Formation of micro-spherulitic barite in association with organic matter within sulfidized stromatolites of the 3.48 billion-year-old Dresser Formation, Pilbara Craton

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Abstract

The shallow marine and subaerial sedimentary and hydrothermal rocks of the ~3.48 billion-year-old Dresser Formation are host to some of Earth's oldest stromatolites and microbial remains. This study reports on texturally distinctive, spherulitic barite micro-mineralization that occur in association with primary, autochthonous organic matter within exceptionally preserved, strongly sulfidized stromatolite samples obtained from drill cores. Spherulitic barite micro-mineralization within the sulfidized stromatolites generally forms submicron-scale aggregates that show gradations from hollow to densely crystallized, irregular to partially radiating crystalline interiors. Several barite micro-spherulites show thin outer shells. Within stromatolites, barite micro-spherulites are intimately associated with petrographically earliest dolomite and nano-porous pyrite enriched in organic matter, the latter of which is a possible biosignature assemblage that hosts microbial remains. Barite spherulites are also observed within layered barite in proximity to stromatolite layers, where they are overgrown by compositionally distinct (Sr-rich), coarsely crystalline barite that may have been sourced from hydrothermal veins at depth. Micro-spherulitic barite, such as reported here, is not known from hydrothermal systems that exceed the upper temperature limit for life. Rather, barite with near-identical morphology and micro-texture is known from zones of high bioproductivity under low-temperature conditions in the modern oceans, where microbial activity and/or organic matter of degrading biomass controls the formation of spherulitic aggregates. Hence, the presence of micro-spherulitic barite in the organic matter-bearing Dresser Formation sulfidized stromatolites lend further support for a biogenic origin of these unusual, exceptionally well-preserved, and very ancient microbialites.

Keywords
dresser formation, organic matter, paleoarchean, spherulitic barite, stromatolites

1 | INTRODUCTION

The ~3.48 Ga Dresser Formation in the North Pole Dome of the East Pilbara Terrane (Western Australia) is famous for hosting exceptional evidence for some of Earth's oldest life. Stromatolites are widespread and common in the North Pole Chert Member of the Dresser Formation, where they occur within shallow water to subaerial deposits that have been variably influenced by circulating hydrothermal fluids (Baumgartner, Van Kranendonk, et al., 2020;
Baumgartner et al., 2019; Djokic, Van Kranendonk, Campbell, Walter, & Ward, 2017; Groves, Dunlop, & Buick, 1981; Van Kranendonk, 2006, 2011; Van Kranendonk, Philippot, Lepot, Bodorkos, & Pirajno, 2008; Walter, Buick, & Dunlop, 1980). A biological origin of these stromatolites is demonstrated by a diverse array of textural features that are indicative of microbiologically mediated formation (Baumgartner et al., 2019; Buick, Dunlop, & Groves, 1981; Van Kranendonk et al., 2008; Walter et al., 1980; among others), and by the presence of associated organic matter, including microbial remains, whose syngeneric origin is demonstrated by relationships with stromatolite geometry and primary mineralogy (Baumgartner et al., 2019). Additional support for ancient life in the Dresser Formation includes: (a) organic matter and methane-rich fluid inclusions in quartz of bedded and hydrothermal vein chert, which show carbon isotope signatures that are expected for biological formation (Duda et al., 2018; Morag et al., 2016; Ueno, Isozaki, Yurimoto, & Maruyama, 2001; Ueno, Yamada, Yoshida, Maruyama, & Isozaki, 2006); (b) sulfur isotope signatures of pyrite mineralization that match the isotopic fractionation trends expected for sulfur-cycling organisms, notably microbes dependent on sulfate reduction and/or disproportionation of elemental sulfur (Baumgartner, Caruso, et al., 2020; Philippot et al., 2007; Shen, Buick, & Canfield, 2001; Shen, Farquhar, Masterson, Kaufman, & Buick, 2009; Ueno, Ono, Rumble, & Maruyama, 2008).

