REVIEW

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Microbial biosignatures in ancient deep-sea hydrothermal sulfides

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Abstract

Deep-sea hydrothermal systems provide ideal conditions for prebiotic reactions and ancient metabolic pathways and, therefore, might have played a pivotal role in the emergence of life. To understand this role better, it is paramount to examine fundamental interactions between hydrothermal processes, non-living matter, and microbial life in deep time. However, the distribution and diversity of microbial communities in ancient deep-sea hydrothermal systems are still poorly constrained, so evolutionary, and ecological relationships remain unclear. One important reason is an insufficient understanding of the formation of diagnostic microbial biosignatures in such settings and their preservation through geological time. This contribution centers around microbial biosignatures in Precambrian deep-sea hydrothermal sulfide deposits. Intending to provide a valuable resource for scientists from across the natural sciences whose research is concerned with the origins of life, we first introduce different types of biosignatures that can be preserved over geological timescales (rock fabrics and textures, microfossils, mineral precipitates, carbonaceous matter, trace metal, and isotope geochemical signatures). We then review selected reports of biosignatures from Precambrian deep-sea hydrothermal sulfide deposits and discuss their geobiological significance. Our survey highlights that Precambrian hydrothermal sulfide deposits potentially encode valuable information on environmental conditions, the presence and nature of microbial life, and the complex interactions between fluids, micro-organisms, and minerals. It further emphasizes that the geobiological interpretation of these records is challenging and requires the concerted application of analytical and experimental methods from various fields, including geology, mineralogy, geochemistry, and microbiology. Well-orchestrated multidisciplinary studies allow us to understand the formation and preservation of microbial biosignatures in deep-sea hydrothermal sulfide systems and thus help unravel the fundamental geobiology of ancient settings. This, in turn, is critical for reconstructing life's emergence and early evolution on Earth and the search for life elsewhere in the universe.

KEYWORDS
astrobiology, black smoker, early Earth, early life, hydrothermal vents, origin of life, SEDEX, VMS

*See glossary for an explanation of specific terms.

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1 | INTRODUCTION

Deep-sea hydrothermal systems provide unique insights into life thriving under extreme conditions by any human standards. Driven by energy from Earth's interior, hot fluids circulate in the ocean crust and locally emanate into cool marine environments. Even in the absence of sunlight, these springs can fuel diverse ecosystems, from chemoautotrophs (i.e., micro-organisms that fix inorganic carbon species such as CO_2) at the base to heterotrophic organisms such as tubeworms and bivalves at higher trophic levels. Metabolically diverse communities of chemosynthetic micro-organisms utilize redox-active gases (e.g., H_2S, CH_4, H_2) and metals (e.g., Fe, Ni, Cu) delivered by hydrothermal fluids (Kelley et al., 2002). Micro-organisms are also ecologically diverse and adapted to highly different temperatures, ranging from psychrophiles and mesophiles that thrive at ambient seawater temperature (ca. 4–45°C) to hyperthermophiles that can tolerate temperatures up to 121°C (Kashefi & Lovley, 2003). The high metabolic and ecologic diversity in these systems is a consequence of steep spatial gradients and temporal variations in various environmental parameters, such as temperature, pH, availability and composition of minerals and organic substrates, and fluid chemistry (e.g., concentrations of metals), resulting in distinct ecological niches (O'Brien et al., 2015; Von Damm, 1995). Therefore, geobiological studies on hydrothermal systems require a combination of geological, geochemical, and microbiological approaches.

Geobiological studies on hydrothermal systems are vital for understanding the emergence and early evolution of life on our planet. Hydrothermal vents were likely much more widespread on the early Earth due to a much higher heat flow from the mantle (Johnson et al., 2014; Russell et al., 2010). Some of these environments provided ideal conditions for the abiotic synthesis of organic molecules via Fischer-Tropsch-type (FTT) reactions linked to the serpentinization* of ultramafic* rocks. More specifically, these processes involve the hydrothermal reaction between minerals (olivine, pyroxene) and H_2O, resulting in the formation of H_2, which then may react with CO_2 from various sources to CH_4 and more complex hydrocarbons (Holm & Charlou, 2001; Konn et al., 2015; McCollom, 2013; McCollom et al., 1999; McCollom & Seewald, 2007; Mißbach et al., 2018; Proskurowski et al., 2008; Rushdi & Simoneit, 2001). Metal sulfide minerals such as pyrite (FeS_2), sphalerite (ZnS), and chalcopyrite ($CuFeS_2$) are essential constituents of hydrothermal deposits, and their redox activity and reactive surfaces may have catalyzed the abiotic synthesis of organic matter under hydrothermal conditions (Huber & Wächtershäuser, 1997; Russell et al., 1994, 2010; Wächtershäuser, 1990). Phylogenetic studies suggest that deep-branching (hyper) thermophilic micro-organisms similar to those found around modern hydrothermal vents appear to be the closest living relatives of LUCA* (Weiss et al., 2016). Similarly, the Asgard archaea—a group of micro-organisms proposed as the "missing evolutionary bridge" between prokaryotes and eukaryotes—were discovered in hydrothermal systems (MacLeod et al., 2019; Spang et al., 2015). Notably, hydrothermal systems may also exist in oceans of icy moons such as Enceladus, fueling the idea that life may also have emerged beyond Earth (Deamer & Damer, 2017).

To understand the significance of deep-sea hydrothermal systems in the emergence and early evolution of life, it is critical to examine their geobiology in deep time. One important reason is that models of potential prebiotic chemical evolution in hydrothermal environments must be consistent with conditions and processes in such systems on early Earth. Also, understanding fluid–microbe–mineral interactions in ancient hydrothermal settings is crucial to identifying metabolic pathways that might have played a vital role in the emergence of the earliest lifeforms. The only direct information on these interactions in our planet's past can be gleaned from the geological record.

The most important ancient equivalents of deep-sea hydrothermal systems are (i) volcanogenic massive sulfide deposits (VMS) and (ii) sedimentary exhalative massive sulfide ores (SEDEX). These deposits form in diverse deep-sea environments (i.e., below the photic zone), ranging from volcanic mid-ocean ridge, ocean-island, and (back-)arc settings to sediment-rich shelves, which accounts for profoundly different facies* (e.g., sulfidic chimney walls vs. sulfide-mineralized shales). Geological evidence for such systems on Earth extends back to more than 3.2 billion years ago (Ga) (Hofmann, 2011; Rasmussen, 2000; Vearncombe et al., 1995). Still, little is known about microbial life in ancient hydrothermal sulfide systems, which is due to (i) the low preservation potential of deep-sea deposits covering oceanic crust, (ii) the decreasing abundance of preserved rocks with increasing geological time, (iii) the obliteration of potential biosignatures by destructive processes in the environment and during later stages in history, and (iv) the difficulty in distinguishing biogenic from abiotic features (Georgieva et al., 2021; Javaux, 2019; Lepot, 2020; Westall, 2005). Indeed, compared with other sedimentary settings, hydrothermal environments are characterized by strong chemical disequilibria, which commonly result in the syn-depositional alteration of biogenic features and self-assembly of mineral textures* that can resemble biological fingerprints (Fowler & L'Heureux, 1996; Rouillard et al., 2018; Southam & Saunders, 2005). Therefore, a robust understanding of the formation and preservation of microbial biosignatures in deep-sea hydrothermal environments over geological timescales is vital to studies concerned with life's emergence and early evolution.

