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Geochemistry and nano-structure of a putative ~3240 million-year-old black smoker biota, Sulphur Springs Group, Western Australia

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ABSTRACT

Filaments of pyrite found within a volcanic hosted massive sulphide (VHMS) deposit from the ~3270–3230 Ma Sulphur Springs Group of Western Australia have previously been interpreted as remnants of some of Earth's oldest thermophilic microbial communities. We here re-examine these pyrite filaments using a suite of *in situ* high spatial resolution techniques and provide new observations on their geochemistry, morphology, texture, distribution and habitat.

A number of the Sulphur Springs filaments retain geochemical evidence for remnants of organic material. This takes the form of patches of carbon and nitrogen enrichment seemingly enclosed within a completely pyritised filament. The distribution of this organic material closely resembles that observed in younger *bona fide* pyritised filamentous microbes. Most filaments also possess a distinctive sponge-like nano-porous pyrite texture, which is replicated in younger pyritised microfossils and bio-mediated pyrite framboids, and is consistent with pyrite nucleation in an organic matrix. New 3D analyses confirm previous observations of approximately uniform filament diameters, lack of branching, clustering of filaments, plus zones of filaments with preferred orientations. Multiple sulphur isotope analyses indicate that the sulphur for pyritisation likely came from a mixture of seawater and magmatic sources, consistent with a black smoker type habitat and permissive of the presence of life in this setting.

While these data are consistent with a biological interpretation for the Sulphur Springs filaments, perhaps as pyritised filamentous microorganisms or bundles of pyritised extra-cellular polymeric substances (EPS), the evidence is not compelling. Solid filament cross-sections and straight lengthwise morphology of most filaments resemble abiotic crystal needles or whiskers, while the parallel and radial alignments of filaments could be replicated by crystal growth patterns. Carbon and nitrogen enrichment could have occurred when organic material entrained within hydrothermal fluids was adsorbed onto these mineral crystals. Further work to obtain larger databases of nano-scale textures and morphologies from both biological and abiotic pyrite is needed before an abiotic formation mechanism can be confidently rejected.

1. Introduction

Low to mid temperature seafloor hydrothermal systems have been put forward as one of the most likely habitats for the origin of life on Earth (Corliss et al., 1981; Russell and Hall, 1997; Shock and Schulte, 1998; Martin and Russell, 2007; Martin et al.,

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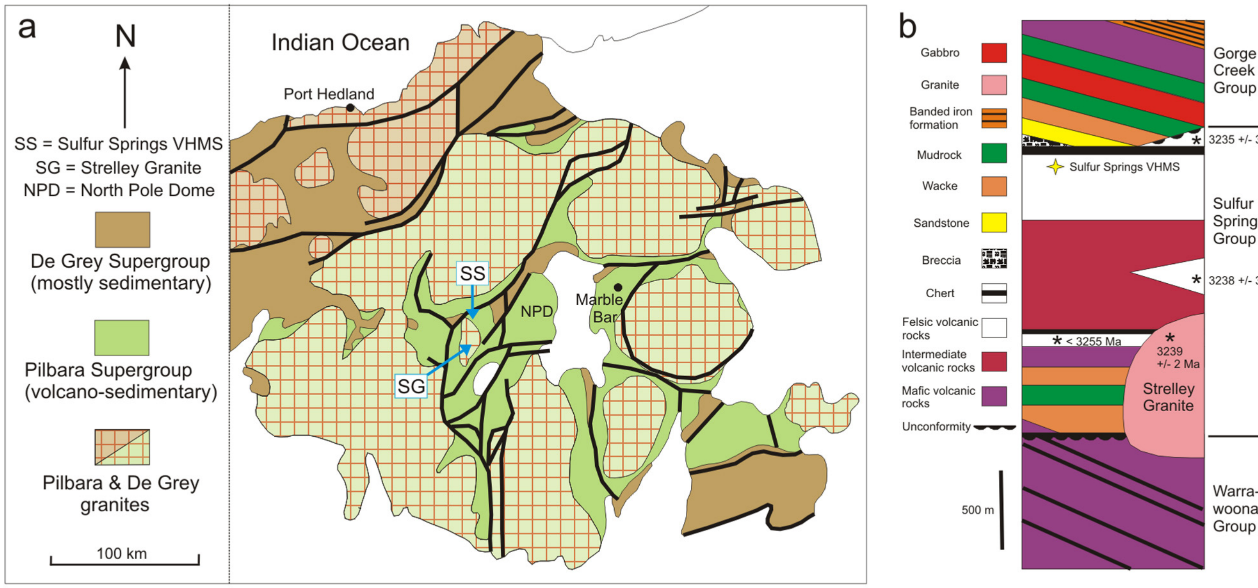

Fig. 1. Location (a) and schematic stratigraphic section (b) of the Sulphur Springs Group, showing the position of the Sulphur Springs VHMS deposit (modified from Wacey, 2012 and Buick et al., 2002).

