Crystallization pathways in the Great Artesian Basin (Australia) spring mound carbonates: implications for life signatures on Earth and beyond

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ABSTRACT

Recent studies of continental carbonates revealed that carbonates with similar fabrics can be formed either by biotic, biologically-induced, biologically-influenced, or purely abiotic processes, or a combination of all. The aim of this research is to advance knowledge on the formation of carbonates precipitated (or diagenetically altered) in extreme, continental environments by studying biotic *vs* abiotic mechanisms of crystallization, and to contribute to the astrobiology debate around terrestrial analogues of Martian extreme environments.

Both fossil (upper Pleistocene to Holocene) and active carbonate spring mounds from the Great Artesian Basin (GAB, South Australia) have been investigated. These carbonates consist of low- to high-Mg-calcite tufa. Four facies have been described: i) carbonate mudstone/wackestone; ii) phytohermal framestone/boundstone; iii) micrite boundstone; iv) coarsely crystalline boundstone. The presence of filaments encrusted by micrite rich in organic compounds, including UV-protectants, in phytohermal framestone/boundstone and micrite boundstone is a clear evidence of the existence of microbial mats at time of deposition. In contrast peloidal micrite, despite commonly being considered a microbial

precipitate, is not directly associated with filaments in the GAB mounds. It has probably formed from nano-crystal aggregation on colloid particulate. Thus, where biofilms have been documented, it is likely that bacteria catalysed the development of fabrics. It is less certain that microbes induced calcium carbonate precipitation elsewhere. Trace elements, including rare earth element distribution from laminated facies, highlight strongly evaporative settings (e.g. high Li contents). CO_2 degassing and evaporation are two of the main drivers for an increase in fluid alkalinity, resulting in precipitation of carbonates. Hence, although the growth of certain fabrics is fostered by the presence of microbial mats, the precipiation of carbonate crystals might be independent from it and mainly driven by extrinsic factors.Non-classical crystallization pathways (aggregation and fusion of nanoparticles from nucleation clusters) may be more common than previously thought in spring carbonate and this should be carefully considered to avoid misinterpretation of certain fabrics as by-product of life. It is proposed here that the term "organic-compound catalysed mineralization" should be used for crystal growth in the presence of organic compounds when dealing with astrobiological problems. This term would account for the possibility of non-classical crystallization that occurred directly from an aqueous solution. More generally biological processes may be responsible for fabric and facies development in micritic boundstones whilst micrite nucleation and growth are driven by abiotic factors.

Key words: spring carbonates, organomineralization, microbial mat, carbonate nucleation, astrobiology, Mars

INTRODUCTION

The aim of this research is to use spring mounds in the Great Artesian Basin (GAB) in Southern Australia (Fig. 1) as case study to investigate processes that resulted in different

carbonate facies formed from groundwater upwelling within an extremely arid environment, and to further explore implications for astrobiological research. The petrographic, chemical and mineralogical investigations presented provide: i) new insights on the interactions between microbial communities and carbonate crystallization mechanisms; ii) details of how varying chemo-physical parameters influence the formation of diverse and peculiar microfabrics. This study will evaluate the ability of routine petrographic, textural and geochemical analyses to unambiguously determine whether spring mound carbonate deposits were produced (directly or indirectly) by microbial metabolism. As such it provides a new perspective in the identification and characterization of potential biosignatures in the extra-terrestrial sedimentary record where similar deposits may be encountered.

Continental carbonates associated with groundwater upwelling are good indicators of palaeo-hydrology and hydroclimate at least for the Pleistocene and Holocene (Valero-Garcés et al., 2008; Capezzuoli et al., 2010, 2014; Toker et al., 2015), and deep-time examples shed light on non-marine carbonate precipitation before the rise of terrestrial vascular plants in the Silurian (Brasier, 2011). The accuracy of spring carbonates as archives of paleoenvironmental and paleoclimatic proxies depends on their processes of formation. There is still much debate about the interplay of abiotic and biotic processes in the formation of terrestrial carbonates (e.g., Brasier, 2011; Della Porta, 2015 for review) and it is therefore important to attempt discrimination of inorganic *vs* biomediated mechanisms of precipitation of minerals (Rainey and Jones, 2009; Fouke, 2011; Della Porta, 2015) and biomineralization (e.g., Addadi et al., 2003; Faatz et al., 2004; Pérez-Huerta et al., 2018). Trichet and Défarge (1995) introduced the term “organomineralization” to describe mineral formation associated with non-biologically derived organic substances in contrast with biologically-induced mineralization. In the process of organomineralization *sensu stricto* (Défarge and Trichet, 1995; Trichet and Défarge, 1995), the organic matrix present in carbonate crystallization

might be provided by non-living organic substrates including acidic amino acids (e.g., Mitterer,1968; Mitterer and Cunningham,1985), negatively charged carboxylic groups, sulphated glycoproteins and amino sugars (e.g., Mitterer and Cunningham,1985; Addadi and Weiner, 1992) and degraded siliceous sponges (e.g., Reitner, 1993; Della Porta et al., 2004, 2013). Dupraz et al. (2009) introduced the term "organomineralization" *sensu lato* "as an umbrella term encompassing biologically-influenced and biologically-induced mineralization". Key components of biologically-induced mineralization are microbial metabolic processes, which includes extracellular polymeric substances (EPS) and may provide a template for carbonate nucleation, while biologically-influenced mineralization can or cannot be related to EPS and is driven by environmental conditions influencing the saturation index for a specific calcium carbonate phase (Dupraz et al., 2009). Despite this clear distinction, many astrobiological studies are still focused on bacterial mats, which imposes the notion of complex metabolic pathways and the formation of organic matrices that may drive mineralization intrinsically (via microbial metabolism) or extrinsically (via evaporation and degassing).

Classical concepts of nucleation and growth were revolutionized when minerals that are commonly associated with life, such as carbonates, were investigated at the nano-scale. High-resolution Transmission Electron Microscopy has revealed that calcite precipitation may be an indirect consequence of biological activity, but also revealed that the physical properties of the carbonates may be determined primarily by inorganic factors (e.g. Nyirő-Kósa et al., 2018).

This view is supported by computational molecular dynamics simulations that demonstrate the existence of pre-nucleation clusters, with populations of small clusters (~0.7 to 1.1nm) coexisting with large clusters (30 to 250nm) produced by a liquid-liquid separation in solutions that are supersaturated with respect to calcium carbonate, without participation of

external compounds (Wallace et al., 2013). Experiments of $CaCO_3$ crystallization have shown that species "significantly large" than ion pairs forms, thus highlighting the limits of the classical nucleation theory to explain the behaviour of many natural systems (Gebauer et al., 2014). The non-classical approach shifts the focus from the direct and/or indirect role of organic molecules in carbonate crystallization, to the actual pathways that result in the final crystals and define their structural and chemical properties. Yet, the crucial process in calcium carbonate fabric formation is that of growth, which ultimately determine the fabrics themselves. Atomic force microscopy has confirmed theories that calcite crystal growth at an atomic scale takes place by propagation of lattice steps at spiral dislocations on the most commonly developed flat rhombohedral faces (De La Pierre et al., 2016), The rate limiting process is probably desolvation of ions and ion pairs, and organic molecules can play a key role in catalysing this. The independence of the first stages of crystallization from microbial metabolic pathways, or microbially-derived substrates, has been highlighted by direct calcium carbonate precipitation experiments from cave dripwaters, where organic compounds in the total dissolved carbon are commonly represented by non-EPS derived (hence, substances that cannot be related to microbial mats) humic and fulvic acids (Frisia et al., 2018).

When it comes to astrobiology, therefore, the terms organomineralization and organomineral (as described in Perry et al., 2007), need to be integrated and/or revised (see discussion in Dupraz et al., 2009), as this might become a defying point in the search for evidence of Life (Reitner, 2004; Défarge et al., 2009; 2010). The assumption that “organomineralization” equates with Life because it is intrinsically tied to microbial metabolism (Perry et al., 2007), is very different from the assumption that carbonates nucleation and growth may be catalysed by inorganic C, O and H compounds (Défarge et al., 2009 and references therein).

The many pathways of calcium carbonate crystal nucleation and growth on non-biologic matrixes (De Yoreo et al., 2015) may result in morphologies and chemical signatures similar to those commonly interpreted as indicative of biologically-induced mineralization (that is: presence of microbes). This is particularly critical if one of the steps in the process is the formation of solid precursors that may form in compartmentalized spaces and/or become anchored to heterogeneous surfaces (Cölfen and Antonietti, 2005; De Yoreo et al., 2015) including clay minerals as colloidal particulates (Nyirő-Kósa et al., 2018). Given that some chemical properties that are commonly being used as "signatures" for microbialites could potentially also be associated with silicate nano-particulate bridging nanometre-scale crystal aggregates (Frisia et al., 2018), it would stand to reason that the most accurate evidence for Life would be the presence of unequivocal biomarkers related to microbes (see Dupraz et al., 2009). This leaves open the question of the role of carbonate fabrics as proxy of Life-related processes.

The GAB carbonate mounds provided an ideal opportunity to investigate the interplay of biotic and purely abiotic processes in a continental extreme environment, which may be an analogue to early Earth settings nurturing the first microbial life forms, or even analogue to ancient Martian conditions, when its climate o still allowed for the presence of liquid water (Rotschild, 1990; Horneck, 2000; Fairén, 2010).

The springs, located along the western margin of the Lake Eyre South (Fig. 1), are fed by discharge of meteoric groundwater originating from the western margin of the GAB in the Northern Territory and South Australia (e.g., Habermehl, 1980, 2001). The significance of the GAB mounds is that they may provide information on a now arid, evaporative setting fed by alkaline groundwater that may be up to 1.5 Ma old (Torgersen, 1994; Love et al., 2000; Fenshman and Fairfax, 2003), which has been transmitted through aquifers for thousands of kilometres (Love et al., 2013a). As such, they are potential analogues of the spring mounds

found in the Equatorial Layered Deposits of Arabia Terra, which have been interpreted as deposited in a playa lake fed by groundwater upwelling (Andrews-Anna et al., 2010; Franchi et al., 2014; Pondrelli et al., 2015; Pozzobon et al., 2019), and in the terrains described in Jezero and Syrtis Major regions (Ehlmann et al., 2011) on Mars. Given that the concept of a habitability implies presence of liquid water at the surface of a planet, the presence of spring mounds, analogous to those outcropping in the GAB, is critical evidence that there was flowing water, likely supporting some forms of life (e.g., Franchi et al., 2014; Pondrelli et al., 2015; Pozzobon et al., 2019). The understanding of microbial adaptive behaviour is important for the investigation of how life thrived on Earth and other planets in the solar system, especially if signatures of their biosynthetic pathways are preserved in the rock record (e.g., Barbieri and Cavalazzi, 2004; Edwards et al., 2005; Javaux, 2006). Therefore, the GAB continental spring mounds are, like other similar sedimentary deposits, important archives for the study of the resilience of life in extreme environments (e.g., Walter and Des Marais, 1993; Horneck, 2000; Clarke et al., 2007; Squyres et al., 2008; Clarke and Bourke 2011; Djokic et al., 2017).