The Dresser Formation also hosts large barite deposits that occur in a dense network of hydrothermal veins, and in laterally extensive, coarse-grained barite layers within bedded cherts (Buick & Dunlop, 1990; Nijman, Bruin, & Valkering, 1998; Pirajno & Van Kranendonk, 2005; Van Kranendonk, Hickman, Williams, & Nijman, 2001; Van Kranendonk et al., 2008). The bedding-parallel barite deposits were originally interpreted as replacive mineralization, formed after gypsum evaporites that precipitated in a restricted lagoon setting (Buick & Dunlop, 1990). However, the recognition of barite as a primary precipitate and that the bedding-parallel, coarse-grained barite has intrusive relationships with the host sedimentary rocks, indicate that it precipitated from circulating and venting hydrothermal fluids in a low-eruptive volcanic caldera setting (Nijman et al., 1998; Runnegar, Dollase, Ketcham, Colbert, & Carlson, 2001; Van Kranendonk, 2006; Van Kranendonk et al., 2008; Van Kranendonk & Pirajno, 2004). In this scenario, \( \text{Ba}^{2+} \) is interpreted to have been sourced mainly from footwall basaltic through leaching by hydrothermal fluids, whereas \( \text{SO}_4^{2-} \) could have been derived from both the hydrothermal systems and intermixed seawater (Baumgartner, Caruso, et al., 2020; Nijman et al., 1998; Philippot, Zuijen, & Rollion-Bard, 2012; Shen et al., 2009; Ueno et al., 2008; Van Kranendonk, 2006; Van Kranendonk et al., 2001; Van Kranendonk & Pirajno, 2004).

Here, we report the discovery of micro-spherulitic barite within exceptionally preserved Dresser Formation sulfidized stromatolites from unweathered drill core samples (Van Kranendonk et al., 2008; Baumgartner et al., 2019). These texturally distinctive barite micro-mineralization occur in two associations: (a) as agglomerations in association with organic matter (including putative microbial remains; c.f., Baumgartner et al., 2019) that are preserved within petrographically earliest dolomite and nano-porous pyrite of the sulfidized stromatolites; (b) as agglomerations within coarse-grained, compositionally distinct (Sr-rich) barite crystals that grew in beds between horizons of the sulfidized stromatolites. Micro-spherulitic barite very similar to that in this study is known to form under low-temperature marine conditions in the presence of microbial activity and/or derived organic matter (e.g., González-Muñoz et al., 2003; González-Muñoz, Martínez-Ruiz, Morcillo, Martín-Ramos, & Paytan, 2012; Smith, Hamilton-Taylor, Davison, Fullwood, & McGrath, 2004; Stevens et al., 2015; Torres-Crespo et al., 2015). Hence, micro-spherulitic barite within the 3.48 billion-year-old Dresser Formation sulfidized stromatolites supports a biological origin for these ancient, exceptionally preserved microbialites.

## 2 | GEOLOGICAL BACKGROUND AND SETTING OF STROMATOLITE GROWTH

The 3.481 ± 2 Ma Dresser Formation of the Warrawoona Group is located in the North Pole Dome of the East Pilbara Terrane, Western Australia (Figure 1a; Van Kranendonk, Smithies, Hickman, & Champion, 2007). A wide variety of stromatolites occur within the North Pole Chert Member at the base of the Dresser Formation, which is a thin (~2–120 m) hydrothermal-sedimentary succession composed of interbedded, white–gray–black chert, thick layers of coarsely crystalline barite, silicified sandstone and conglomerate, carbonates, siliceous hot spring sinter deposits, and jaspilite chert (Djokic et al., 2017; Groves et al., 1981; Van Kranendonk, 2006, 2011; Van Kranendonk et al., 2008; Walter et al., 1980). Stromatolites are strongly weathered in surface outcrops, but were found to consist predominately of pyrite and dolomite in unweathered drill cores (Van Kranendonk et al., 2008). The Dresser Formation was metamorphosed under prehnite-pumpellyite to lower greenschist facies conditions (Dunlop & Buick, 1981; Terabayashi, Masada, & Ozawa, 2003).