This paper on microbial biosignatures in Precambrian VMS- and SEDEX-type deposits aims to provide a resource for scientists from across the natural sciences whose research is concerned with life's emergence and early evolution. First, we introduce a range of candidate biosignatures for these environments and discuss their preservation potential under sulfidic hydrothermal conditions and over geological time scales. We then highlight examples of Precambrian deep-sea hydrothermal sulfide deposits for which biosignatures have been reported. Our review stresses the need to understand better the formation and preservation of microbial biosignatures in hydrothermal environments, which is of paramount importance for the search for the earliest life on Earth and, perhaps, beyond.

2 | MICROBIAL BIOSIGNATURES—CONCEPT AND DEFINITIONS

The Precambrian comprises the first 4 billion years in Earth's history, and most of this time, life was exclusively microbial (Knoll et al., 2016). Problematically, micro-organisms do not possess hard parts such as bones, shells, or wood. Therefore, reconstructing the earliest evolution of life on Earth cannot rely on such "classic" fossils. However, rocks can preserve various other types of evidence that indicate the presence of micro-organisms in ancient environments. These include rock fabrics* and textures, microbial microfossils, as well as minerals and organic matter with specific characteristics that are diagnostic for biologic activity (e.g., morphology, trace element signatures, stable isotope compositions; Figure 1). These features can be understood as *microbial biosignatures*, that is, signatures preserved in sediments and rocks that potentially testify to the presence of microbial life during their formation deposition.
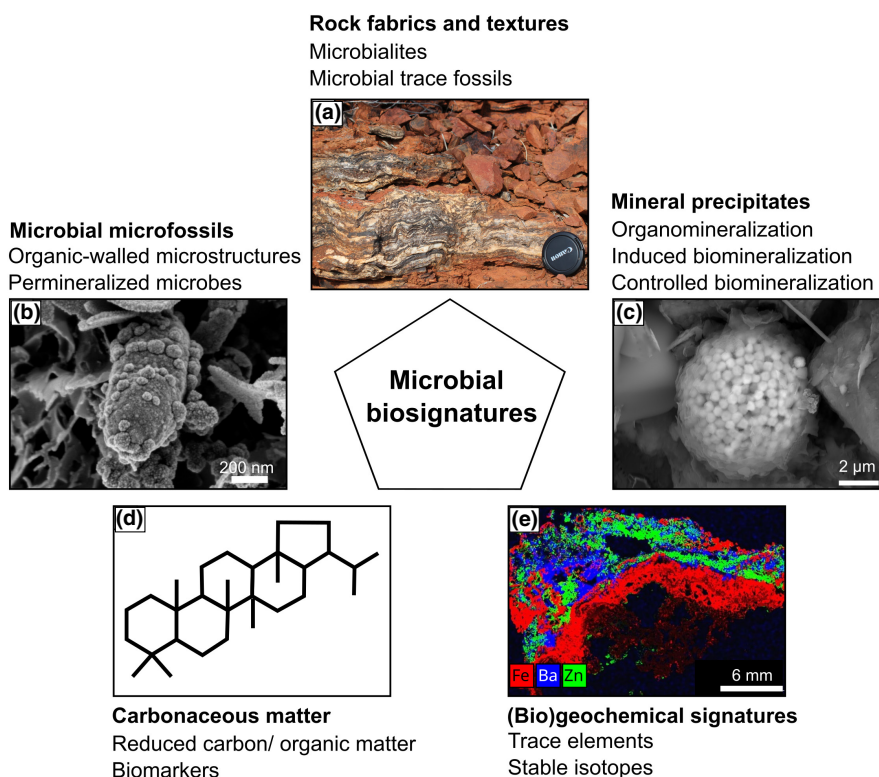
The identification and interpretation of microbial biosignatures in the geological record are challenging. For one, this is because Earth's oldest rocks may preserve primary features that resemble diagnostic biosignatures but have an abiotic origin (i.e., pseudo-biosignatures) (e.g., Brasier et al., 2002; Lowe, 1994; McCollom & Seewald, 2007; McLoughlin et al., 2008; McMahon, 2019; Zawaski et al., 2020). Discussing an abiotic explanation for observed features is relevant in rocks of any age but most critical for studies investigating periods in Earth's history for which the presence of life is not well constrained (i.e., before the Paleoarchean). Furthermore, biosignatures tend to get obscured over geological time scales by various processes. Alteration and destruction of biosignatures commence in

the paleoenvironment and continue throughout diagenesis* and perhaps later stages (e.g., metamorphism*, metasomatism*, surface exposure; Manning-Berg et al., 2019; Pinti et al., 2009; Westall, 2005). Primary signatures preserved in rocks might also be obscured by the formation of secondary minerals or the intrusion of organic matter during much later stages (e.g., Rasmussen et al., 2008; Summons et al., 2021; van Zuilen et al., 2002; Westall & Folk, 2003). For these reasons, a robust knowledge of biosignature formation and preservation (i.e., taphonomy*) is critical to studies concerned with Precambrian geobiology and astrobiology, and the geological context of target records must always be considered.

3 | MICROBIAL BIOSIGNATURES RELEVANT TO PRECAMBRIAN DEEP-SEA HYDROTHERMAL SULFIDE SYSTEMS

Geobiological studies on Earth's oldest rocks ideally start at the outcrop scale and then progressively zoom in, perhaps down to the micron- or even nanoscale. Accordingly, this survey begins with morphological features ("rock fabrics and textures" and "microbial microfossils": Figure 1a,b), continues with mineralogical and organic components ("mineral precipitates" and "carbonaceous matter": Figure 1c,d), and concludes with chemical and isotopic fingerprints in rocks ("(bio)geochemical signatures": Figure 1e). All the potential biosignatures discussed here may occur independently; that is, macroscopic life-like structures in rocks are not necessarily associated with mineralogical and chemical fingerprints of life and vice versa. However, this integrative multi-scale strategy is essential to critically

FIGURE 1 Examples of microbial biosignatures comparable to those that might form and preserve in deep-sea hydrothermal sulfide deposits; (a) microbial rock fabrics and textures (here: originally sulfidized stromatolite in the ca. 3.48 Ga Dresser Formation, Pilbara Craton); (b) microbial microfossils (here: a Fe(II)-oxidizing bacterium encrusted by Fe-(oxyhydr)oxides that formed through microbially induced precipitation); (c) microbial mineral precipitates (here: recent framboidal pyrite in sediments from the Norsminde Fjord, Denmark); (d) (bio)geochemical signatures (here: µXRF scan showing chemical zoning in the exterior part of a recent black smoker chimney from the Manus Basin, Western Pacific Ocean); (e) carbonaceous matter (here: structural formula of a C_{30} hopane, a geologically stable organic molecule that is diagnostic for commonly used bacterial biomarker).