Definition of terms

Mound Springs - The terms ‘mound spring’ (e.g., Keppel et al., 2011), ‘spring mound’ (e.g., Pentecost and Viles, 1994; Crombie et al., 1997; Keppel et al., 2012 and references therein), and spring deposits (Jones and Renaut, 2010) show mounded morphologies consisting of continental carbonates associated with groundwater discharge or hydrothermal flow.

Tufa - Carbonate tufa deposits were defined by Capezzuoli et al. (2014) as ‘*continental carbonates generally produced from meteoric water at ambient temperature and characterized by low depositional rates, high porosity and high content of microphytes and macrophytes phytohermal or stromatolitic build-ups deposited by ambient temperature*

176 *waters'* (see also Pedley 1990; Riding, 1991; Ford and Pedley 1996; Capezzuoli et al., 2010;
177 Camuera et al., 2014).
178 Micrite - The term micrite is used here for calcite crystals with size of 4μm or less
179 (microcrystalline calcite) with no differentiation between allomicrite and automicrite (Reitner
180 1993; Reitner et al., 1995). The term microsparite is used here to identify a calcite matrix (as
181 seen under the optical microscope) with uniform crystal size (between 4 and 62 μm) and
182 equant crystal shape (e.g., Dunham, 1962; Flügel, 2004).
183 Peloids and pellets - The term peloid is used here to identify grains composed of
184 cryptocrystalline and microcrystalline carbonates regardless from their origin (McKee and
185 Gutschick, 1969; Bathurst, 1971). Clotted peloidal micrite is a textural term that refers to a
186 fabric consisting of granular micritic aggregates (peloids) typically silt sized (20-60 μm;
187 Riding, 2000) forming amalgamated clots (Flügel, 2004). Pellets, on the other hand, are
188 spherical to ovoidal shaped grains without internal structure, consisting of excreta of aquatic
189 organisms (i.e., faecal pellets, algal pellets) and as such they have a narrow uniform size
190 distribution within the same sample (cf. Scholle and Ulmer-Scholle, 2006).
191
192 **GEOLOGIC AND HYDROGEOLOGICAL SETTING**
193 The GAB underlies one-fifth of the Australian continent (Fig. 1A) and is one of the largest
194 groundwater basins in the world (e.g., Love et al., 2013a), consisting of multi-layered
195 Mesozoic marine to continental sandstones (Krieg et al., 1995). The spring mounds of the
196 GAB of Australia form where artesian groundwater reaches the surface in an otherwise
197 extremely dry landscape situated in an arid climate zone (e.g., Keppel et al., 2012). The main
198 aquifers are the Jurassic Algebuckina Sandstone and Cretaceous Cadna-Owie Formation
199 (Habermehl, 2001; Prescott and Habermehl, 2008; Keppel et al., 2012 and references
200 therein). The confining unit for the principal GAB aquifers is a Cretaceous marine mudstone

known as Bulldog Shale Formation (Prescott and Habermehl, 2008; Keppel et al., 2011). The main water recharge occurs along the coastal area of north-east and north Australia (e.g., Keppel et al., 2012), with minor amount of water infiltrating along the north-western side of the GAB (e.g., Prescott and Habermehl, 2008). Water infiltrating in the north-eastern and northern side of the GAB has a residence time of thousands up to millions of years before discharge occurs (Torgersen, 1994; Love et al., 2000, 2013a; Keppel et al., 2012). The spring mounds in the south-west of the GAB are aligned along the central Australian NW-SE faults cutting across Mesozoic and Proterozoic units (Prescott and Habermehl, 2008; Keppel et al., 2012; Love et al., 2013a; Ring et al., 2016). Most of the springs rest unconformably on the Cretaceous bedrocks (Clarke and Bourke, 2011).

In present day conditions, precipitation of carbonates occurs at near-ambient water temperatures of ca. 15 - 30 °C (Keppel et al., 2011; 2012; 2018). The average annual rainfall is ca. 125mm/yr (Keppel et al., 2012). Mean maximum daily temperature at the surface is 28.4°C (Clarke and Bourke, 2011; Keppel et al., 2011, 2012; Love et al., 2013a, b). The evapotranspiration rate varies from 22% to 6% for Warburton and Beresford Springs, whereas values from Wabma Kadarbu National Park - WKNP ('the Bubbler') are approx. 3% (Keppel et al., 2012). The water chemistry composition of the studied springs is presented in Table 2.

Morphology of the spring complexes

The locations selected for this study, WKNP Spring complex, Warburton and Beresford Hill Spring complex and Strangways Spring complex, are located along the Oodnadatta track between Maree in the south and William Creek in the north (Fig. 1B). The 3 locations are all characterized by spring mounds with low-angle shield morphology including asymmetric

flanks and a flat top where, for the active springs, a circular pool of spring water is located (Fig. 2A). Mounds are normally 2 to 5m in height, with exceptions in Strangways Springs mound complex where active mounds can reach >10m height, but they are extremely variable in width. Most of the mound pools are vegetated by hydrophytes such as *Phragmites* sp. and *Typha* sp. (Keppel et al., 2012 and references therein) whereas the flanks of the mounds are always non-vegetated (Fig. 2). For this study 7 mounds from WKNP, one from Warburton and 5 from Strangways Springs have been selected (Table 1). Except for Warburton, where only one active mound exists, the mounds selected cover both active and inactive springs and represent different mound sizes and morphologies including flat-topped and asymmetrical mounds.

Wabma Kadarbu National Park Spring Complex (WKNP)

WKNP spring complex, at the southern edge of the study area (Fig. 1B), has several large active and inactive mounds, including two of the largest mounds in the region, 'The Bubbler' and 'Blanche Cup' (e.g., Prescott and Habermehl, 2008; Keppel et al., 2018). The Bubbler has an overall surface of ca. 38,500m^2 (including surrounding wetlands, Keppel et al., 2012) and a mound radius of 39.7m (Keppel et al., 2018). Blanche Cup consists of prominently layered spring carbonates and pool deposits (Fig. 2A-F). The layering is sub-horizontal at the base of the mound while it is blanketing the morphology toward the top of the mound (Fig. 2F). This mound has a radius of ca. 31m and a concentric shape formed by spring deposits, with a circular active pool at the summit, ca. 6m across, which is surrounded by thick vegetation (Fig. 2A), where formation of coated grains ("oolites", Keppel et al., 2011) still occurs (Fig. 2B). The vegetation surrounding the mound pool mainly consists of hydrophytes (i.e. *Phragmites* sp., *Typha*, *Cyperus*, *Baumera*, *Fimbristylis*, *Gahnia* and *Juncus*; Keppel et al., 2012 and references therein) adapted to the chemical composition of the water in a highly

saline and evaporative environment (see also Lewis et al., 2013; Love et al., 2013a). The top of the mound is characterized by a rim of tufa, the mound barrage structure *sensu* Keppel et al. (2011), and by a phytoherm framestone cut by an active outflow channel (Fig. 2C). The flanks of the mound are draped by phytoherm framestone/boundstone (Fig. 2D) and micrite boundstone (Fig. 2E). Along the flanks of the mound, well cemented tufa are interbedded with poorly cemented beds (or lenses) of reddish silt- and sand-sized terrigenous sediments (Fig. 2E). The base of the mound is characterized by sub-horizontal layers of carbonate mudstone and wackestone (Fig. 2F).

The mound WKNP 1 (Table 1) shows a flat top covered by vegetation and sub-horizontal bedding at the base (Fig. 2G). This inactive mound has no pool at the summit and the only evidence of water upwelling is at the base of the mound, where there are a few, small ephemeral springs associated with the precipitation of evaporites (mainly halite and thenardite; WKNP 1 and WKNP 2 in Table 1) on the floor of the evaporitic lake (playa, Fig. 2G).

The inactive mounds WKNP 3-6 commonly show a concave-up upper rim consisting of phytoherm framestone (Fig. 2H) with plant in life position, which are encrusted by halite and gypsum (Fig. 2I).

Warburton and Beresford Spring Complexes

In the Warburton and Beresford Spring area (Fig. 1B) there is only one active spring (Warburton mound; Keppel et al., 2018), which is surrounded by macrophytes (Fig. 2J). This mound is ca. 2m in height, covers an area of ca. 6,713m^2, and is characterized by very gentle slope. Self-Potential measurements suggest that spring location is on faults that provide conduit to the surface (Inverarity et al., 2016). Flowing waters created shallow stream

channels along the flanks of the mound (Fig. 2J) that are cutting through the phytoherm framestone and boundstone that compose most of the mound build-up (Fig. 2K).

Strangways Spring Complex

The Strangways Spring Complex (Fig. 1B) is characterized by tens of mounds (Ring et al., 2016), most of which are inactive and have slightly asymmetrical shapes (Fig. 2L, StSp1 mound in table 1). These mounds lie unconformably onto the bedrock with the largest active feature located in the northern part of the region (StSp 3, Table 1). This is associated with surface runoff that precipitates thin layers of calcite and other spring minerals with abundant fungal hyphae (Fig. 2M). Another actively growing mound (StSp 5) is characterized by the presence of a water pool at the top, tufa terracettes and cascades along abandoned outflow channels (Fig. 2N-O).

Age of the GAB spring deposits

A sample of sand collected right below the ”Blanche Cup” spring carbonates at WKNP (SM16_06 in figure 2F) was dated by Prescott and Habermehl (2008) at 10.9±1.5 ka using thermoluminescence of quartz sand grains. This provides the maximum age of the first phytoherm framestone tufa formation at this site (Table 1), and coincides with early in the wet, high level phase I of Lake Eyre (Prescott and Habermehl, 2008; Priestley et al., 2018). Despite the age uncertainty it could also coincide with climate instability in Australia following the end of the Younger Dryas (Black and Mooney, 2006).