The interpretation for a hydrothermally influenced depositional setting of stromatolite growth is supported by the recognition of syngenericity between emplacement of the Dresser Formation and underlying swarms of hydrothermal chert–barite veins (Nijman et al., 1998; Van Kranendonk & Pirajno, 2004). This is demonstrated by the fact that hydrothermal veins transect basal basalt and komatiitic basalt but terminate within the North Pole Chert Member of the Dresser Formation and that clasts of hydrothermal, coarse-grained barite occur in sandstones and conglomerates of the North Pole Chert Member (Van Kranendonk, 2006; Van Kranendonk & Pirajno, 2004). Hence, the growth of stromatolites has likely occurred in proximity to, and perhaps was directly linked with, shallow marine to subaerial vents of hydrothermal fluids within a closed, evaporitic to subaerial volcanic caldera basin (Djokic et al., 2017; Van Kranendonk, 2006; Van Kranendonk et al., 2008).
3 | MATERIALS AND METHODS

The stromatolite samples examined in this study are derived from ~89 m depth in a fresh diamond drill core (Pilbara Drilling project; PDP) that was obtained from the North Pole Chert Member of the Dresser Formation (Figure 1b; Philippot et al., 2007; Van Kranendonk et al., 2008). Details on the stratigraphy of the drill core, spatial correlation with stromatolites in surface outcrops, and inferences on the geological context of stromatolite formation, are reported in Van Kranendonk et al. (2008). The micro-textures, mineralogy, and chemistry of the drill core stromatolites samples are documented in Baumgartner et al. (2019), Baumgartner, Van Kranendonk, et al. (2020). One polished thin section and two polished epoxy mounts that were prepared in the study of Baumgartner et al. (2019) from centimeter-sized rock slabs taken from the center of the drill cores were examined in detail for contained barite mineralization.

3.1 | Synchrotron radiation X-ray fluorescence microscopy (SR–XFM)

Element mapping by SR–XFM was performed on polished epoxy mounts at the XFM beamlne at the Australian Synchrotron in Melbourne. Parts of the acquired SR–XFM data were already reported in Baumgartner, Van Kranendonk, et al. (2020). The beam was focused using the Kirkpatrick Baez mirror microprobe end-station, which resulted in a monochromatic 2 µm beam with energies in the range 4–20 keV. The XFM beamline is equipped with the high solid-angle, energy–dispersive multi-element detector MAIA, which allows for element mapping of large areas with ~2 µm² resolution (Paterson et al., 2011). Spectral maps were acquired over areas of several square centimeters using count rates of 4–10 M/s. The energy resolution was 0.3–0.4 keV. The spectral maps were processed using GeoPIXE (CSIRO) into element concentrations by standardless correction of the raw data (Ryan et al., 2010). The results are presented as tricolor (red, green, and blue) multi-element maps.

3.2 | Scanning electron microscopy (SEM)

Backscattered Electron imagery and Energy Dispersive X-ray Spectroscopy analysis was performed using a FEI XHR–Verios 460L field-emission SEM at the Centre for Microscopy, Characterisation and Analysis (CMCA), University of Western Australia (UWA). The analytical setup involved 3–20 kV acceleration voltage and 0.1–0.8 nA beam current for imaging, whereas up to 15 kV and 0.8–1.6 nA was used for EDS analysis. Both the electron imagery and chemical analysis were done without the use of conductive coatings. Elements were determined using characteristic Kα and Kβ X-ray emission lines.
3.3 | Nitric acid etching

Following initial textural, mineralogical, and chemical examination, the epoxy mounts were ground and repolished, cleaned with ethanol and distilled water, and then etched for ~60–90 s with 70% nitric acid (HNO₃). After rinsing with distilled water and air-drying in an exicator, the exposed organic matter and mineralogy were analyzed and imaged by Raman Spectroscopy and SEM–EDS analysis.