Rock fabrics and textures
Microbialites
Microbial trace fossils

Microbial microfossils
Organic-walled microstructures
Permineralized microbes

Mineral precipitates
Organomineralization
Induced biomineralization
Controlled biomineralization

Microbial biosignatures

Carbonaceous matter
Reduced carbon/ organic matter
Biomarkers

(Bio)geochemical signatures
Trace elements
Stable isotopes

assess the integrity and validity of potential microbial biosignatures in Earth's most ancient rocks and, simultaneously, helps avoid analytical and interpretative pitfalls.

3.1 | Rock fabrics and textures

3.1.1 | Microbialites

Benthic microbial communities organized as mats or biofilms can directly influence sedimentation by trapping and binding allochthonous* particles (Black, 1933; Reid et al., 2003; Suarez-Gonzalez et al., 2019) or, perhaps more importantly, by facilitating authigenic mineral formation (Arp et al., 2001; Dupraz et al., 2009; Labrenz et al., 2000; Reitner, 2011; Reitner et al., 2005; Riding, 2000). These processes are commonly linked to organic extracellular polymeric substances (EPS) produced by micro-organisms. They often result in specific fabrics and textures that may be preserved in rocks over geological time scales (e.g., domal or columnar shapes and layered or clotted macro- and microfabrics; Arp et al., 2003; Grey & Awramik, 2020; Riding, 2011; Suarez-Gonzalez et al., 2019). Lithified sediments formed by benthic microbial communities such as biofilms or microbial mats are termed microbialites (Burne & Moore, 1987; Riding, 2000; Figure 1a). Perhaps the most famous type of microbialite are stromatolites, that is, organosedimentary growth structures that are characterized by distinct layering and/or lamination (Kalkowsky, 1908; Semikhatov et al., 1979).

Biofilms, microbial mats as well as microbialite-like rock fabrics formed by benthic microbial communities are present in today's deep-sea hydrothermal systems (Baumgartner et al., 2022; Blumenberg et al., 2007; Flemming & Wuertz, 2019; Moeller et al., 2014; Reysenbach & Cady, 2001; Van Dover, 2000, 2019). Moreover, numerous Fe sulfide-bearing microbialites in the Precambrian hydrothermal deposits demonstrate their preservation potential over billion-year timescales (Baumgartner et al., 2019; Baumgartner, Caruso, et al., 2020; Baumgartner, Van Kranendonk, et al., 2020; Duda et al., 2016; McGoldrick, 1999; Mißbach et al., 2021; Van Kranendonk et al., 2008; Figure 1a). For these reasons, microbialites are a prime target for geobiological studies on ancient deep-sea hydrothermal systems.

The formation of microbialites in deep-sea hydrothermal sulfide systems results from a complex interplay of abiotic and biological processes. It may be fostered by biologically induced precipitation and/or encrustation of organic templates of biofilms and microbial mats in Fe and S minerals (see the section on Mineral precipitates). These structures may serve as precursors for the secondary sulfidation of Fe minerals and organic matter driven by reduced sulfur species from volcanic exhalation or microbial sulfur cycling (Baumgartner et al., 2022; Campbell, 2006; Kelley et al., 2002; Little et al., 1998; Russell, 1996). The fabric, texture, and mineralogy of microbialites in deep-sea hydrothermal systems will likely depend on temperature, pH, and fluid chemistry. For instance, these parameters' steep gradients and substantial temporal variations might result in distinct

ecological niches occupied by different (stratified) microbial communities and characterized by specific microbe–mineral interactions (O'Brien et al., 2015; Toner et al., 2013). Furthermore, the (trans) formation of various metal sulfides in hydrothermal environments is influenced by metal concentrations (Ehrlich et al., 2021; Park & Faivre, 2022) and gradients in fluid temperature, pH, and redox state (e.g., from hot to cooler: pyrrhotite ± magnetite > chalcopyrite to pyrite > sphalerite ± galena: Hannington, 2014; Figure 1d). These gradients may also control the identity of minerals precipitated in microbial mats and biofilms, potentially resulting in mineralogically and/or geochemically zoned microbialites in ancient hydrothermal deposits.

Abiotic processes, such as chemical precipitation or tectonic deformation of laminated rocks, can form rock fabrics resembling microbialites (Allwood et al., 2018; Buick et al., 1981; Grotzinger & Rothman, 1996; McLoughlin et al., 2008; Zawaski et al., 2020). This is particularly critical in hydrothermal settings, where physico-chemical disequilibria may drive abiotic precipitation of colloform, botryoidal, and domal textures (Maslennikov et al., 2017; Revan et al., 2014). These precipitates mostly exhibit uniform, concentric, or laterally continuous banding (Foley et al., 2001; Gao et al., 2016; Pirajno, 2010). Further complicating, stromatolite-like fabrics, including wrinkly laminae (Allwood et al., 2009; Buick et al., 1981; Riding, 2000, 2011; Van Kranendonk, 2011), have also been replicated in abiotic laboratory experiments (McLoughlin et al., 2008). Although the experimental conditions differed from those prevailing in deep-sea hydrothermal vent environments, this report cautions that features commonly associated with microbialites can also derive from abiotic processes.

3.1.2 | Microbial trace fossils

Microbial trace fossils (not to be mistaken with microfossils, see next section) are μm-scale morphological or textural features formed by rock-inhabiting (i.e., endolithic) micro-organisms. These organisms may actively create channels, voids, or cavities within rocks or minerals (Golubic et al., 1981; Ivarsson et al., 2021; Marlow et al., 2015). For instance, oxidative dissolution of Fe sulfides by Fe(II)-oxidizing bacteria can result in distinct cell-sized (i.e., μm-scale) etch-marks or pits on mineral surfaces (Andrews, 1988; Rojas-Chapana & Tributsch, 2004; Thorseth et al., 2001). Such features and associated Fe (oxyhydr)oxides resulting from oxidative dissolution were reported on surfaces of sulfide minerals in modern seafloor hydrothermal deposits (Liu et al., 2020). To the best of our knowledge, there are no reports of microbial trace fossils in Precambrian hydrothermal sulfides. However, etch marks and channels associated with Fe oxides and carbonaceous matter in detrital pyrite in the ca. 3.4 Ga Strelley Pool Formation were interpreted as evidence for microbially induced pyrite oxidation (Wacey, Saunders, et al., 2011). This suggests that microbial trace fossils may be preserved in ancient hydrothermal sulfides.

