular polymers and in space occupied by the cytoplasm, by increasing the calcium carbonate oversaturation. Ultra-small precursor amorphous grains of calcium carbonate and other minerals (depending on the ionic composition in the mat microenvironments) could have been generated during

the lifetime of the colonies in the EPS (cf. Kühl et al., 2003; Kremer et al., 2008). This most likely happened due to activity of heterotrophic bacteria which probably used the polysaccharide components as a source of food (cf. Lange, 1971). During later diagenesis, these often amorphous precursor mineral phases can be transformed into

various authigenic minerals, as observed in the case of Nauga Formation cyanobacterial sheaths and capsules and, for example, in the mineralized coccoid colonies from modern Lake Van microbialites (comp. Figs. 5–8). The $\delta^{13}\text{C}$ values measured on the calcareous layers enclosing the remains of cyanobacterial sheaths and on the flat pebble clasts range between -2.7 and -3.1 per mil. (Kazmierczak and Altermann, 2002). This indicates that the calcification occurred within the biodiagenetic zone of bacterial oxidation (e.g. Mazzullo, 2000; Wetzel and Allia, 2000), perhaps with some contribution from the bacterial sulphate reduction processes.

Our SEM observations in Neoproterozoic carbonates are supported by direct comparison to the calcification activity and taphonomy of benthic colonial cyanobacteria (particularly forms assigned to the genera *Entophysalis*, *Stanieria* and *Pleurocapsa*) from Lake Van, Turkey (Figs. 5–8 and 10). Microfossils have been described previously from the same geographic area and stratigraphic group or its correlatives in the Transvaal succession. Altermann and Schopf (1995) reported nine different taxa from partially silicified limestones, including filaments of *Siphonophycus transvaalensis*, *Eomycetopsis* cf. *filiformis*, *Archeotrichion* sp. and coccoids interpreted as *Eoentophysalis* sp., in addition to other unnamed colonial coccoids and hematitized filaments. From the same stratigraphic level, and partly based on the thin section of Klein et al. (1987), Wright and Altermann (2000) reported on possible microbial mediation of calcification and dolomitisation processes, in microbial laminites and oolites. Earlier multiple descriptions of coccoid microfossils including *Eoentophysalis*, from a similar stratigraphic level of the Campbellrand Subgroup (Altermann and Schopf, 1995) and from the age-equivalent Chuniespoort Group (Transvaal Supergroup, Transvaal preservational basin; Lanier, 1986) support our findings and interpretation. Further support can be derived from the report of cyanobacterial molecular fossils (steranes and related products of carbon maturation) in Archean shales of similar age, but from Australia (Brocks et al., 1999; Eigenbrode et al., 2008).

Rare occurrences of carbonate rocks from inferred shallow marine environments are known from early Archean successions, including the 3.45 Ga Warrawoona Group (Hofmann et al., 1999). Their genesis and the sudden appearance of widespread and thick stromatolitic carbonate platforms at about 2.9–2.6 Ga remains, however, unexplained, and the mechanism of biocalcification and carbonate precipitation for the entire Precambrian is still vigorously debated (Altermann and Kazmierczak, 2003; Altermann et al., 2006). Equally puzzling is the genesis of large masses of Phanerozoic fine grained (micritic) carbonate deposits under normal marine conditions. High calcium carbonate oversaturation of the seawater, caused either by higher alkalinities (Kempe and Kazmierczak, 1990, 1994) or higher calcium concentrations (Kazmierczak et al., 1985; Hardie, 1996, 2003) might have increased calcification potential of benthic cyanobacterial communities, leading to mass production of fine grained (micritic) and peloidal limestones in Phanerozoic seas (Kazmierczak et al., 1996).

Extant cyanobacteria are capable of direct calcification in highly CaCO_3 supersaturated (i.e. $\text{SI} > 0.8$) environments provided either by hard waters (karstic fresh waters) or by alkaline waters (alkaline lakes of various salinity) although exceptions from this rule have been reported (e.g. Kremer et al., 2008), but most Precambrian stromatolites presumably thrived under marine conditions. Many early Precambrian stromatolites are extremely finely laminated and often do not show much evidence for sediment trapping and binding. Evidence for trapping and binding is, however, to some extent also present in Archean stromatolites (Altermann, 2008). Nevertheless, rates of sediment accumulation and organic production on Archean carbonate platforms were comparable to those on modern carbonate platforms and in recent microbial mats (Lanier, 1986; Altermann and Nelson, 1998).