3.4 | Focused ion beam (FIB) milling and scanning transmitted electron microscopy (STEM)

A STEM wafer of micro-spherulitic barite was prepared from nitric acid-etched sample material using a FEI Helios NanoLab G3 CX DualBeam FIB–SEM (installed at CMCA, UWA). Preparation involved deposition of a thick protective Pt layer, following which the ultrathin wafer was milled to a thickness of ~150 nm using a Ga ion beam. Bright- and dark-field STEM imagery was performed at CMCA, UWA, using a FEI Titan G2 80–200 TEM/STEM with ChemiSTEM Technology operated at 200 kV. Element maps were obtained by EDS with a Super-X detector using a probe size of ~1 nm and a probe current of ~0.9 nA. Elements were determined using characteristic Kα and Kβ X-ray emission lines. The EDS maps were produced using ESPRIT 2 (Bruker Corporation).

3.5 | Raman Spectroscopy (RS)

Raman Spectroscopy analysis of organic matter that occurs in association with micro-spherulitic barite was carried out at CMCA, UWA, using a WITec alpha 300RA + Raman probe combined with a peltier-cooled 1,024 × 1,280 pixel CCD detector, and a Toptica Photonics Xtra II 785 nm laser source. A 50×/0.9 objective was used for laser focussing. The laser power was ~5 mW. Data were acquired in the 900–1,800 Δ cm⁻¹ range with 600 L/mm spectral grating. Calibration involved the analysis of a silicon wafer with a distinctive 520 Δ cm⁻¹ band. The acquisition time was 15 s with 10 accumulations. Project Four (WITec GmbH) was used for background correction.
FIGURE 3  SEM and STEM images of micro-spherulitic barite from the Dresser Formation stromatolites and compared with modern analogues. (a) Backscattered Electron (BSE) image of platy tabular to lenticular barite (Brt) that occurs in association with dolomite (Dol) and pyrite (Py) of the sulfidized stromatolites. (b) Platy tabular to lenticular barite grains embedded within nano-porous pyrite (red arrow) and organic matter (Om) (c) Assemblage of micro-spherulitic barite and organic matter. The white arrow indicates nano-porous pyrite enriched in organic matter. The arrow in the inset indicates the outer shell of a barite micro-spherulite. The asterisk indicates the location of Raman Spectroscopy analysis of organic matter (Figure 5b). (d) Dark-field STEM image showing the poorly crystallized, to irregular or radiating crystalline interiors of some barite micro-spherulites (arrows from left to right, respectively). See their chemical analysis in Figure 6. (e) Smooth-surfaced barite micro-spherulites in dolomite (Dol). The image of the inset was taken at relatively higher acceleration voltage (5 vs. 20 kV). It indicates the partially hollow to entirely nano-crystalline interiors of the spherulites. (f) Barite micro-spherulites encrusting a coherent organic matter strand. The red arrows indicate nano-porous pyrite and associated organic matter. (g–h) Spherulitic barite of laboratory experiments using marine microbes. The images are taken from Torres-Crespo et al. (2015) and González-Muñoz et al. (2012), respectively. The inset in (g) shows the hollow interiors (red arrow) of precipitating barite micro-spherulites; compare with (e) in this figure panel. Note in (h) the radiating crystalline micro-texture (red arrow) of spherulites. Images in (a–f) were acquired on nitric acid-etched surfaces. See the imaging locations in Figure DR2.
RESULTS

4.1 | Texture, petrography, and chemistry of stromatolites and barite

The Dresser Formation sulfidized stromatolites analyzed here consist of wavy to gently undulating and wrinkly sulfide-dolomite laminae, as well as millimeter- to centimeter-scale sulfide-dolomite columns that exhibit microns-scale lamination (Figure 2a; c.f., Baumgartner et al., 2019; Baumgartner, Van Kranendonk, et al., 2020). These well-preserved, strongly sulfidized stromatolite structures lie within centimeters thick beds of chert and dolomite, but finely laminated stromatolite layers also occur within horizons of euhedral to subhedral, coarsely crystalline barite (plus minor quartz and dolomite) that are interlayered with the stromatolites (Figures 2a–c, DR1 and DR2).