A common challenge in studying ancient microbial trace fossils is ensuring their endogeneity* and syngenicity* to the host rock.

Endolithic micro-organisms can inhabit a rock any time after its formation, even billions of years after deposition (Hoshino et al., 2014; McLoughlin et al., 2007; Westall & Folk, 2003). Moreover, it has been shown for other rock types (e.g., pillow basalts, seafloor volcanic glasses, and chert) that microbial trace fossils can be confused with abiotic post-depositional features such as ambient inclusion trails or metamorphic titanite microtubes (e.g., Grosch & McLoughlin, 2014; Knoll & Barghoorn, 1974; Lepot et al., 2011; McCollom & Donaldson, 2019). The degree to which abiotic processes can mimic sulfide bio-alteration features is currently unknown. Moreover, experimental exposure of bio-alteration features to high temperatures is necessary to illuminate their preservation potential in hydrothermal systems.

3.2 | Microbial microfossils

Microbial microfossils are organic remains or permineralized* microstructures of micro-organisms preserved within rocks (Figure 1b). In Precambrian cherts, microfossils typically range between 10 and 100 μm in size and exhibit spheroidal or filamentous shapes (Duck et al., 2007; Glikson et al., 2008; Golubic & Hofmann, 1976; Javaux & Lepot, 2018; Knoll & Barghoorn, 1977; Rasmussen, 2000; Sugitani et al., 2007). The morphological preservation of such delicate structures may be aided by sulfide- and silica-bearing fluids causing mineral-coating or permineralization in sulfide minerals and/or chert (Alleon, Bernard, Le Guillou, Daval, et al., 2016; Alleon, Bernard, Le Guillou, Marin-Carbonne, et al., 2016; Delarue et al., 2017; Duda et al., 2016; Georgieva et al., 2018; Gong et al., 2020; Konhauser et al., 2004; Manning-Berg et al., 2019; Manning-Berg & Kah, 2017; Peter & Scott, 1988; Rasmussen, 2000; Reinhardt et al., 2019). Chert formation typically occurs in the lower temperature zones of deep-sea hydrothermal systems and is often associated with (microbial) Fe oxide formation, resulting in a characteristic jasper facies (Hannington et al., 1998). These rocks could provide promising targets for studying ancient microbial microfossils; indeed, various reported microbial Fe oxide filaments were found in such jasper (Dodd et al., 2017; Little et al., 2004, 2021; Papineau et al., 2022).

Despite this potential, recognizing microbial microfossils in the rock record remains difficult. One important reason is their small size and simple morphology (Brasier et al., 2002; Buick, 1990). Furthermore, abiotic processes, such as self-assembly during syndepositional or diagenetic mineral (trans)formations, can produce structures that morphologically resemble microbial microfossils (i.e., "biomorphs": Cosmidis & Templeton, 2016; Criouet et al., 2021; García-Ruiz et al., 2003; McMahon, 2019; Nims et al., 2021; Rouillard et al., 2018). Abiotic biomorphs may also be present in hydrothermal sulfide systems. Experimental studies demonstrated the auto-assembly of mackinawite and elemental sulfur into filamentous structures in the presence of organic matter (Cosmidis & Templeton, 2016; Picard et al., 2021). Significantly, these minerals are essential precursors to pyrite in lower temperature (<121°C) inhabited niches of hydrothermal environments (Kotopoulou

et al., 2022). Moreover, the organic compounds contributing to this auto-assembly may derive from the degradation of primary organic matter that does not testify to a biogenic origin of associated minerals (Brasier et al., 2002; Simoneit, 1993; Simoneit et al., 2004). Pyritization of such abiotic filaments may yield features resembling previously reported pyritized microfossils in hydrothermal sulfides (Baumgartner et al., 2022; Rasmussen, 2000). The morphological preservation of abiotic biomorphs needs to be tested for hydrothermal conditions, but likely, such features can easily be confused with microbial microfossils in ancient rocks.

Microfossil-like structures ("mimics") may also form during later stages in the history of a rock, for instance, through the reorganization of carbonaceous matter during silica recrystallization or its migration into pre-existing voids or gas bubbles (Brasier et al., 2002, 2005; Jones & Renaut, 2007; Rasmussen et al., 2021; Wacey, Noffke, et al., 2018; Wacey, Saunders, & Kong, 2018). Given the complexity of such alteration processes, it may not be surprising that many purported microfossils from early Archean hydrothermal deposits have been re-interpreted as younger contaminants or abiotic mimics (Brasier et al., 2002, 2005, 2006; Schopf & Packer, 1987; Wacey et al., 2016). Because of these limitations and potential pitfalls, studying microbial microfossils requires careful and detailed microscopic observation. Critical morphological criteria include population-scale morphometric characteristics, cell-like ultrastructure, and taphonomic features such as cell-like deformation behavior (Grey & Sugitani, 2009; Javaux et al., 2003; Rouillard et al., 2019). Additional geochemical evidence (e.g., $\delta^{13}C^*$ signatures in carbonaceous matter, thermal maturity consistent with the metamorphic grade of the host rock) can help establish the syngenicity and biogenicity of organic microstructures (Javaux et al., 2010; Lepot et al., 2013; Sforna et al., 2014).

3.3 | Mineral precipitates

3.3.1 | Organomineralization and induced biomineralization

Micro-organisms can facilitate extracellular mineral formation in various ways. One pathway is the nucleation of crystal growth on organic templates, such as cell wall surfaces or within EPS (i.e., "organomineralization": Addadi & Weiner, 1985; Reitner, 1993; Trichet & Défarge, 1995; or "biologically influenced mineralization": Cosmidis & Benzerara, 2022). In this case, the structural and chemical properties of the organic template facilitate mineral precipitation. Another possible pathway is the modification of the physicochemical microenvironment in microbial communities through their metabolic activity (i.e., "induced biomineralization": Beveridge, 1989; Lowenstam, 1981; or "biologically induced mineralization": Cosmidis & Benzerara, 2022). Organomineralization and induced biomineralization are not mutually exclusive and may co-occur. However, organomineralization is not necessarily linked to metabolic processes or limited to living organic matter and, therefore, can proceed during

an organisms' lifetime and/or after its death (i.e., as a taphonomic process). Induced biomineralization, in contrast, requires metabolic activity and, thus, living organisms.