Samples from inactive mounds at Strangways Spring (Fig. 1B) yielded thermoluminescence age of ca. 60±8 ka (Prescott and Habermehl, 2008), which corresponds with the final part of Lake Eyre’s wet, high lake-level phase III, the last deep-water perennial lake episode in the basin (Priestley et al., 2018).

Priestley et al. (2018) demonstrated that spring carbonate deposition occurred episodically at around 465 ka, 370 ka, 335 ka, 285-240 ka, 185 ka, 160-150 ka, 110-100 ka and during the past 30 ka. They also demonstrated that high carbonate deposition rates were synchronous with humid periods within glacial cycles and that carbonate deposition followed rainfall and increased evaporation rate cycles (Magee et al., 2004; Priestley et al., 2018). Past changes in surface water levels in the Lake Eyre Basin and formation of large expanses of wetland during the Pleistocene might have been caused by groundwater discharge, which was controlled by both climatic conditions and fault re-activation during the Pleistocene (e.g., Krieg et al., 1991; Hesse et al., 2004; Prescott and Habermehl, 2008; Ring et al., 2016). Available data indicate that artesian water has episodically fed spring carbonates for at least 465 ka allowing the survival of life under extreme arid conditions during important global climatic variations such as those associated with Quaternary glacial maxima and the post-Younger Dryas instability (e.g., Ayliffe et al., 1998).

MATERIALS AND METHODS

Forty-five samples of carbonates from 13 spring mounds were collected from WKNP, Warburton Spring and Strangways Springs (Fig. 1; Table 1). X-ray diffraction (XRD) analyses on 36 selected samples had the objective of characterizing the phases present in the specimens and were performed with a Bruker D8 Advance X-ray diffractometer (Cu Kα X-ray source) at Botswana International University of Sciences and Technology (BIUST) Palapye (Botswana). Raw XRD data were then processed by Rietveld refinement by using the FullProf4 software (Rodríguez-Carvajal, 2001). The $MgCO_3$ content in calcite phases was obtained by measuring changes in the d-spacing of calcite (Table 1), as determined from the shift of calcite {112} peak in the diffractograms (Goldsmith et al., 1955; Gayathri et al., 2007; Taviani et al., 2015). Twenty-nine samples were selected among the most

representative of the 4 facies in the three localities for geochemical investigation (Table 3). The major and minor element distributions were measured by using X-ray fluorescence (XRF) on fusion beads at the Council for Geoscience (COG) in Pretoria (South Africa). Milled samples (<75 μ fraction) were roasted at 1000 °C for at least 3 hours to oxidize Fe^{2+} and S, and to determine the loss on ignition (L.O.I.). Glass disks were prepared by fusing 1 g roasted sample and 10 g flux consisting of 49.50% $Li_2B_4O_7$, 49.50 $LiBO_2$ and 1.00% LiBr at 950 °C. For trace element analysis 12 g milled sample and 3 g Licowax was mixed and pressed into a powder briquette by a hydraulic press with the applied pressure at 25 ton. The prepared glass disks were analysed by a PANalytical Axios X-ray fluorescence spectrometer equipped with a 4 kW Rh tube and the wax pellets by a PANalytical Zetium X-ray fluorescence spectrometer fitted with a 4 kW Rh tube.

The WKNP mounds were chosen for detailed petrographic and geochemical study because this area has the best water chemistry record (Table 2) and the mounds cover a broad spectrum of size and morphologies (Fig. 2). The basis of carbonate petrographic classification was modified from that presented by Della Porta (2015), based on the classifications of Dunham (1962), Embry and Klovan (1971) and Wright (1992). Four facies have been identified based on the textures of the spring carbonates.

Ten samples representative of the four carbonate facies identified at WKNP were selected for petrographic investigation (SM_01, _02, _03, _05, _06A and B, _07, _15, _16 and _20; Table 1). Standard 30 μm thick polished and uncoated sections, were prepared at the University of Botswana (UB) in Gaborone (Botswana) and at theCOG. The petrographic and epifluorescence microscopy observations were carried out at BIUST and at the University of Newcastle, Australia. Epifluorescence observations have been conducted on samples selected for the abundance of filaments and putative microbial features (SM_07, SM_15A and

SM_22B; see Table 1) illuminated with UV and green light (excitation wavelengths of 365nm and 470nm respectively).

Morphological and textural observations, and element distribution analyses were performed on freshly broken fragments from 7 boundstone samples (SM_01, _04, _05, _15A and B, _20 and _22A) deemed most representative for the presence of encrusted filaments. In addition, one sample of evaporite crust (SM_11) has been analysed (Table 1). Morphological and textural observations, and element distribution analyses were performed with a JEOL JSM-7100F field emission scanning electron microscope (FE-SEM) equipped with electron dispersive spectrometer (EDS) at BIUST. Specimens were carbon coated and operating conditions were 15-25kV accelerating voltage and 15-20 mm working distance.

Laser ablation – inductively coupled plasma – mass spectrometry (LA-ICP-MS) analysis was carried out on 4 samples from WKNP (Table 4) deemed most representative of the micrite boundstone with bushes of putative microbial filaments. Analyseswere performed at the Laser Ablation ICP-MS Agilent 7700x facility at University of New Brunswick (UNB), Canada, using a Coherent CompexPro 110 (193 nm Excimer laser) with a Resonetics M-50-LR laser ablation system. A 33μm spot size, repetition rate of 3Hz and an on-sample energy of 5J/cm^2 were used, with a 30s ablation and a 30s gas blank between each ablation. Carrier gasses were ultra-pure helium (300 ml/min), ultra-pure nitrogen (2ml/min), and standard Argon (930 ml/min). A second rotary pump was used to increase sensitivity for heavy isotopes. The ICP-MS was tuned for a full suite of elements (Z = 7, 47, 118, and 207 were monitored during tuning) to ensure maximum sensitivity over the range of masses analysed, while keeping double-charged ions and oxides at a level below 0.3% for each. Standards used were NIST610 and MACS-3 (see Online Materials). Calcium was used as internal standard for data reduction of Ca-carbonate samples. The dwell times for most isotopes were kept at 0.01 sec per isotope, thus allowing the lowest possible sweep time for each method.

375 Non-destructive geochemical analyses were performed with the use of a HORIBA LabRAM
376 HR Evolution Raman microscope equipped with 532nm laser (LAS-532-100HREV) at
377 BIUST for *in situ* identification of the distribution of organic compounds and mineral phases
378 on one sample of micrite boundstone (SM16_20, Table 1), on the assumption that this sample
379 identified a mixture of bio-induced and inorganic processes (cf. Frisia et al., 2000). Raman
380 spectroscopy results were processed by using the LabSpec 6 software (Horiba Scientific®),
381 and then compared with reference spectra from the RRUFF mineral phases database (Laetsch
382 and Downs, 2006), and from literature for the organic compound peaks (Edwards et al., 2005;
383 Marshall et al., 2009). The REE ratios and anomalies have been calculated following the
384 linear equations in Lawrence et al. (2006) and in Franchi et al. (2016; 2017). The LREE (light
385 REE, from La to Eu) and HREE (heavy REE, from Gd to Lu including Y) ratio has been
386 calculated as Pr_{SN}/Yb_{SN} (cf. Franchi et al., 2015) and, to avoid negative values and below
387 detection limit values, as ∑LREE/∑HREE (Table 4).
388
389 **RESULTS**
390 **Petrography and mineralogy of GAB spring carbonates**
391 XRD and XRF analyses (Tables 1, 3) revealed that the main carbonate phase in the WKNP
392 and Warburton Spring mounds consists of high-Mg calcite with minor amounts of aragonite,
393 whereas in the mounds from Strangways Springs it is low-Mg calcite. In the studied samples,
394 the {112} peak shift indicates that $MgCO_3$ content in the calcite varies from ac. 4 to c.
395 8mol.% (Table 1).
396 The carbonates from WKNP mounds are grouped into the following four major lithofacies
397 (Figs. 3-5): i) carbonate mudstone/wackestone (cf. Clarke and Bourke, 2011) often grading
398 into oncoidal grainstone with abundant gastropods shell relicts and little to no evidence of
399 plant relicts (Fig. 3A-C); ii) phytoherm framestone and boundstone characterized by micrite-

coated roots and stems and coated grains (Fig. 3D-F); iii) micrite boundstone (Fig. 3G-H, 5) and iv) coarsely crystalline boundstone (Fig. 4).

Petrography of the WKNP carbonates

1. Carbonate mudstone/wackestone. This facies consists of massive, highly porous, poorly-consolidated deposits (Fig. 2C) which, in thin section, reveal textures consisting of clotted peloidal micrite cemented by microsparite containing terrigenous particulates (Fig. 3A). Gastropod shells and coated grains (oncoids) are engulfed by micrite peloids and cemented by microsparite (Fig. 3A, C). The coated grains in the wackestone facies are commonly "oncoid-like" with cortex layers of sparite and microsparite grown around fossils, intraclasts or micrite peloids (Fig. 3A, C). Coarsely crystalline calcite is present as displacive cement (Fig. 3B) or filling the mouldic porosity. Calcite crystals radiating from a micritic substrate in fan-like textures show either clear translucent or turbid (impurity ridden) areas and the growth phases of each crystal are often blurred (Fig. 3B). The last cement phase in this lithofacies is a thin fringe of isopachous calcite lining primary and mouldic porosity (Fig. 3A-B).In addition to an apparent lack of both laminites and few phytoherm remains, a diagnostic characteristic of this lithofacies is the abundance of terrigenous grains of quartz (Table 3) and mouldic porosity (Fig. 3A-B).

2. Phytohermal framestone and boundstone. A major component of the GAB spring mounds consists of phytohermal facies (cf. Keppel et al., 2011) including framestone and boundstone with plant moulds (Fig. 3D-E). This lithofacies consists of clotted peloidal micrite with abundant micritic intraclasts, peloids and pellets, and thin gastropod shells (Fig. 3D). Terrigenous clasts commonly consist of angular clasts of quartz (<100 μm) (Fig. 3D-E).

This phytoherm lithofacies can also contain oncoidal packstone/grainstone (Fig. 3F; cf. ooidal phytoherm framestone in Keppel et al., 2011) or peloidal packstone. The coated grains, ca. 350 μm to 1 mm across, are surrounded by micrite pellets (probably faecal pellets) and clotted peloidal micrite (Fig. 3F). Mouldic porosity is observed where plant remains decayed and the resulting voids were lined by fringes of isopachous calcite cements and then filled by terrigenous materials (Fig. 3E). The last generation of cement in this lithofacies consists of thin, isopachous calcite rims lining the pores (Fig. 3F).