In the attempt to solve the problem of the genesis of Archean sedimentary carbonates and stromatolites, it is noteworthy that, *post-mortem*, the cellular content in modern cyanobacterial mats is degraded fairly rapidly by anaerobic bacteria but the extracellular polymers appear to be more resistant to decomposition and are commonly well preserved, even around highly degraded cells (Horodyski and Vonder Haar, 1975; Kempe and Kazmierczak, 1993; Kazmierczak et al., 1996; Kazmierczak and Iryu, 1999). Heterotrophic bacteria occupying or degrading EPS layers of living and dead cyanobacterial cells have the ability to bind various ions and may serve as nucleation centers for a variety of minerals. It has been found (e.g. Ferris et al., 1987; Konhauser et al., 1994; Urrutia and Beveridge, 1994; Schultze-Lam et al., 1995; Fortin et al., 1997; Tazaki, 1997; Barker and Banfield, 1998; Douglas and Beveridge, 1998) that an array of authigenic minerals, including clay minerals, can nucleate and grow within the extracellular matrices. It is also significant for the present discussion, that microprobe analyses of calcified modern coccoid cyanobacterial mats forming huge, tower-like calcareous structures in the highly alkaline Lake Van, Turkey (Kempe et al., 1991) show elemental composition (Fig. 8), indicative of authigenic carbonate and silicate minerals, almost identical to those in the studied Neoproterozoic samples (see also Kazmierczak and Altermann, 2002, their Fig. S4, in the supplementary online material).

6. Conclusions

From the striking morphological and mineralogical–chemical similarity between the Neoproterozoic microfossils presented here and modern benthic colonial coccoid cyanobacteria it can be concluded that analogous, if not identical, biological, taphonomic and fossilization processes were in operation during the early history of life. Thus, our observations may help to solve the problem of the genesis of micritic Archean calcium carbonate deposits. They also cast a new light on the rock-building potential of microbiota in the formation of the Archean carbonate platforms and stromatolitic reefs (Grotzinger, 1989). In the light of our observations it is difficult to accept statements claiming a negligible role for calcified cyanobacteria in Precambrian seas (Arp et al., 2001). The abundant cyanobacterial mats in the Nauga Formation and consequently in the entire Transvaal Supergroup stromatolitic carbonates, suggest mass production of fine-grained calcium carbonate by benthic coccoid cyanobacteria in the Neoproterozoic. This process helps to explain the finely laminated nature of most Archean (particularly stromatolitic) calcareous sediments.

We infer that microbially produced fine-grained carbonates (micrite) must have been abundant in the Archean, but are difficult to recognise because of strong diagenetic and metamorphic neomorphism. Giant Neoproterozoic stromatolitic reefs are common on most cratons. Current and wave abrasion of stromatolitic reefs produced carbonate silts and sands, as are abundant in the 2.9 Ga Wit Mfolozi carbonate platform of the Pongola Supergroup, most likely for the first time in Earth history, and in the giant 2.6–2.5 Ga carbonate platforms of South Africa. It can be argued that the sudden appearance of carbonate platforms at about 2.9 Ga is connected to the evolutionary advancement of life and the appearance of cyanobacteria at that time. Although the occurrence of cyanobacterial biomarkers in rocks as old as 2.8 Ga (Brocks et al., 1999, 2003) has been recently questioned (Brocks et al., 2008; Rasmussen et al., 2008) independent investigation confirm such findings (Eigenbrode et al., 2008). Thus, cyanobacterial calcification is plausible at that time and was probably the most important rock-forming process of biomineralization (Altermann, 2002, 2004). As life probably existed on Earth already at 3.8 Ga (Mojzsis et al., 1996; Rosing, 1999; McKeegan et al., 2007; Schopf et al., 2007), it would

not be surprising to find evidence for cyanobacteria even in the 3.5 Ga Streeley Pool stromatolitic reefs of Western Australia (Allwood et al., 2006). Thus, cyanobacteria may not only have shaped the face of the Earth by their influence on the composition of the atmosphere, but primarily by introducing a new rock type to the sedimentary inventory of our planet Earth.

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