Fe and S minerals are the most promising minerals of potential biogenic origin in hydrothermal sulfide systems because their formation in most sedimentary environments dominantly results from microbial Fe and S cycling (Kappler et al., 2021; Picard et al., 2016). Important examples are Fe (oxyhydr)oxides such as ferrihydrite (Kappler et al., 2005; Widdel et al., 1993) and magnetite (Chaudhuri et al., 2001; Köhler et al., 2013; Lovley et al., 1987). These minerals commonly exhibit nm-scale particle size and association with organic matter (Han et al., 2021; Miot et al., 2009). The reaction of Fe minerals and dissolved metals (e.g., Fe^{2+}, Zn^{2+}) with aqueous sulfide in anoxic to low-oxic settings drives sedimentary sulfide mineral formation (Berner, 1970, 1984; Labrenz et al., 2000; Popa et al., 2004; Rickard, 1975; Schieber, 2002). Notably, sulfate-reducing bacteria can influence the nucleation, particle size, and morphology of sulfide minerals via templating on cell walls and EPS, as well as through sulfur redox cycling (Donald & Southam, 1999; Ferris et al., 1987; Mansor et al., 2019; Park & Faivre, 2022; Picard et al., 2018; Thiel et al., 2019; Xu et al., 2016; Figure 1c). Pyrite framboids are prominent examples that are often interpreted to result from biological mediation of sulfide mineral (trans)formation (Duda et al., 2016; Popa et al., 2004; Wilkin & Barnes, 1997), although the mechanisms leading to framboid assembly in microbial systems remain enigmatic (Ohfuji & Rickard, 2005). Similarly, the formation of metastable elemental sulfur can be induced by microbial oxidation of reduced sulfur species and facilitated by organic templates, which may also aid in the stabilization and preservation of elemental sulfur (Breier et al., 2012; Cosmidis et al., 2019; Cron et al., 2019).

Identifying the products of induced biomineralization or organomineralization in ancient hydrothermal deposits is challenging. One important reason for this problem is that biological and abiotic precipitates might be texturally and compositionally similar. For instance, magnetite can form during diagenesis or low-grade metamorphism via thermochemical reduction of primary Fe oxyhydroxides such as ferrihydrite and lepidocrocite with sedimentary organic matter (Halama et al., 2016; Köhler et al., 2013; Posth et al., 2013, 2014). Also, sulfides that abiotically precipitate from supersaturated fluids may exhibit colloform or framboid-like features (Foley et al., 2001; Fowler & L'Heureux, 1996; Ohfuji & Rickard, 2005; Wilkin & Barnes, 1997), which resemble microbial textures from modern analog settings (Nozaki et al., 2020; Figures 2e,f). Furthermore, primary biogenic minerals might be overprinted or replaced by abiotic precipitates resulting from intense fluid circulation in hydrothermal systems (Kesler et al., 1989; Southam & Saunders, 2005). Consequently, biogenic and abiotic precipitates might co-exist in hydrothermal sulfide deposits and are potentially not or only barely distinguishable.

Despite these limitations, potential biogenic sulfide minerals have been reported from numerous ancient hydrothermal environments, ranging from the Phanerozoic (<541 million years, Ma) back to the early Archean (>3.2 Ga) (Baumgartner et al., 2019; Duda et al., 2016; Fallick et al., 2001; Georgieva et al., 2018; Kucha

et al., 2005; Rasmussen, 2000; Schroll & Rantitsch, 2005; Tornos et al., 2014; Wacey et al., 2015; Wilson et al., 2003). While the biogenicity of precipitates has not been unequivocally demonstrated in all of these cases, the combination of petrographic analyses with various mineralogical and geochemical approaches has helped reach a higher degree of confidence.

3.3.2 | Controlled biomineralization

Some micro-organisms can directly control the nucleation and growth of specific minerals within their cells (Mansor & Xu, 2020; Weiner & Dove, 2003). For instance, some S-oxidizing bacteria, such as *Allochromatium*, *Beggiatoa*, or *Thiothrix*, form intracellular deposits of amorphous S^0 (Dahl, 2020; Nims et al., 2019; Prange et al., 2002). Notably, the bacterium *Achromatium* occurs in modern deep-sea hydrothermal systems and precipitates both S^0 and $CaCO_3$ intracellularly (Benzerara et al., 2020; Ionescu et al., 2020). Perhaps most prominently, magnetotactic bacteria (MTB) precipitate nanocrystals of ferromagnetic minerals (magnetite [Fe_3O_4] or greigite [Fe_3S_4]) within membrane-bound organelles ("magnetosomes") (Amor et al., 2020). Understanding the preservation potential of these precipitates could open new possibilities for detecting biominerals in the rock record.

Magnetite crystals in MTB have characteristic features that differ from their abiotic counterparts, making them a potential biosignature in sedimentary rocks (i.e., "magnetofossils": Kirschvink & Chang, 1984). These features include narrow size/shape distributions, diagnostic crystal morphologies (e.g., bullet-shaped, elongated prismatic), an arrangement of crystals in chains, crystallographic perfection, major and trace element chemical purity, high Fe(II)/Fe(III) ratios, and isotopic fingerprints (e.g., Amor et al., 2015, 2016; Lam et al., 2010; Thomas-Keprta et al., 2000). Greigite magnetosomes show distinctly different magnetic properties than abiotic greigite (Bai et al., 2022). Still, greigite magnetosomes exhibit more crystallographic defects and chemical impurities than magnetite magnetosomes, making their identification more difficult (Kopp & Kirschvink, 2008).

MTB occur in suboxic to anoxic environments in freshwater and marine settings (Amor et al., 2020). Magnetite-producing MTB are generally more abundant near the oxic-anoxic transition zone, while greigite-producing MTB more widely occur in sulfidic environments (Amor et al., 2020; Reitner et al., 2005). The MTB strain *Magnetobacterium bavaricum* was found to inhabit recent deep-sea hydrothermal vent chimneys, supporting the potential presence of magnetofossils in ancient deposits from such settings (Suzuki et al., 2004). Indeed, magnetite magnetofossils are widespread in modern deep-sea sediments (Chang & Kirschvink, 1989). Putative magnetofossils preserved in the ca. 1.9 Ga Gunflint Chert (Chang et al., 1989) and the ca. 2.7 Ga Tumbiana Stromatolite (Akai et al., 1997) suggest that MTB may be traced back to late Archean to early Paleoproterozoic times. This is supported by molecular clock studies suggesting an origin of controlled Fe biomineralization at ca.