Epifluorescence microscopy of sample SM16_022B (Fig. 6A-C) shows that micrite encrusted filaments excited with 365nm and 470nm wavelengths emit both blue and green fluorescence, whilst microsparite infill is non-luminescent (Fig. 6B-C). Areas of clotted peloidal micrite may appear dull (red oblong in Fig. 6A-B). Isopachous cement crusts consisting of sparry calcite show zonation, with increase of emitted blue and green fluorescence toward the centre of the voids (arrows in Fig. 6B-C).

3. Micrite boundstone. Unconsolidated silt, sand and phytoherm framestone are lined by layers, few cm-thick, of micrite boundstone along the flanks of the mounds, (Fig. 2E). Laminae result from the alternation of whitish and greenish carbonates consisting of clotted peloidal micrite and microsparite (Fig. 3G-H) often showing shrub-like fabrics (*sensu* Gradziński, 2010). Peloids are normally <50 μm across and have a well-rounded, sub-spherical shape with microsparite replacements. The stacked boundstone laminae contain micrite-encrusted filaments with average length from 100 to 250 μm (Fig. 5). These are either cemented by microsparite (Fig. 5A, C-E) or embedded in clotted peloidal micrite (Fig. 5B, F). Hollow filaments appear to be filled by microsparite cements (Fig. 5A-B) or micrite (Fig. 5C-D, F). Micrite-encrusted filaments can be isolated (Fig. 5A, D) or grouped into small

449 shrubs or palisade-like sub-millimetre structures (Fig. 5B, C, E-F), a typical texture found in
450 modern freshwater tufa (Gradziński, 2010).
451 In the micrite boundstone and the phytoherm framestone/boundstone, calcified filaments
452 occur, which are clearly visible in scanning electron microscope micrographs (SEM; Fig. 7).
453 They appear both as hollow, sinuous filaments, few tens of micrometres across arranged in
454 shrubs (Fig. 7A-B) or as less than 5 µm across, isolated rods (Fig. 7C). These filaments are
455 surrounded by clotted peloidal micrite (Fig. 7A, D) and cemented by euhedral microsparite
456 crystals (Fig. 7B-C). The larger filaments have a central hollow cavity surrounded by thin
457 micrite crusts and microsparite crystals radiating from the centre (Fig. 7E-F). Shrubs of
458 filaments can be several hundreds of micrometres across (up to 0.5 mm; Fig. 5) and are
459 characterized by original high porosity, with most pores now partially filled by NaCl (Fig.
460 7F). Euhedral crystals of calcite grew directly on micrite crusts, creating 'armoured'
461 filaments (Fig. 7G-H). The external wall of the filaments is commonly lined by a generation
462 of euhedral, high-Mg calcite crystals with same crystal orientation growing from the thin
463 micrite crust (Fig. 7G-H). The longitudinal section of the filaments reveals that the micrite
464 encrusting the filaments is aggregated in a clotted fabric (Fig. 7I). The central conduit of the
465 filaments is lined by euhedral calcite growing perpendicular to the inner surface (Fig. 7I-J).
466 The external surfaces of micrite peloids are lined by high-Mg microsparite (bottom left in
467 Fig. 7I).
468 Filaments up to several tens of micrometres across (cf. figure 7) in the GAB mounds were
469 previously identified by Keppel et al. (2011) as shrubs of *Rivularia*. The filaments observed
470 in the micrite boundstone can been attributed to the cyanobacteria *Phormidium incrustatum*
471 (Freytet and Verecchia, 1998). The shape and size of these filaments suggests affinity with
472 the *Vaucheria*, a Xanthophyceae algae, and *Oocardium*-like algae which have been found in
473 calcareous tufa deposits (cf. Freytet and Verrecchia, 1998; Gradziński, 2010).

4. Coarsely crystalline boundstone. Coarsely crystalline boundstone (Fig. 4), shows thinly laminated cement crusts entirely consisting of palisade calcite, microsparite and sparite (Fig. 4A-B), micrite and crystal fans (Fig. 4C-E). Thin Mn-Fe-rich shrubs and reddish micrite are intercalated with the coarse calcite laminae (Fig. 4D-E). The dominant fabric is a coarse mosaic of non-planar sparite that cements fans and relicts of acicular crystals radiating from micrite peloids and intraclasts (Fig. 4A-B). The laminated cement crusts commonly separate laminae < 10μm thick consisting of clotted peloidal micrite with shrub-like micrite fabrics (Fig. 4C-D). The coarsely crystalline boundstone contains multiple erosional surfaces and multiple generations of cements (Fig. 4D-E). The last generation of cements consists of isopachous fringes of elongated calcite rhombohedra and sparite (Fig. 4D). Thinly laminated palisades of calcite fans change from colourless to reddish/brown in the hand specimen, because of the increasing presence of Mn-Fe-rich arborescent dendrites growing perpendicular to the laminae (Fig. 4E). Locally the coarsely crystalline boundstone includes micrite peloids and pellets cemented by sparite (Fig. 4F) and by acicular cements (Fig. 4G), as well as isopachous crystal-fans crusts (Fig. 4H). Micrite peloids appear to be a substrate for the thin (< 100μm; Fig. 4G), isopachous layers of acicular crystals, which are followed by thicker (> 200μm; Fig. 4H) fans of sparite cements, which grew radially from the substrate and displaced peloids and/or micrite pellets.

The coarse crystalline banded tufa in sample SM_15A (Fig. 6D) is characterized by calcite showing dull to bright fluorescence emission in the range of green light (Fig. 6E). The thin Mn-Fe-rich shrubs and the reddish micrite on the crystal fans are non-luminescent (Fig. 6E-F). Laminae show regions with high fluorescence in Figure 6E (arrow), which are likely related to the presence of sub-micrometre scale organic inclusions. Figure 6G shows crystals

fan of calcite and rod-shaped crystals surrounded by micrite. In blue incident light (365nm) the boundaries of rods are evident while the crystal fans are non-luminescent (Fig. 6I). The coarse crystalline banded tufa is characterized by a mesh of rod-shaped nano-scale filaments with section < 0.5µm (Fig. 7K). These filaments consist of aggregates of nanocrystals of calcite. The larger, hollow, micrite-encrusted filaments (Fig. 7A-I) have not been observed in this facies.

Geochemical composition of the WKNP spring carbonates

Major and trace elements

The XRF analyses carried out on bulk rock samples reveal very low contents of Na_2O, P_2O_5, K_2O, TiO_2 and MnO, with values always < 0.5 wt.% (Table 3). Al_2O_3 and SiO_2 content ranges from 0 to 1.9 wt.% and from 0.6 to 41.8 wt.%, respectively (Table 3), with the mudstone/wackestone showing the highest SiO_2 contents, which is likely to be related to terrigenous material trapped within the carbonate mud. The Fe_2O_3 concentration varies from 0.1 to 2.6 wt.% (Table 3). MgO and CaO values range from 0.9 to 7.6 wt.% and from 25.6 to 54.8 wt.%, respectively (Table 3).

The XRF results have been normalized against Post-Archean Australian Shale (PAAS) composition (Taylor and McLennan, 1985) (Fig. 8). The Na_2O, Al_2O_3, SiO_2, P_2O_5, K_2O, TiO_2 and Fe_2O_3 contents are depleted in the studied samples with respect to the PAAS (Fig. 8). MgO is particularly enriched in samples from WKNP and Warburton Springs (Table 3) reflecting dominant high-Mg calcite mineralogy (Table 1). Samples from Strangways Springs are enriched in MnO (Fig. 8).

Trace element results from LA-ICP-MS analysis have been normalized against the PAAS composition (Taylor and McLennan, 1985) (Fig. 9). Results from coarse crystalline boundstone and micrite boundstone reveal a heterogeneous distribution (Table 4; Fig. 9). The

micrite boundstone shows a consistent pattern characterized by high Rb and a general depletion in other analysed elements, with Cu, Pb and Th showing high concentration variability (Fig. 9A, D). The coarsely crystalline boundstone shows a distinctive peak of Rb in most of the analyses, whilst other trace metal and element contents are highly variable (Fig. 9B-C). In particular, Mn and Fe reflect the alternation of thin laminae of crystal fans and Fe-Mn-rich dendrites (Supp. Mat. 3).

Clotted peloidal micrite in both micrite boundstone and coarsely crystalline boundstone is commonly enriched in Li (3.3 to 75.6 ppm) and V (up to 6.0 ppm) relative to PAAS (Table 4). Iron and Rb are enriched in the peloidal micrite (Supp. Mat. 3C), reaching maximum concentrations of up to 26900 ppm and 24300 ppm, respectively (Table 4). Manganese is particularly enriched in the laminae of dark micrite within the coarse crystalline boundstone (Table 4), with peaks of up to 6980 ppm (Supp. Mat. 3B).

Rare earth elements distribution

The REE content is commonly very low in all studied samples (∑REE including Y <1 ppm for most of the points analysed) as most REE LA-ICP-MS measurements yielded values below the detection limit of the instrument (Table 4). The average ∑REE content is 1.022 ppm with a maximum of 12.608 ppm yielded by the clotted peloidal micrite from the coarse crystalline boundstone (Table 4; Supp. Mat. 3D).