The stromatolites are primarily composed of organic matter-rich, nano-porous pyrite that is overgrown by a later generation of non-porous, massive pyrite; dolomite, quartz, and sphalerite are intergrown with these pyrite types (c.f., Baumgartner, Van Kranendonk, et al., 2020; Baumgartner et al., 2019). Element mapping by SR–XFM documents strong enrichments of Ni within pyrite of the stromatolites. This technique also reveals that stromatolitic sulfide laminae within barite generally continue across intrusive, anhedral to subhedral, barite macro-crystals, which generally show well-developed growth zonation and Sr enrichment (Figures 2c–e and DR1).

4.2 | Micro-mineralogy and chemistry of micro-spherulitic barite

High-resolution electron imaging of the sulfidized Dresser Formation stromatolites following nitric acid etching reveals the presence of generally submicron-scale, platy tabular to lenticular barite grains, and submicron-scale barite spherulites that are intimately associated with dolomite and organic matter-rich, nanoporous pyrite (Figures 3a–f and DR3). The barite micro-spherulites show smooth- to rough-textured surfaces, as well as hollow to well-crystallized, irregular (framboid-like) to radiating, crystalline interiors (Figures 3c–e and DR3a–c). Most barite micro-spherulites with well-crystallized cores exhibit unattached outer shells (e.g., Figure 3c,d). Both the platy tabular/spherulitic barite morphotypes usually have narrow size distributions (i.e., ~0.3 to ~1 μm), but some localities in the samples have greater grain size variations and grains that are significantly smaller than 100 nm (e.g., Figure 3a,f).

Some barite micro-spherulites have been pseudomorphed to pyrite, particularly at contacts between sulfidized stromatolites and overlying, or underlying, coarse-grained barite layers (Figures 4a, DR3d and DR4). Indeed, nitric acid etching reveals that some parts of the coarse-grained barite crystals that lie in proximity to stromatolite layers are actually composed of close-packed to intergrown agglomerations of micro-spherulitic barite (Figures 4b, DR2 and DR3e,f), whereas barite crystals located away from the stromatolite layers show homogeneous internal textures and well-developed growth zonations (Figure DR1).

More than 40 chemical analyses (EDS) of barite micro-spherulites and platy tabular/lenticular barite reveal that they contain variable concentrations of Na, Mg, Al, Si, P, K, Ca, and Sr (Figure 5a). However, the small sizes of barite micro-spherulites precluded their accurate analysis and assessment of eventual relationships between barite chemistry and morphology. High-resolution electron imaging, EDS analysis, and Raman Spectroscopy analysis reveal that both barite morphotypes are ubiquitously associated with thermally mature, kerogen-like organic matter (Figures 3a–f, 5 and DR3c–d), including some notable examples where nanoscopic barite spherulites encrust clumps and coherent strands of organic matter (Figure 3f). Complementary TEM–EDS analysis of a barite micro-spherulite assemblage resolves C enrichments in their interiors (Figure 6).