FIGURE 2 Comparison of modern and ancient hydrothermal sulfide deposits and microbial sulfide precipitates. (a) modern black smoker chimney (Manus Basin), (b) modern massive hydrothermal sulfide (Indian Ocean), (c) pyritized biofilm (white arrow) in modern hydrothermal sulfide deposit (Indian Ocean), (d) potential pyritized biofilm laminated sulfides in the ca. 390 Ma Rammelsberg SEDEX deposit (Harz mountains, Germany) (white arrow), strongly resembling recent pyritized biofilm structure in (c), (e) loose aggregates of sub-μm scale pyrite crystals (white arrow; 1) and pyrite framboids (2) associated with organic matter in modern marine sediments from the Norsminde Fjord (Denmark), (f) loose aggregate of sub-μm scale pyrite crystals (1), pyrite framboids (2), and infilled framboids (3) in the ca. 390 Ma Rammelsberg SEDEX deposit.
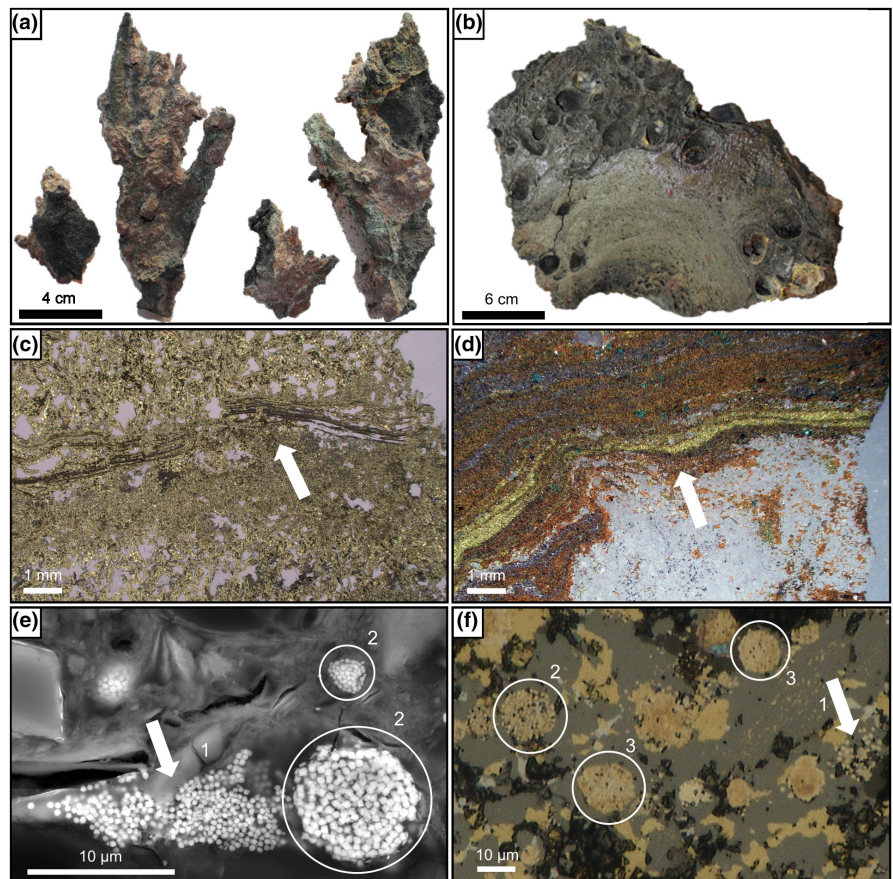
3.2–3.4 Ga (Lin et al., 2017). Taken together, magnetofossils seem to be promising candidate biosignatures for geobiological studies on ancient hydrothermal deposits.

The preservation potential of magnetofossils for microbial habitats in hydrothermal sulfide systems needs to be better understood. Sulfidation reactions may promote the reductive dissolution of magnetite and/or its transformation to Fe sulfide minerals (Bendt et al., 2019; Canfield & Berner, 1987; Poulton et al., 2004; Qian et al., 2010, 2013). More experimental work is required to identify whether the transformation products of such reactions preserve biogenic characteristics. Moreover, high-temperature metamorphic reactions may produce magnetite crystals in the size range of MTB magnetite. Indeed, putative magnetofossils in the Martian meteorite ALH84001 are now widely considered abiotic products of high-temperature reactions (e.g., Bell, 2007; Brearley, 2003; Treiman, 2003; but see McKay et al., 1996; Thomas-Keprta et al., 2000). Therefore, the unambiguous identification of magnetofossils in ancient hydrothermal deposits requires distinct criteria that collectively differentiate them from abiotic precipitates (for a detailed review, see Kopp & Kirschvink, 2008).

3.4 | Carbonaceous matter

All known life is based on reduced carbon, and organisms are the primary source of organic matter in sediments and rocks on Earth

(Peters et al., 2005a, 2005b; van Zuilen, 2019). Particularly interesting are organic molecules with specific biological sources (e.g., lipids, pigments) and their hydrocarbon derivates that are stable over geological timescales and retain source diagnostic structural characteristics. These compounds are commonly termed "molecular fossils" or "biomarkers" (Eglinton et al., 1964; Peters et al., 2005a, 2005b; Figure 1e). Organic matter in modern and ancient deposits can be chemically and compositionally complex. It is operationally divided into proportions that are extractable and non-extractable with organic solvents (i.e., bitumen and kerogen, respectively) (Durand, 1980; Figure 3). Bitumen comprises mixtures of organic compounds that were directly preserved as free molecules or released through the thermal degradation of macromolecular fractions such as kerogen (Vandenbroucke & Largeau, 2007; Figure 3). The kerogen is particularly important since it usually comprises the bulk of the total organic matter in sediments and sedimentary rocks (typically >90% w/w: e.g., Peters et al., 2005a, 2005b). Kerogen formation is complex but essentially involves the degradation, polymerization, and condensation of biomolecules (Durand, 1980; Farrimond et al., 2003; Vandenbroucke & Largeau, 2007). Given that a post-depositional emplacement can be excluded, most of the bitumen preserved in ancient samples is derived from the thermal degradation of the corresponding kerogen during burial.

During burial, the degradation of organic matter is mainly driven by increasing temperatures, resulting in a progressive loss

of N, S, O, and H. At ca. 200–300°C, extensive thermal cracking and aromatization of organic matter result in recalcitrant, high molecular-weight residues (Rouzaud et al., 2015). Under metamorphic conditions, carbonization and crystallization processes transform organic matter within rocks into pure residual carbon or crystalline graphite, respectively (Bernard & Papineau, 2014; Rouzaud et al., 2015; Figure 3). Despite their high maturity, pure residual carbon and graphite may still bear morphological or stable C isotopic characteristics related to biogenic precursor materials, thus serving as biosignatures (Bell et al., 2015; Hayes & Waldbauer, 2006; Mojzsis et al., 1996; Schidlowski, 2001; Schiffbauer et al., 2007; for discussion on C isotopes, see also Section 3.5.2). However, as detailed above (see the section on Microbial microfossils), life-like morphologies may result from secondary reorganization and hydrothermal overprint of the precursor materials, which can, in turn, be abiotic or biogenic in origin (Brasier et al., 2005; Rouillard et al., 2018).