2008) and host a wide variety of microbial life today (Jannasch and Mottl, 1985; Karl, 1995). The ~3270–3230 Ma Sulphur Springs Group (Van Kranendonk et al., 2007) from the Pilbara region of Western Australia houses one of Earth's oldest and best preserved volcanic hosted massive sulphide (VHMS) deposits (Morant, 1995), providing an ideal opportunity to study seafloor hydrothermal environments on the early Earth. The VHMS deposit occurs in the Soanesville greenstone belt of the East Pilbara Terrane around 50 km west of Marble Bar and around 100 km south east of Port Hedland (Fig. 1a). Hydrothermal mineralisation was driven by heat associated with the intrusion of the Strelley Granite at 3238 Ma (Morant, 1995; Vearncombe et al., 1995; Brauhart et al., 1998; Buick et al., 2002) and massive sulphide mineralisation is hosted within felsic volcanics and a marker chert of the Kangaroo Caves Formation, the uppermost member of the Sulphur Springs Group (Fig. 1b). The geological setting and sulphide textures indicate that the VHMS deposit formed in a manner analogous to modern black smoker chimneys, in water depths of around 1000 m (Vearncombe et al., 1995, 1998; Golding et al., 2010). The deposit has suffered very little subsequent tectonic deformation or metamorphism, with a maximum metamorphic grade not exceeding prehnite–pumpellyite facies (Buick et al., 2002). Primary textures (Morant, 1995; Vearncombe, 1995; Vearncombe et al., 1995; Rasmussen and Buick, 2000) and potentially a primary biota (Rasmussen, 2000; Duck et al., 2007) are well-preserved.

Pyritic filaments (0.5–2.0 μm in diameter) from this VHMS deposit have been interpreted as perhaps Earth's oldest examples of a thermophilic chemotrophic biota (Rasmussen, 2000). This interpretation was based upon morphological and textural characteristics of the filaments observed at the micrometre (μm) to millimetre (mm) scale. These characteristics include: filament occurrence in paragenetically early minerals and across multiple thin sections from diamond drill core; some filaments have sinuous and sharply curved morphologies; filaments are of uniform thickness along their length and are unbranched; some filaments are intertwined; filaments change their orientation across different micro-environments (Rasmussen, 2000). Subsequent work showed that hydrothermal petroleum generation was occurring prior to and during sulphide mineralisation in the Sulphur Springs region, and these hydrocarbons may have provided a carbon source for this biota (Rasmussen and Buick, 2000). Further signs of life in the Kangaroo Caves Formation were reported by Duck et al. (2007), in the form of tiny tubular (<1 μm) and spheroidal (<100 nm) microstructures, plus associated carbonaceous material with bulk $\delta^{13}C$ of −34‰ to −27‰, consistent with biological carbon fixation. The tiny tubes could plausibly be examples of carbonaceous precursors to the pyritic filaments studied here.

A number of reviews of Archaean life have classed the pyritic filaments as probable chemotrophic prokaryotes (Schopf, 2004, 2006; Wacey, 2009, 2012). However, little geochemical or nanostructural evidence exists in favour of this biological interpretation. Here we revisit these putative filamentous micro-organisms, using a suite of high spatial resolution techniques including focused ion beam milling (FIB), transmission electron microscopy (TEM), scanning electron microscopy (SEM), secondary ion mass spectrometry (SIMS and NanoSIMS), plus three dimensional nano-tomography to investigate their geochemistry, nano-texture, three dimensional morphology and organisation. We also compare potential biosignals preserved in these pyritised filaments with definitive biosignals seen in younger *bona fide* pyritic microfossils from the 1900 Ma Gunflint Formation of Canada.

2. Materials and methods

2.1. Samples and petrography

Samples come from a diamond drill core (SSD7) through the Sulphur Springs VHMS deposit (Fig. 2a), drilled by *Sipa Resources* in the 1990s and collected by us from the Port Hedland Core Facility in 2002. Twenty-two samples were collected at ~5 m intervals through the massive sulphide zone and associated silicified laminites; data in this contribution come from a depth of 173.4 m within the core. Petrography was conducted on 30 μm and 100 μm thick polished thin sections using *Nikon Optiophot-2* and *Optiophot-pol* microscopes, and preliminary SEM examination and mapping was done using a *Zeiss Supra 1555*. Petrography revealed zones of pyritic filaments (Fig. 2b and c) identical to those described by Rasmussen (2000). Younger pyritised *bona fide* filamentous microfossils, that here act as comparative material, come from the