The PAAS-normalized REE patterns show an overall enrichment of HREE with respect to LREE (Fig. 10). The LREE enrichment factors are mostly above 1 (average 1.37, Table 4) showing an overall LREE enrichment in the non-normalized values. The Y/Ho ratios, excluding outliers with extremely low Ho contents, show overall near-chondritic values throughout the data set (Table 4). Ce and Eu anomalies are highly variable, although this could be the consequence of incomplete REE series (Table 3). Among the samples with

548 complete REE series, Ce anomaly ranges from 0.45 to 1.64 with average value of 0.91 (Fig.
549 10) and the Eu anomaly varies from 0.76 to 2.45, with average of 1.46.
550
551 **Organic matter composition**
552 Raman spectroscopy of micrite boundstone sample SM16_20 revealed that calcite is the
553 dominant mineral phase, followed by halite (Fig. 11). The calcite spectrum has strong bands
554 at 281 cm^{-1}, 540 cm^{-1}, 1085 cm^{-1} and 1613 cm^{-1} and the halite peak is at ca. 540 cm^{-1} (Fig.
555 11) (cf. Sun et al., 2014). Raman spectra also contain bands than can be ascribed to the
556 following functional groups, cellular compounds and substructures: hopanol, DNA-RNA, ß-
557 carotene, chlorophyll, aliphatic (Naumann et al., 1995; Edwards et al., 2005; Guedes et al.,
558 2005; Marshall et al., 2009) (Fig. 11). The bands at ca. 1155-1188 cm^{-1} is a marker for β-
559 carotene. The other typical β-carotene band, at ca. 1522 cm^{-1}, is within the shoulder of the
560 1613 cm^{-1} band of calcite (Fig. 11). Broad bands at 1330 cm^{-1} and the band at ca. 770 cm^{-1}
561 are ascribed to chlorophyll (Fig. 11). Characteristic bands of hopanol can be identified at c.
562 642 cm^{-1} and 1437 cm^{-1}. Other bands at 540 cm^{-1}, 770 cm^{-1} 964 cm^{-1} likely correspond to
563 vibrational groups ν(C–S), DNA-RNA, ν(C–C), respectively (Fig. 11). The characteristic first
564 and second order bands of Disordered Organic Matter (DOM; Guedes et al., 2005) have been
565 detected at 1580-1630 cm^{-1} (G and D2, Marshall et al., 2009) and ca. 2900 cm^{-1} (S2). The
566 former probably overlaps with characteristic bands of other aliphatic compounds, namely
567 ν(C–N), ν(C=C) and C–PC groups, while the latter is within the shoulder of ν(CH_3) and C-H
568 groups (Fig. 11). Most of the spectra in figure 11 show aliphatic ν(CH) stretching band with
569 strong components at ca. 2965 cm^{-1}.
570
571 **DISCUSSION**
572 **Interpretation of the genesis of the GAB mounds lithofacies**

573 *Carbonate mudstone/wackestone.* This is by far the most abundant carbonate lithofacies in
574 the WKNP Spring complex, Warburton and Beresford Hill Spring complex and Strangways
575 Spring complex. It does not seem to be genetically related to active pools and it is distributed
576 across the spring wetlands and in the streams. Along the streams, in particular, the surface
577 area of the substrate in contact with the spring water is large. This is believed to facilitate
578 nucleation of carbonates (Pentecost, 2005; Keppel et al., 2011). Both pH and SI_C of the
579 spring water show a gradual increase away from the pool (from 7.15 to 8.90 and from 0.05 to
580 1.36, respectively for 'The Bubbler' (Keppel et al., 2012; 2018), while Ca^{+2} concentration has
581 opposite trend (Keppel et al., 2011; 2012; 2018). This is likely due to increase of calcium
582 carbonate precipitation along the streams and across the wetlands driven by degassing and
583 evaporation. Both processes contribute to keep the SI_C of the solution high even though there
584 is calcite precipitation and removal of calcium upstream. Thus, it is reasonable to infer that
585 the formation of micrite and microsparite in the mudstone/wackestone is primarily driven by
586 two inorganic processes. Notably, in the mudstone/wackestone facies clotted peloidal micrite
587 texture has been observed (Fig. 3A) to be un-associated with filaments and laminites. The
588 laminites have been observed to contain clotted peloidal micrite. Although previously
589 interpreted as cyanobacterial precipitates (Frisia, 1996), more recent work has shown them to
590 consist of aggregated nanocrystals that could have precipitated directly from supersaturation
591 changes in the ambient waters without any biological agency (Frisia et al., 2018; Meister and
592 Frisia, 2019). In the WKNP Spring, Warburton and Beresford Hill and Strangways Spring
593 complexes, water analyses (Table 2) document variability in pH and supersaturation, in an
594 environment that may be analogous to the evaporative setting where nanocrystal aggregates
595 have been found in micrite (Preto et al., 2015; Meister and Frisia, 2019). There are also
596 analogies to cave settings where nanocrystal aggregation triggered by degassing has been
597 documented (Frisia et al., 2018).

598 The principle behind inorganic formation of clotted peloidal micrite is the formation of a
599 liquid-like phase of calcium carbonate through a binodal process, leading to pre-nucleation
600 clusters (PNC) when differences in supersaturation occur in the solution (Gebauer et al.,
601 2014). From PNC the next step is the formation of amorphous phases and/or nano-crystal
602 aggregation. Thus, on the basis of emerging data on the pathways that lead to the
603 crystallization of micrite, which imply fluctuations in a chemical environment, rather than the
604 active/passive contribution of microorganisms, the formation of carbonate
605 mudstone/wackestone facies is interpreted as due to purely inorganic processes. Micrite
606 precipitated from a parent solution subjected to subtle variations of SI_C. Microsparite is
607 considered as a cement phase that is also inorganic and driven by degassing and evaporation.
608 In this perspective, the formation of this facies can be explained as not requiring biological
609 agency, and therefore does not necessarily represent an example of organomieralization.
610
611 *Phytohermal framestone and boundstone.* The abundant vegetation thriving within pools and
612 streams (Fig. 2) provided a favourable, passive substrate for nucleation and growth of micrite
613 within the phytoherm tufa facies (e.g., Capezzuoli et al., 2010; Keppel et al., 2011; Camuera
614 et al., 2014). Simultaneously, it may have also had an active role by changing water
615 chemistry by consuming CO_2 through photosynthesis (e.g., Liu et al., 2006; 2008). It appears
616 likely that the phytoherm tufa described from the WKNP Spring complex, Warburton and
617 Beresford Hill Spring complex and Strangways Spring complex mounds and also reported for
618 Billa Kalina Spring (Keppel et al., 2011) formed in vegetated pools similar to those currently
619 active. Microbial communities thrived among hydrophytes roots and stems, thus identifying
620 more proximal deposits to the springs than the carbonate mudstone and wackestone.
621

Micrite boundstone. Micrite boundstone is characterized by shrubs of hollow, sinuous filaments, few tens of micrometres across (Fig. 7A-B) interpreted as putative microbial filaments of *Rivularia* sp. (cf. Kepple et al., 2011) and/or *Phormidium incrustatum* (cf. Freytet and Verecchia, 1998). These filaments are encrusted by micrite with high organic matter contents as demonstrated by epifluorescence observation (Fig. 6). Figure 7 shows that filaments are encrusted by well-formed rhombohedral crystals with size as small as 0.5 μm, although in Fig. 7H there are rhombohedra in the range of 0.1μm embedded in what seems an organic (amorphous) material. Epifluorescence images (Fig. 6A-B) suggest that filaments may have acted as a substrate for micrite growth. The band assignments for Raman spectra of the encrusted microbial filaments from the micrite boundstone facies revealed the presence of organic compounds including UV-protectant molecules (Fig. 11). All the samples are characterized by clear markers for β-carotene. The production of key protectant biomolecules such as β-carotene is typical of cyanobacteria from highly stressed environments (e.g., Edwards et al., 2005). Other UV-protectant molecules such as scytonemin might be present within the shoulder of calcite bands at ca. 1600 cm^{-1} (1593 cm^{-1}; Edwards et al., 2005). This suggests presence of cyanobacteria in the micrite boundstone from the GAB mounds, and particularly those cyanobacteria that developed strong defence systems over an extreme arid habitat where the UV index at solar noon in summer is commonly in excess of 12-13 (source: Cancer Council, Australia). The presence of cyanobacteria can be also inferred through the presence of characteristic Raman spectral bands pertaining to unresolved aliphatic, such as ν(CH) stretching (Fig. 11). The UV-protectant molecules are the best evidence of an ecosystem where cyanobacteria thrived because of their capability to protect cells from death caused by high UV radiation (e.g., Pérez et al., 2017). The effect of extreme UV radiation on the microbial community can be regulated by the secretion of EPS that will disintegrate under the effect of the UV radiation and shield the microbial mat (Dupraz and Visscher, 2005).

As discussed for the carbonate mudstone/wackestone facies genesis, micrite in the boundstone facies may have formed exclusively via inorganic steps related to degassing and evaporation. Even though Raman spectra reveal presence of organic compounds, which may be related to relicts of cyanobacterial mats, the role of microorganisms in crystallization pathways is equivocal. No studies have been carried out on the living microbial communities to address this conundrum.

., It is therefore important to discriminate between crystallization pathways and carbonate facies when considering direct or indirect involvement of microbial processes in the boundstone. Crystallization processes may be purely inorganic, whilst microfacies are the expression of complex interactions between all processes (organic and inorganic) that characterize micro-environments of deposition. This distinction opens a possibility of addressing the difficulty identified by Della Porta (2015) of ascribing calcium carbonate precipitation to any specific mechanism in carbonates where microbes and higher organisms are present. Della Porta's (2015) seminal summary on continental carbonate build-ups, highlights that their formation "*results from a continuum of abiotic and biologically influenced/induced processes in settings where carbonate supersaturation is largely driven by physicochemical mechanisms and microbial biofilms, even if acting as passive low-energy surface sites for nucleation, are widely present*". Micro-morphologies alone cannot, therefore, unambiguously point to biologically-controlled/induced crystallization processes, or even organomineralization, but microfabrics provide information on the presence or absence of microorganisms that influence the crystal size, how crystals are spatially organized between each other and how crystals aggregate into specific morphological objects within a sediment/rock. When biomarkers are identified, such as in the micrite boundstone of the GAB, and specifically when EPS are present, it is possible to invoke living or dead organisms in micro-fabric formation. In these situations the term organomineralization is

672 appropriate to explain microfabrics, rather than referring to crystallization pathways that can
673 equally be accounted for, through experiments and observations, as the result of non-classical
674 nucleation processes driven by subtle changes in supersaturation of the parent solution.
675 The debate about microbial contribution to calcium carbonate formation in dark and nutrient-
676 poor cave environments is also pertinent. There, calcium homeostasis may act as a first step
677 in the nucleation processes (Banks et al., 2010). Calcium homeostasis is a physiological
678 adaptation of bacteria to remove "toxic" Ca^{2+} ions, which is particularly beneficial in caves,
679 but its contribution to secondary calcium carbonate precipitation to form speleothems has yet
680 to be demonstrated (Banks et al., 2010). Calcium homeostasis cannot be ruled out in GAB,
681 being useful also in such a Ca-rich setting (Table 2), but to support bio-mineralization for the
682 micrite boundstone, one would have to demonstrate experimentally that the microbes are
683 using this pathway to expel excess Ca^{2+}. By considering all data presented hereit can be
684 suggested that microbes catalysed calcium carbonate crystal arrangement into a boundstone
685 texture. The micrite boundstone *fabric* is the result of biologically influenced processes, but
686 the crystallization pathways may have been purely driven by inorganic processes. Therefore,
687 the micrite crystals may not be organominerals (*sensu* Dupraz et al., 2009). In fact, if
688 supersaturation changes in the parent solution alone are needed to start non-classical
689 crystallization processes, the degassing and evaporation are sufficient to drive nucleation and
690 growth of micrite. There is no need for microbial metabolism to catalyze calcium carbonate
691 nucleation and growth.
692
693 *Coarsely crystalline boundstone.* Calcite crystals fan and palisade calcite laminae in the
694 coarsely crystalline boundstone (Fig. 4A-E) alternate with Fe-Mn shrub-like fabrics (Fig. 4D-
695 E) indicating stages of calcite growth interruption (inhibition), which could be ascribed to
696 variations in water chemistry, such as mixing with undersaturated waters, reduced flow rates,

enhanced microbial respiration (evolving excess CO_2) and/or organic matter oxidation (see discussion in Camuera et al., 2014). Similar fabrics have been reported for rapidly growing deposits under high-flow rates that favour rapid CO_2 loss (Okumura et al., 2012; Camuera et al., 2014). In the laminated coarsely crystalline boundstone (Fig. 4A-H), Li, Y and Rb concentration increases within the thinner laminae (Supp. Mat. 3B points 1-6), which record an increase of evaporation rather than high-flow rates.