The fate of organic matter in deep-sea hydrothermal vent systems is poorly understood. One important reason is that organic matter might be exposed to elevated temperatures at any stage, which is very different from conventional sedimentary environments where, in the absence of magmatic activity, thermal maturation is a function of burial depth (Greenwood et al., 2013; Logan et al., 2001; McCollom & Seewald, 2007; Figure 3). For instance, immature kerogen in hydrothermal surface environments might be thermally altered by percolating fluids, leading to the formation of "hydrothermal petroleum" and the degradation of hydrocarbons before deposition and burial (Simoneit, 1993; Simoneit et al., 2004). Further complicating, hydrothermal fluid circulation can cause in situ mixing of organic matter from various sources and environments, resulting in time- and space-averaged signals (Blumenberg et al., 2007, 2012; Duda et al., 2018; Konn et al., 2009). On the other hand, early encapsulation of organic

matter into hydrothermal sulfide minerals may promote its preservation (Greenwood et al., 2013; Holman, Grice, et al., 2014; Picard et al., 2019, 2021). The removal of organic matter from hot zones and subsequent sequestration in minerals can also facilitate its preservation, as proposed for hydrocarbons that may have formed abiotically via FTT reactions linked to serpentinization (Delacour et al., 2008).

Organic matter is widespread in modern deep-sea hydrothermal systems and potentially provides valuable insights into geomicrobiological key processes (Holman, Grice, et al., 2014; Konn et al., 2009; Logan et al., 2001; McCollom & Seewald, 2007; Reeves et al., 2014; Simoneit, 1993; Simoneit et al., 2004). For instance, massive sulfide deposits from the Mid-Atlantic ridge as well as sediments and chimneys of the arctic Loki's castle hydrothermal vent, were shown to contain bacterial fatty acids and archaeal isoprenoid lipids (Blumenberg et al., 2007, 2012; Jaeschke et al., 2014). Organic matter and source-diagnostic hydrocarbons were also reported from ancient hydrothermal sulfide ores (Blumenberg et al., 2007, 2012; Greenwood et al., 2013; Logan et al., 2001; Mycke et al., 1988). Genuine molecular records from the very ancient Earth are scarce. However, several early Archean hydrothermal deposits contain indigenous organic compounds that are demonstrably syngenetic to the host rock and, in some cases, assuredly of biological origin (Duda et al., 2018; Marshall et al., 2007; Mißbach et al., 2021). These studies demonstrate that molecular information on microbial life can be preserved under hydrothermal conditions.

Organic matter in hydrothermal systems may also derive from abiotic processes, such as FTT synthesis linked to serpentinization (Delacour et al., 2008; Holm & Charlou, 2001; Konn et al., 2015; McCollom, 2013; McCollom et al., 1999; McCollom & Seewald, 2007; Ménez et al., 2018; Milesi et al., 2016; Mißbach et al., 2018; Proskurowski et al., 2008; Rushdi & Simoneit, 2001;
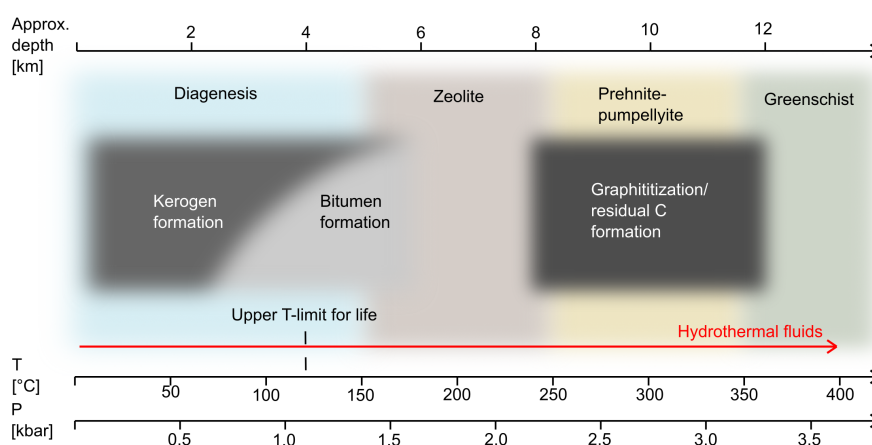

FIGURE 3 Temperature and pressure conditions relevant to the preservation of biosignatures in hydrothermal deposits. The increase in temperature (30°C/km) and pressure (0.27 kbar/km) as a function of depth are given for continental crust since the geothermal gradient is highly variable in the oceanic crust (ca. 40–80°C/km). Note that the heat flow can drastically increase in proximity to hydrothermal vents at oceanic spreading centers (red arrow). Boundaries between metamorphic facies are not sharp, and the relationship between temperature and pressure conditions during metamorphism varies strongly between different plate tectonic settings. Note that diagenetic processes commence at temperatures lower than the upper limit of microbial life and can thus affect, and be affected by, living microbial communities.

Sforna et al., 2018). However, the involved processes are complex, and the abiotic synthesis of organic matter is by no means an inevitable consequence of serpentinization. Furthermore, it has not been demonstrated that FTT-derived compounds would evolve into kerogens (Mißbach et al., 2018), a crucial prerequisite for preserving over geological time scales. These fundamental uncertainties may result from the facts that FTT products show no distinct characteristics that would allow their discrimination from biotic compounds (McCollom & Seewald, 2006; Mißbach et al., 2018) and that the presence of potential abiotic organics in Earth's history could have been masked by organic matter from biological sources. Hence, the quantitative significance of organic matter deriving from FTT synthesis under hydrothermal conditions remains unknown for any time in Earth's history.

Hydrothermal deposits may also contain secondary carbonaceous matter formed during metamorphic reactions (i.e., temperatures >200°C; Figure 3), such as the thermal decomposition of siderite [$FeCO_3$] (Halama et al., 2016; Köhler et al., 2013; Lepland et al., 2002; McCollom, 2003; Milesi et al., 2015; Posth et al., 2013; van Zuilen et al., 2002, 2003). Notably, such secondary abiotic graphite can exhibit $\delta^{13}C$ signatures consistent with a biogenic origin (e.g., −30‰: van Zuilen et al., 2002). Graphite may also precipitate from reactions of abiotic CO_2 and CH_4 dissolved in hydrothermal fluids (Luque et al., 2012; Ortega et al., 2010; Rumble & Hoering, 1986). Thus, graphite in ancient metamorphic rocks may originate from the mixing of fluids containing carbon from either abiotic or biogenic sources and may be emplaced both syngenetically or from exogenous sources during younger metamorphic events (Heijlen et al., 2006; Lepland et al., 2011; Papineau et al., 2011; Papineau, De Gregorio, Cody, et al., 2010; Papineau, De Gregorio, Stroud, et al., 2010). These potential sources of carbonaceous further complicate the identification of primarily biogenic materials in the rock record.