FIGURE 4 Backscattered Electron (BSE) images of micro-spherulitic pyrite (a) and micro-spherulitic barite (b) at contacts between stromatolite laminae and layers of coarsely crystalline barite. Chemical analysis of micro-spherulitic pyrite in (a) is shown in Figure DR4. Note in (b) the range of textures from closely packed micro-spherulites (left red arrow), to intergrown, globular agglomerations of micro-spherulites (right red arrow). See imaging locations in Figure DR2. Brt = barite; Om = organic matter; Py = pyrite.
Barite is a common mineral in Earth’s crust and may be used as a proxy for the geological environment and the ambient conditions at the time of formation. For instance, barite in marine hydrothermal systems generally forms well-developed, tabular and bladed crystals, acicular/radiating tapered crystals, and/or dendritic crystals (e.g., Ray et al., 2014; Griffith & Paytan, 2012; Harris et al., 2009; Jamieson et al., 2016). On the other hand, barite in the water column and within pelagic sediment typically occurs as rounded, elliptical, or platy tabular grains (e.g., Bertram & James, 1997; Dehairs, Stroobants, & Goeysens, 1991; Griffith & Paytan, 2012). Although the detailed factors in the development of a specific barite morphotype are not entirely understood, laboratory experiments show that variations can be controlled by physical factors such as saturation index, crystal growth rate, and temperature, as well as chemistry, especially the ratio of Ba$^{2+}$/SO$_4^{2−}$ in solution, the presence/abundance of organic molecules, and the availability of ions that may substitute for Ba$^{2+}$ in the crystal lattice (Mg$^{2+}$, Ca$^{2+}$, and Sr$^{2+}$; e.g., Godinho & Stack, 2015; Jones et al., 2007; Judat & Kind, 2004; Kowacz, Putnis, & Putnis, 2007; Ruiz-Agudo, Putnis, Ruiz-Agudo, & Putnis, 2015; Smith et al., 2004; Widanagamage, Waldron, & Glamoclija, 2018). The incorporation of organic molecules, and perhaps Sr$^{2+}$ cations into the crystal lattice of barite, plus organics promoting supersaturation and inhibiting crystal growth, are known to promote the development of both platy tabular/lenticular grains and polycrystalline barite aggregates with spherulitic shape (e.g., Jones et al., 2007; Smith et al., 2004; Widanagamage et al., 2018). The importance of organics in the formation of spherulitic barite is further demonstrated by experiments involving marine microbial cultures, which revealed that cellular surfaces and EPS can act as a nucleation site of spherulitic barite (Figure 3g–h, and see additional data in González-Muñoz et al., 2012, Stevens et al., 2015, Torres-Crespo et al., 2015). This observation, in addition to the fact that high concentrations of biomass/dissolved organic matter help in overgrowing barite under-saturation (Bertram & James, 1997; Dehairs et al., 1991; Deng et al., 2019; Goldberg & Arrhenius, 1958; Horner et al., 2017; Martinez-Ruiz, Jounidi, et al., 2018; Martinez-Ruiz, Paytan, et al., 2018; among others), suggest that precipitation of spherulitic barite may be common in the pelagic zones of the oceans, such as at cold seeps where such mineralization have been found to occur in association with communities of sulfur-cycling microbes (Stevens et al., 2015).

Whereas microbial activity and/or the presence of degrading biomass can facilitate the formation of spherulitic barite aggregates, their sizes, as well as their detailed micro-textural and micro-mineralogical characteristics, may vary in relation to even subtle differences in ambient physical and chemical parameters during precipitation. For instance, laboratory experiments involving humic substances have produced framboid-like spherulitic agglomerations of euhedral barite nanocrystallites (Smith et al., 2004). On the other hand, microbial experiments by Torres-Crespo et al. (2015) have formed both densely crystalline spherulites and nano-scale hollow spheres with diameters in the ~1 µm to >10 µm range (Figure 3g), whereas biogenic barite precipitates in González-Muñoz et al. (2012) generally have consistent sizes and form radiating compact spherical clusters of acicular crystals (Figure 3h). Importantly, the 3.48 billion-year-old barite micro-spherulites described in this study not
only share several micro-textural features with these spherulitic barite types known from laboratory experiments and natural examples (compare Figure 3a-f with Figure 3g–h, and with additional data in González-Muñoz et al., 2012, Stevens et al., 2015, and Torres-Crespo et al., 2015), they also have poorly crystallized, in part nano-porous interiors that could indicate formation from amorphous precursors (compare Figure 3d with Figure 6 in Martinez-Ruiz, Paytan, et al., 2018), and they contain trace concentrations of P (Figure 5a), as is found in some biogenic barite examples.