The coarse crystalline boundstone likely precipitated along streams, cascades and similar environments where large surface area and the unstable flow of water favoured evaporation and, consequently, increased alkalinity. Degassing increased pH and SI_C promoting calcite mineralization, so calcite nucleation and growth was not necessarily driven by metabolic processes. As already discussed for carbonate mudstone and micrite boundstone facies in the GAB mounds, this does not mean that microbial activity was absent in the development of fabrics, but it cannot be proven in the actual crystallization process. Microbial metabolism likely changes the chemistry of the parent water, but similar changes are attained through degassing and evaporation. The presence of putative microbial filaments (Fig. 7K) shows that microorganisms were present in the system, but a major issue in interrogating carbonates associated with evaporative settings such as the GAB concerns the energy environments surrounding the "building blocks" of the carbonates. Under evaporative conditions, it is known that the parent fluid may reach growth sites "*per ascensum*", via capillary flow. This has obvious influence on the SI_C of the parent solution and on crystal fabrics (see Caddeo et al., 2015; Vanghi et al., 2017). When excited by the 470 nm incident light the sparite crystal fans of this facies are non-luminescent, which suggests that the minerals do not contain organic compounds (Fig. 6H), so they likely grew abiotically. By contrast, the layer of luminescent micrite around non-luminescent rods suggests that micrite preserves organic molecules, suggesting that organic compounds catalysed the precipitation of small, equant

calcite crystals (Fig. 6H). In analogy to what was discussed for the carbonate mudstone and the micrite boundstone facies it is reasonable to infer that the coarsely crystalline boundstones are the product of predominantly inorganic crystallization processes, driven by evaporation, and the microbial role was simply that of a catalyst for fabric development.

The importance of REE in deciphering the environmental conditions during precipitation of spring carbonates and water provenance

Several studies, especially in marine environment, suggested that microbialites record the ambient aqueous REE distributions (e.g., Webb and Kamber, 2011), but it is also well known that microbial metabolism can result in biogenic fractionation of REE (Pourret et al., 2008; Chagas et al., 2016 and references therein). As a result of this biogenic fractionation the REE distribution within microbialites might not reflect that of the water (Takahashi et al., 2005; Pourret et al., 2008). A study carried on carbonates precipitated from CO_2-rich waters in absence of microbial mats showed that the REE pattern of precipitates was very similar to that of the original waters, indicating that no significant REE fractionation into carbonates occurred (Choi et al., 2009). Therefore, the fractionation of REE into microbial mats has been often used as evidence for organomineralization when textural and fabric evidence was inconclusive (Takahashi et al., 2005; Franchi et al., 2015; Franchi, 2018).

The REE distribution into carbonates can also highlight partitioning effects into the organic colloidal fraction (e.g., Pourret et al., 2008). In organic-rich alkaline waters this partitioning effect might result in carbonate phase enriched in HREE with a negative Ce anomaly and organic colloids with LREE enrichment and positive Ce anomaly (Pourret et al., 2008). The REE distributions of micrite boundstone and coarse crystalline boundstone from GAB spring mounds (Table 4) reveal an overall LREE enrichment and Ce anomalies close to 1, showing affinity with organic colloids described by Pourret et al. (2008). At high carbonate alkalinity

747 and a pH over 8.0, Ce(III) is oxidized to Ce(IV) that can be easily adsorbed by organic matter
748 leading to a positive Ce anomaly of the organic-rich colloids and consequent negative Ce
749 anomaly of the carbonate precipitates (Pourret et al., 2008; Himmler et al., 2010; Kim et al.,
750 2012; Hu et al., 2014). The original negative Ce anomaly of carbonate phases can be altered
751 if organic colloids are dissolved during diagenesis (e.g., Franchi et al., 2015), as it seems to
752 be the case for the GAB samples.
753 The average ∑REE content in the micrite boundstone (Table 4) is around 1ppm and shows a
754 clear enrichment into the filaments shrubs (Supp. Mat 4B) with respect of micrite peloids
755 (Supp. Mat. 4A). This suggests that there was a biologic fractionation of REE associated with
756 polymeric substances during encrustation, which would support a catalytic function for the
757 filaments. The ∑REE content in the coarsely crystalline boundstone (Supp. Mat. 2-3; Table
758 4) is as low as 0.01 ppm with a slight, but consistent, partitioning of the REE into the clotted
759 peloidal micrite, which shows the highest REE contents, up to a maximum of 12.608 ppm
760 (Supp. Mat. 3D). The enrichment of REE into the clotted peloidal micrite is coupled with a
761 high Mn-Fe contents (up to 437 and 7780ppm, respectively) in the peloids (e.g. points 2-4
762 Supp. Mat. 3D; Table 3). Interestingly, the Fe-Mn-rich dendrites in the coarsely crystalline
763 boundstone of sample SM16_15A (Supp. Mat. 3B) yielded ∑REE values below 1 ppm
764 revealing that the REE are not coupled with Fe and Mn oxides in this facies (e.g., Bau and
765 Koschinsky, 2009; Franchi et al., 2015).
766 Very low ∑REE values and the lack of correlations between REE and Zr, Th and Rb (Table
767 3), indicate that the influence of REE-bearing terrigenous material is negligible, with the
768 exception of the peloidal micrite from the coarse crystalline boundstone. It is reasonable to
769 assume that crystallization pathways explain the concentration of REE into clotted peloidal
770 micrite. The presence of abundant organic matter (Moffet, 1994; Franchi et al., 2016), may be
771 more important for calcite authigenesis than any site-specific microbial metabolism

(Neuweiler et al., 2003). The observed decoupling of REE and Fe-Mn suggest that the environment of micrite formation was oxidising, inhibiting reductive dissolution of iron-manganese oxyhydroxides. Alternatively, clay minerals under the form of colloidal particulate may have favoured non-oriented nano-particles attachment during stages of micrite crystallization (cf. Cölfen and Antonietti, 2005; Nyirő-Kósa et al., 2018). The spatial precision of the LA-ICP-MS technique does notdiscriminate effects due to presence of nano-inclusions, which would be better detected by micro- and nano-scale techniques such as synchrotron radiation-based micro XRF (Vanghi et al., 2019). Although such a nanoscale approach would be advisable, it is not always feasible and may not detect elements at very low concentrations.

The REE in continental carbonates can be useful proxies for the characterization of fluid/rock interactions between the groundwater and the substratum (e.g., Uysal et al., 2007; 2009; Teboul et al., 2016; Kokh et al., 2017) and for the characterization of the sources of calcium and other elements that constitute tufa and travertines (Teboul et al., 2016; Kokh et al. 2017). A pattern of HREE enrichment, LREE depletion (Bau and Dulsky, 1996; Bolhar et al., 2004) in the PAAS-normalized REE patterns, and low Th indicate prolonged interaction of groundwater with carbonate aquifers (Choi et al., 2009; Kokh et al. 2017). In contrast, GAB carbonates are characterized by LREE and Eu enrichment (Eu-anomaly values >1; Table 3), which suggests contribution of deep crustal fluids that were in contact with volcanic rocks and assimilated Ca from breakdown of plagioclase (Michard, 1989; Douville et al., 1999; Klinkhammer et al., 1994; Franchi et al., 2015).

Non-classical crystallization pathways in the GAB carbonates

796 The Australian GAB spring carbonate facies are associated with filamentous microbial mats,
797 macrophyte roots and stems (Keppel et al., 2011). Classically, this association would be
798 interpreted as one in which the biological material provided favourable sites for calcium
799 carbonate nucleation and growth with a strong likelihood of biological agency (directly or
800 indirectly) in the crystallisation mechanism (Castanier et al., 1989; Buczynski and Chafetz,
801 1991; Pentecost, 2005; Gradziński, 2010; Camuera et al., 2014). However, non-classical
802 crystallization pathways involving pre-nucleation clusters are now known to drive micrite
803 precipitation. These arise through binodal processes in a parent solution whose saturation
804 state is modulated by degassing and evaporation alone (Wolf et al., 2008; Gebauer et al.,
805 2014). This paradigm has already been applied to continental carbonate formation (e.g.,
806 Rogerson et al., 2008; Pedley et al., 2009; Riding, 2011) and are equally likely for calcite
807 nucleation in the GAB mounds.
808 Environmental and petrographic data from the GAB carbonates suggest that the first steps of
809 crystallization may have occurred in the water column driven by fluctuations in pH and
810 supersaturation. There is also petrographic evidence for the presence of non-carbonate
811 particles, of both biological and inorganic origin, trapped within the micrite fabric (Fig. 6A-
812 C). Colloids are known to serve as catalyst substrates for attracting aggregates of
813 nanoparticles formed in the water column to filament surfaces, leading to encrustation
814 (Meister and Frisia, 2019). The enrichment of REE and the Ce-anomaly close to 1 detected in
815 the GAB micrite crystals strongly suggests that micrite is an aggregate of nanoparticles
816 bridged by colloids as observed elsewhere (Frisia et al., 2018). The REE, and particularly Ce,
817 are preferentially scavenged by colloids during the formation of carbonates (Pourret et al.,
818 2008). The peak of ∑REE in clotted peloidal micrite (and Fe-Mn-rich micrite pellets; Supp.
819 Mat. 3B-C) then is reasonably interpreted as due to REE scavenging onto inorganic and
820 organic colloids (Dia et al., 2000; Della Porta et al., 2015). Similarly, the lack of clear Ce

anomaly (Ce/Ce* values close to 1) can be interpreted as evidence for Ce complexation on organic colloids (e.g., Pourret et al., 2008) and indirectly related to microbial scavenging of Ce(IV) during subsequent diagenesis of microbialites (Kim et al., 2012; Hu et al., 2014; Franchi et al., 2015; 2016; 2017).

Implications for the "organomineralization" concept and exobiological studies

In the GAB mounds, peloidal micrite, commonly considered a microbial precipitate (e.g., Riding, 2000; Flügel, 2004), is not directly associated with the filaments that are unequivocal evidence for microbial life (Fig. 6H-I). Where biofilms (microbial mats) and therefore EPS around the filaments have been documented, it is likely that bacteria catalysed the development of fabrics. What is less certain is that bacteria induced calcium carbonate crystallization, given that evaporation and degassing alone may have been sufficient to trigger nucleation and growth. Overall, GAB mound petrographic and chemical data suggest that the concept of organomineralization is best associated with fabrics, whilst does not provide information on crystallization pathways. In fact, when the term is associated with fabrics, one immediately understands that the spatial arrangement of calcium carbonate crystals is related to the presence of organic compounds that may have directly or indirectly influenced size, chemistry and spatial arrangement of crystals. If associated with crystallization pathways the concept would obscure the importance of non-classical crystallization pathways

The direct precipitation of micrite from the water column has been a long-standing problem (Morse and McKenzie, 1990). Keppel et al. (2011) suggested that micrite grown in their GAB microcosms experiments was similar to that associated with low-energy, EPS-

846 influenced carbonate depositional environments, in which EPS templating and/or microbial
847 metabolismcircumvented the energy barrier related to calcite nucleation and growth.
848 However, micrite crystallization may follow non-classical pathways (De Yoreo, 2013). When
849 considering all possible nucleation pathways for carbonate crystals, it becomes almost
850 impossible to define whether inorganic CO_2 degassing or metabolic-induced precipitation
851 leads to the precipitation of micrite and the formation of micritic-rich facies (e.g., Arp et al.,
852 2010). This uncertainty encapsulates the debate surrounding "organomineralization", because
853 the concept of organomineralization was mostly derived from micrometre-scale observations
854 of fabrics, whilst nano-scale observations are broadening the discussion to include nucleation
855 processes that occur within the aqueous solution because of simple changes in the chemical
856 environment. The risk is for researchers to use indiscriminately the term
857 "organomineralization" to explain the formation of carbonate crystals when kinetic barriers
858 prevent it. In this sense it bears no relationship to what process drove the crystallization
859 pathways, merely information on a potential participation of anything organic in the
860 crystallization process. Carbonates consist of C and O, and both molecules are in one way or
861 the other related to Life accounting for the fact that O on Earth's atmosphere is a by-product
862 of microbial metabolism (Kasting and Siefert, 2002; Riding et al., 2014), so any carbonate
863 formed at Earth's surface could be considered an organomineral, even if the product of
864 exclusively inorganic processes. Extrapolating to an astrobiological perspective, use of this
865 definition is inadequate as an indicator of life because it negates information on a crucial
866 process of carbonates nucleation and growth. From this astrobiological perspective, it is
867 therefore best to associate organomineralization to fabrics, rather than to the carbonate
868 crystals as "organominerals" formed by a particular biological agency.
869 It is, therefore, proposed that when dealing with astrobiological problems, the term "organic-
870 compound catalysed mineralization" should be used for crystal growth in the presence of

organic compounds. This would account for the possibility of non-classical crystallization directly from an aqueous solution.

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Implication for extra-terrestrial research for Life

The discovery of widespread evaporitic playa deposits on Mars) linked to regional scale groundwater upwelling (e.g., Rossi et al., 2008; Andrews-Hanna et al., 2010; Franchi et al., 2014; Pondrelli et al., 2015; Pozzobon et al., 2019) has boosted the interest for microbial mats living in spring deposits formed under extreme evaporitic and hypersaline conditions. Recent discoveries have revealed that hypersaline conditions may promote polymerization of prebiotic molecules and therefore can be suitable incubators for life (Dalai et al., 2016). In this regards the GAB provides unparalleled opportunity for comparison of Martian layered evaporitic sediments with terrestrial counterparts because of their complex formation that involves groundwater upwelling, springs, evaporative conditions, high UV radiation and evidence of organomineralization (e.g., Mann et al., 2004; Clarke and Bourke, 2011; Franchi et al., 2014).

Although GAB spring mounds are often highly vegetated and present products linked to metabolism of complex organisms, the overall spring system provides a good laboratory for testing hypothesres of how playa deposits on Mars formed and of their potential relationship with life. Especially considering the abundance of biosignatures of UV-protectant compounds that allow organisms to thrive also when exposed to extreme radiation. UV protection is in fact a quality to be expected in extra-terrestrial microbial associations where UV radiation is high (e.g., Mars).

The open question remains how to identify that the minerals and microfacies of the Martian mounds are reliable testimony of past life. Non-classical crystallization pathways may be more common than previously thought in spring and carbonate sedimentary environments (cf. Rodriguez-Navarro et al., 2016) and should be considered in astrobiology to avoid considering calcite crystals as a *de facto* by-product of life (cf. Perry et al., 2007 and discussion in Défarge et al., 2009; 2010). This becomes particularly important for the interpretation of extra-terrestrial micrites, either laminated or showing peloids.

As an example, the sedimentary deposits of the Martian Gale crater consist of evaporite minerals associated with clay, which likely deposited in a progressively drying lake. On Earth, clay minerals, particularly smectite, help in the crystallization pathway known as "oriented nanoparticle attachment" (Cölfen and Antonietti, 2005). This process has been documented in Lake Balaton, where smectite acts as template for the development of calcite crystals (Nyirő-Kósa et al., 2018) as it seems the case for peloids in the GAB boundstone. Similarly, the presence of organic compounds, may guide nano-particle attachment and result in some of the microfabrics observed in the GAB mounds (i.e., organomineralization s.s., Trichet and Défarge, 1995). Thus, by considering the evidence provided by GAB spring mound fabrics and the existing data available on Mars sediments, the crystals alone are not unequivocal evidence of life even if they are characterized by fluorescence that can be related to the presence of organic compounds. It is a clear association with microbial mats in fabrics, coupled with the presence of EPS and organic compounds, which allows carbonate rock/sediment to be interpreted as the result of direct or indirect biological processes.

The concepts outlined in Dupraz et al. (2009) for carbonate authigenesis are here shifted from the mineral to the facies perspective. In particular, if one applies the concept of organominerals as defined by Perry et al (2007), even metamorphic carbonates become organominerals, since large C-H molecules can also be associated with carbonatites

(Belonoshko et al., 2015). This is because it may lead to equivocal interpretation when it comes to astrobiology, as their organomieralization definition does not account for the actual processes of nucleation and growth of crystals.

Only a multi-proxy approach, which should include the nanoscale observation of crystals with high-resolution electron microscopes (HR-TEM), or the investigation of biosignatures such as UV-protectant compounds would determine whether the minerals preserved in mounded morphologies such as those identified in the equatorial region of Mars in the Firsoff and Crommelin craters are due to bio-mediation or biomineralization or not (Franchi et al., 2014; Pondrelli et al., 2015; Pozzobon et al., 2019).

CONCLUSIONS

The complex spring mound deposits in the GAB, at the south-western edge of the Lake Eyre South (South Australia), can be morphologically and genetically compared with spring mounds on Mars as in both areas the layered sediments are formed by processes linked to regional scale groundwater upwelling. Thus, GAB mounds represent a unique analogue of what are believed to be the conditions under which layered spring deposits were formed on Mars, i.e. high evaporation rate and high UV radiation. In this perspective, GAB carbonates, with their complex mixture of biotic and abiotic mineralization processes driven by changes in supersaturation in the parent solutions in a dry, evaporative setting are perfect laboratories for astrobiological studies.

Carbonate spring mound deposits from GAB consist of four facies: i) carbonate mudstone/wackestone; ii) phytoherm framestone and boundstone; iii) micrite boundstone; iv) coarsely crystalline boundstone. Micrite boundstone and phytoherm boundstone are characterized by shrubs of putative microbial filaments interpreted as *Rivularia* sp. and/or *Phormidium incrustatum*. There are also evidences for the presence of non-carbonate

colloids, of both biological and inorganic origin trapped within the micrite fabrics. Colloids are known to serve as catalyst substrates for attracting aggregates of nano-particles formed in the water column to filament surfaces, leading to encrustation.

Overall, GAB mound petrographic and chemical data suggest that the concept of organomineralization is associated with fabrics, and does not provide information on crystallization pathways. It is proposed here that the analysis of microfacies may not be sufficient to provide robust evidence that microbial Life somewhat participated to the formation of evaporative minerals in the Martian mounds. Biochemical and nano-scale, high-resolution investigation of crystals and micro(nano)-morphologies will be needed to reconstruct mineralization pathways.

In synthesis, as GAB facies consist of both organominerals and abiotic/inorganic carbonates, a clear distinction is needed between organomineralization and abiotic mineralization. The term organic-compound catalysed crystallization is here proposed as alternative, in astrobiological studies, of the term organomineralization as defined by Trichet and Défarge (1995) and modified by Dupraz et al. (2009). It is here proposed to confine the term organomineralization to fabrics where the presence of organic compounds is unequivocally demonstrated (i.e. presence of EPS, biomarkers, etc.). This term bears no relation to the crystallization pathway drivers but provides information on a potential participation of organic compounds in the crystallization process. The discussion around the original definition of organomineralization s.s. has been expanded by new concepts of crystallization pathways, which are purely inorganic, and, as such, the concept of organomineralization should be focused only on the interpretation of fabrics and the microfacies. It will be only through future nano-scale investigation that light will be shed on the nature of the drivers of GAB carbonate crystallization, and by extension, to other spring deposits.

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TABLE CAPTIONS

Table 1. Location and description of the studied samples.

Table 2. Hydrochemistry of the GAB spring water. From Keppel et al. (2011, 2018).

Table 3. Oxides composition (XRF analysis) of selected samples from GAB mounds. Numbers in the first raw correspond to sample names in table 1.

Table 4. Major and trace elements distribution from LA-ICP-MS analyses of samples SM16_05, SM16_07, SM16_15A and SM16_20.

FIGURE CAPTIONS

Figure 1. A) Outline of the Great Artesian Basin in Australia showing the study area and the locations of the mound springs under investigation (B): Wabma Kadarbu National Park (WKNP) spring mounds, Warburton Springs and Strangways Springs. Modified from Keppel et al.(2012).