An additional, critical observation in this study is that barite micro-spherulites are ubiquitously found in the earliest formed mineral assemblages that make up the Dresser Formation sulfidized stromatolites; that is, dolomite and nano-porous pyrite containing organic matter and enriched in various transition metals (e.g., Ni and Zn); Figures 3a–f and DR3a–c; c.f., Baumgartner et al. (2019), Baumgartner, Van Kranendonk, et al. (2020). The texture and chemistry of this organic matter-rich, texturally distinctive nano-porous pyrite is consistent with an origin through sulfidization of biofilms as early as during stromatolite growth (c.f., Baumgartner, Van Kranendonk, et al., 2020; Baumgartner et al., 2019), as is found in some biogenic barite examples.

Interestingly, we note that spherulitic barite is also common in close vicinity to stromatolite layers within bedding-parallel, coarse-grained barite (Figures 4b and DR3e,f). These large, euhedral to subhedral, strongly zoned barite crystals are similar to barite that typically forms in hydrothermal vein systems and marine hydrothermal vents (compare Figure 2d,e and Figure DR1 with figure 2 in Jamieson et al., 2019, their Figure 4)). Hence, while all the physical and chemical factors that can control barite morphology are still not entirely understood (c.f., Widanagamage et al., 2018), our data suggest that intimately associated organics have been important factors for micro-spherulite formation. These organics were likely derived from (decaying) ancient microbial mats that flourished in a hydrothermally influenced, low-temperature, shallow water depositional environment (Djokic et al., 2017; Nijman et al., 1998; Van Kranendonk, 2006; Van Kranendonk et al., 2018; Van Kranendonk et al., 2008; Van Kranendonk & Pirajno, 2004; among others).

The barium and sulfate for precipitating barite may have been sourced from hydrothermal fluids and intermixed seawater (c.f., Baumgartner, Caruso, et al., 2020; Philippot et al., 2007; Philippot et al., 2012; Shen et al., 2009; Ueno et al., 2008). Living microbial communities and/or dead microbial biomass could have served as precipitation sites for micro-spherulitic barite, through direct formation on EPS, or promoted by strong chemical gradients established by degrading biomass and the presence of organic matter.

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A late-stage origin for the coarse-grained barite in the Dresser Formation sulfidized stromatolite samples studied here is indicated by the fact that some barite crystals have deformed, intruded into, and ripped apart some stromatolite laminae (Figure 2c–e). By comparison, spherulitic barite within sulfidized stromatolites is intimately associated with petrogenetically earliest dolomite and organic matter-rich, nano-porous pyrite. An early formation of micro-spherulitic barite is further supported by the fact that these mineralizations are locally pseudomorphed to pyrite (Figures 4 and DR3d), and clearly are overgrown by the coarse-grained barite crystals. Hence, these textural/petrographical relationships and the correspondent variations in barite morphology allow for detailed inferences on the temporal evolution of barite precipitation: (a) precipitation of the barite micro-spherulites in a low-temperature regime, as early as during growth and sulfidization of the stromatolites; (b) precipitation of the coarse-grained barite crystals in relation to fluid percolation at some stage following demise and burial of the stromatolites.

6 | CONCLUSION

Sulfidized stromatolites from the ~3.5 Ga Dresser Formation that contain abundant organic matter, including potential microbial remains (Baumgartner et al., 2019), host micro-spherulitic barite aggregates and platy tabular/lenticular barite grains. These barite morphotypes, which are associated with petrographically earliest dolomite and nano-porous pyrite enriched in autochthonous organic matter, show striking textural and chemical similarities with barite precipitates that are known to develop under low-temperature conditions in the presence of microbial activity or degrading biomass. This finding lends further support to a biogenic origin of the Dresser Formation stromatolites.

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AUTHOR CONTRIBUTIONS

The methodology was conceived by R.J. Baumgartner, M.J. Van Kranendonk, and M.L. Fiorentini. All analytical work was carried out by R.J. Baumgartner, with assistance by D. Wacey, M. Saunders and C. Kong (Focused Ion Beam Milling and Transmission Electron Microscopy), as well as A. Pagès and C. Ryan (Scanning Electron Microscopy and/or Synchrotron Radiation X-ray Fluorescence Microscopy). The manuscript was written by R.J. Baumgartner, with input from all co-authors.

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