Figure 2. Outcrop view and hand specimens from WKNP, Warburton Springs and Strangways Springs mounds (see Figure 1 for location). A-B) Active pool on top of 'Blanche Cup' spring mound at WKNP characterized by formation of 'oncoid-like' coated grains at the edges of the active pool (B). C) Location of samples MS16_01 and MS16_02 along an active outflow channel on top of 'Blanche Cup'. D) Phytoherm boundstone from the south-western flank of the mound 'Blanche Cup' (sample SM16_04). The inset shows sample SM16_03

collected few meters from SM16_04. E) Micrite boundstone characterized by alternation of greenish and whitish laminae overlying a bed of poorly lithified, fine grained siliciclastic sediments (under the lens). The inset shows sample SM16_05 collected from this same outcrop along 'Blanche Cup'. F) Horizontal bedding at the bottom of the mound 'Blanche Cup' (sample SM16_06). G) Panoramic view of the mounds WKNP2 (S-29.45108; E136.85736) with gentle flanks and flat top. H) Plant remains along the flank of the mound in G. I) PHalite and other evaporites along the flank of mound WKNP5 characterized by ephemeral spring (top). J-K) Outcrop view of the Warburton Spring mounds. J) Running water along the main mound at Warburton Spring (S29.274335; E136.671733). K) Phytoherm framestone along the flank of the mound in J. L-O) Outcrop view of Strangways Springs active and inactive springs. L) Asymmetrical shape of mound StSp1 (Table 1). The top of the mound is vegetated although no evidence of spring activity has been recorded. M) Active mound StSp3 in the northern sector of Strangways Springs (S29.15857; E136.54327) characterized by precipitation of carbonates and thin crust of evaporites with fungi (red arrows). N) Abandoned terraccettes (white arrows) of calcareous tufa along the flank of mound StSp5 at Strangways Springs (S29.15938; E136.54692). O) Fossil cascade made up by phytoherm framestone (white arrow) along the flank of a mound StSp5 at Strangways Springs (S29.15938; E136.54692).

Figure 3. Photomicrographs of samples from spring mounds at WKNP. A-C) Carbonate mudstone and wackestone from 'Blanche cup': sample SM16_06. See location of sampling points in Figure 2F. The tufa in this sample is made of clotted peloidal micrite and putative faecal pellets surrounded by microsparite with diffuse fenestral porosity (A). Coated grains are abundant in this lithotype (red arrows in A). B) Crystal fans of calcite surrounded by clotted peloidal micrite. C) Close up of a single coated grain showing well developed cortex

layers of crystal fans and microsparite surrounding a central agglomerate of micrite peloids (red arrow). D-F) Phytoherm framestone and boundstone photomicrographs: samples SM16_01, 02 and 03. D) This lithofacies is made up by abundant intraclasts and gastropod shell remains (red arrow). Peloids of micrite have been partially replaced by microsparite (sample SM16_01). E) Moldic porosity from phytoherm framestone (sample SM16_02). The cavity left by the plant has been filled by terrigenous materials, mainly quartz grains (red arrows). F) Coated grain from phytoherm framestone (sample SM16_03) surrounded by micrite peloids and putative faecal pellets, cemented by microsparite and by a fringe of early diagenetic isopachous cement (red arrows). G-H) Micrite boundstone: sample SM16_05. The bulk of this lithofacies is made up by clotted peloidal micrite cemented by microsparite. A-F, H: Plane polarized light. G: crossed polarized light.

Figure 4. Photomicrographs of coarse crystalline boundstone micromorphologies and fabrics: samples SM16_07, 15 and 16. A) Microsparite and coarse calcite fans with evidence of micritization (arrows) from sample SM16_07. B) Micrite peloids and intraclasts of micrite radially coated by fans of sparite retaining relicts of fibrous crystals. C) Wackestone (bottom left) and reddish micrite encrusted by superimposed laminae of calcite crystal fans and clotted peloidal micrite (upper part of the photomicrograph). Note the acicular mesh of rod-shaped crystals filling the fracture in the reddish micrite (arrows). Sample SM16_15A. D) Superimposed laminae of calcite crystal fans and clotted peloidal micrite arranged in a shrub-like fabric. Toward the top (top right of the photomicrograph) the stacked laminae are coated by isopachous fringes calcite (elongated rhombohedra) and sparry calcite. Sample SM16_15A. E) Thinly laminated fabric with laminae of calcite crystal fans separated by films of micrite (bottom). Toward the top the fabric is dominated by arborescent Mn-Fe-rich dendrites and sparry calcite. Sample SM16_15A. F) Peloids and pellets of micrite cemented

by sparry calcite. Sample MS16_16. G) Peloids of micrite overgrowth by radial acicular cements and sparry calcite. Sample SM16_16. H) Acicular crystals of calcite growing radially from peloids of micrite and lined by isopachous crystal fan cements. The crystal fans show evidence of corrosion and displacive growth (arrows). Sample SM16_16. A-H: plane polarized light.

Figure 5. Micrite boundstone with putative microbial filaments (red arrows): samples SM16_05 and 20. A-B) Micrite and microsparite encrusted bacterial filaments from sample SM16_05. A) Note that microsparite cements have cemented the filaments and partly replaced the micrite coating (arrows in A). Microsparite is nucleated on the micrite crust and the overall texture is increasing away from the filament. B) Small bush of hollow filaments (arrows) growing perpendicular to the lamination surrounded by clotted peloidal micrite. C-F) Micrite encrusted filaments of supposed microbial origin from sample SM16_20. C) Small shrub of filaments (arrows) and micrite peloids encrusted by clear microsparite. Crosses and letters refer to the points investigated by Raman spectroscopy (Fig. 11). D) Single dark micrite filament (arrows) encrusted by micrite and isopachous cements. E) Palisade of hollow filaments (arrows) encrusted by micrite and cemented by microsparite. Crosses and letters refer to the points investigated by Raman spectroscopy (Fig. 11). F) Palisade of dark micrite filaments (arrows) surrounded by clotted peloidal micrite and cemented by microsparite.

Figure 6. Epifluorescence images of selected samples of phytoherm framestone (A-C) and coarse crystalline banded tufa (D-I). A-C) Clotted peloidal micrite (red circle in A) and micrite encrusted filaments (white circle in A) cemented by microsparite from sample SM16_22B. In the 470nm fluorescence range (B) the filaments show a lining of bright luminescent micrite. The clotted peloidal micrite is dull to bright luminescent whereas the

microsparite is non-luminescent and locally shows thin lamination with alternation of bright and non-luminescent cements (arrows in B and C). D-F) Coarse crystalline boundstone from sample SM_15A (same as Supp. Mat. 3D). In the 470 nm fluorescence range (E) the cements are dull to bright luminescent and the thin Mn-Fe-rich dendrites are opaque. In blue light (365nm) the reddish micrite (arrow) appears clearly non-luminescent (F). G-I) Rods of calcite growing on the surface of crystal fans and sparite from sample SM16_07 coarse crystalline boundstone (same as Supp. Mat. 2C-D). In the 470 nm fluorescence range (H) the boundaries of the rods (dark in transmitted light) are highly fluorescent and the crystal fans carbonate are dark. In blue light (365nm) the boundaries of rods are evident (I) But some carbonate also fluorescent. The spots in figures 6D-I are the ablation spots of the LA-ICP-MS analyses.

Figure 7. Scanning electron microscope photomicrographs of the spring carbonates and evaporites from WKNP. A) Shrubs of hollow filaments surrounded by peloids of micrite (arrows) from sample SM16_05. B) Isolated filaments encrusted by microcrystalline calcite and cemented by microsparite from sample SM16_04. C) Close up of one of the filaments (square in B) showing the microcrystalline structure of the filament encrusted by euhedral crystals of microsparite (arrows). D) Micrite and microsparite encrusted filaments cemented by microsparite from sample SM16_04. E) Transversal section of filaments from sample SM16_04 showing microcrystalline calcite encrusted by euhedral crystals of microsparite. F) Transversal section of a hollow filament made up by micrite encrusted by microsparitic cements; voids are partially filled by halite. Sample SM16_05. G) Close up of a filament from sample SM16_04 encrusted by euhedral crystals of calcite (arrows). Note that the crystals of calcite have the same orientation. H) Close up of a filament made by micrite overgrowth by euhedral crystals of calcite growing perpendicular to the filament. Sample SM16_04. I) Longitudinal section of a hollow filament showing the central part of the wall

made up by aggregates of micrite lined by an isopachous crust of microsparite. Sample SM16_05. Note the peloids in the bottom left of the picture are lined by microsparite as well. J) Close up of the inner wall of a hollow filament showing the euhedral crystals of calcite growing perpendicular to the wall of the filament. Sample SM16_05. K) Mesh of rod-shaped filaments from sample SM16_15A. L) A sample of a thin evaporitic crust (SM16_11; Table 1) revealing the presence of peloids of micrite trapped within a mesh of tightly packed acicular crystals of thenardite (SEM-EDS spectrum).

Figure 8. PAAS-normalized distribution of major oxides from WKNP, Warburton Springs and Strangways Springs carbonates.

Figure 9. PAAS-normalized trace elements (LA-ICP-MS) distribution from 4 selected samples from WKNP. The numbers in the keys refer to the sample number (e.g. 01) and ablation spots (e.g. _03) shown in the Supplementary Materials 1-4 and in Table 4.

Figure 10. PAAS-normalized REE distribution from 3 samples from WKNP. Note that figure reports only the patterns obtained for samples with complete REE series (Table 4) and these are mostly micrite encrusted filaments (20_03_4), peloids of micrite (15A_03_7, 8, 10, 20_04_6) and micrite (all other points). The numbers in the keys refer to the ablation spots shown in the Supplementary Materials 2-4 and in Table 4.

Figure 11. Raman spectra of two filament palisades from sample SM16_20 (see sampling location in figure 5).

Supplementary Material 1. Photomicrographs of sample SM16_05 showing the location of the LA-ICP-MS ablation points (Table 4). A-B: crossed polarized light; C-E: plane polarized light.

Supplementary Material 2. Photomicrographs of sample SM16_07 showing the location of the LA-ICP-MS ablation points (Table 4). B, D: crossed polarized light; A, C, E: plane polarized light.

Supplementary Material 3. Photomicrographs of sample SM16_15A showing the location of the LA-ICP-MS ablation points (Table 4). A, C: crossed polarized light; B, D: plane polarized light.

Supplementary Material 4. Photomicrographs of sample SM16_20 showing the location of the LA-ICP-MS ablation points (Table 4). B-D: crossed polarized light; A: plane polarized light.