3.5 | (Bio)geochemical signatures

3.5.1 | Trace elements

Trace elements partitioning from fluids into minerals is a function of their abundance in the fluid and their compatibility in the mineral. Together, this can be mathematically expressed as the partition coefficient (K)*. Micro-organisms can affect K when mineral formation occurs in equilibrium with their cytoplasm (intracellularly), as is the case for many trace elements in magnetite produced by MTB (e.g., Ni, Zn, Cu, Pb: Amor et al., 2015). Also, mediation of mineral formation by organic templates (e.g., cell wall surface, EPS; extracellularly) can affect K in magnetite formed by dissimilatory Fe-reducing bacteria (e.g., Ni, Zn in magnetite: Han et al., 2021), or in sulfide minerals in microbial mats (e.g., As, Zn, Pb, Ni: Huerta-Diaz et al., 2012; Labrenz et al., 2000; Valdivieso-Ojeda et al., 2014). This suggests that trace element signatures in minerals could be used as fingerprints of microbial activity.

Metals and metalloids also form the active centers of many essential enzymes (e.g., Ni, Mo, Zn: Fraústo da Silva & Williams, 2001), resulting in the enrichment of these elements in organic matter in sediments and rocks (Cameron et al., 2012; Cavalazzi et al., 2021; Hickman-Lewis et al., 2020; Liermann et al., 2007; Reitner et al., 2015). Moreover, the affinity of many trace elements to organic matter can result in their enrichment in living and dead biomass during diagenesis (Huerta-Diaz et al., 2012; Petrash et al., 2016; Sforna et al., 2016). These processes are by no means restricted to "normal" sedimentary environments and may also occur in hydrothermal environments. Indeed, sulfidic stromatolites from the ca. 3.48 Ga Dresser Formation (Pilbara, Western Australia) with enrichments of transition metals and metalloids in early diagenetic pyrite were interpreted to reflect their binding to organic matter (Baumgartner, Van Kranendonk, et al., 2020).

Nevertheless, using trace elements as biosignatures is highly challenging. This is because K is also influenced by other parameters that are usually not well-constrained for paleoenvironments (e.g., mineral precipitation rates and temperature). Also, trace element concentrations in seawater have changed through geological time (Saito et al., 2003; Williams & Fraústo Da Silva, 2003) and are unknown for local paleoenvironments. These problems are amplified in hydrothermal systems, where element concentrations show steep spatial gradients and strong temporal variations (Kelley et al., 2002; Von Damm, 1995). The high capacity of sulfide minerals to abiotically sequester a broad range of metal(loid)s may result in enrichments of trace elements that are commonly associated with biological influence (e.g., Ni) (Berner et al., 2013; Dellwig et al., 2002; Gregory et al., 2015; Raiswell & Plant, 1980; Reitner et al., 2015). Also, trace metals may bind to organic matter of abiotic origin, which may originate from FTT synthesis in specific hydrothermal systems (Holm & Charlou, 2001; Konn et al., 2015; McCollom, 2013; McCollom et al., 1999; McCollom & Seewald, 2007; Ménez et al., 2018; Mißbach et al., 2018; Proskurowski et al., 2008; Rushdi & Simoneit, 2001; Sforna et al., 2018). Finally, mineral-fluid exchange during diagenesis or metamorphism might cause secondary modification of primary trace element signatures (Houghton et al., 2004; Monecke et al., 2002; Petrash et al., 2016; Schad et al., 2021). Future research must address these issues by improving paleoenvironmental proxies and conducting experimental studies to understand the long-term preservation of biogenic trace element fingerprints in minerals under hydrothermal conditions.

3.5.2 | Stable isotopes

Metabolic processes are commonly associated with mass-dependent stable isotope fractionation*, leading to different isotope ratios in the products compared with the reactants (Hoefs, 2021). For instance, photo- and chemoautotrophic organisms prefer the lighter over the heavier stable C isotope (^{12}C and ^{13}C, respectively) for carbon fixation. Consequently, biological organic matter is

isotopically depleted relative to the inorganic carbon pool, as expressed in negative $\delta^{13}C_{Org}$ values (Eigenbrode & Freeman, 2006; Hayes, 2001; Hoefs, 2021; Schidlowski, 2001). Since heterotrophic organisms usually conserve the isotopic composition of their substrates with only minor variations, modern, and ancient biological organic matter typically exhibits $\delta^{13}C$ signatures between ca. −20‰ and −30‰. Thus, ^{13}C-depleted carbonaceous matter preserved in rocks and minerals may be a valuable fingerprint of life.

Organic compounds in fluids and sediments from modern deep-sea hydrothermal vent sites typically exhibit negative $\delta^{13}C_{Org}$ signatures (ca. −20‰ to −50‰: Blumenberg et al., 2007; Jaeschke et al., 2014; Konn et al., 2009). However, $\delta^{13}C_{Org}$ values consistent with photo- or chemoautotrophic C fixation do not provide stand-alone evidence for microbial carbon cycling. Similar $\delta^{13}C_{Org}$ values have been reported for abiotic bulk organic matter and organic compounds in carbonaceous meteorites (down to −21.0‰ and −38.7‰, respectively: Sephton et al., 2003; Sephton & Gilmour, 2001). Significantly, abiotic synthesis of CH_4 and other organic compounds under hydrothermal conditions (e.g., via FTT reactions) can fractionate C isotopes by a magnitude similar to biological fractionation (down to −60‰ in CH_4 and −36‰ in higher molecular weight compounds: Horita & Berndt, 1999; McCollom & Seewald, 2006). However, compounds from these experiments also yielded highly variable offsets between $\delta^{13}C_{org}$ and $\delta^{13}C_{inorg}$ (30‰ to −36‰: McCollom & Seewald, 2006). Therefore, a consistent offset between $\delta^{13}C_{org}$ and $\delta^{13}C_{inorg}$ of at least 20‰ to 30‰ across different facies within one system might serve as a biosignature in hydrothermal deposits (cf. Schidlowski, 2001).

Another stable isotope system that is relevant for hydrothermal sulfide deposits is sulfur. In non-hydrothermal environments, stable sulfur isotopes (^{32}S, ^{33}S, ^{34}S, ^{36}S) are mainly fractionated during microbial sulfur cycling (Hoefs, 2021; Jørgensen et al., 2019; Strauss, 1997). Substantial kinetic fractionations occur during dissimilatory sulfate reduction and disproportionation of elemental sulfur (Böttcher et al., 2001; Canfield & Thamdrup, 1994; Habicht & Canfield, 1997; Sim et al., 2011). The most commonly analyzed sulfur isotopic ratio is $^{34}S/^{32}S$ because the $^{34}S/^{32}S$ of sulfide species can be fractionated during microbial sulfur cycling by more than −70‰ (Jørgensen et al., 2019). In contrast, the $\delta^{34}S$ signature of volcanogenic H_2S typically ranges from −2‰ to 2‰ (Hoefs, 2021; Ohmoto, 1996). However, multiple abiotic processes in hydrothermal systems may also substantially fractionate S isotopes. For instance, experiments on thermochemical sulfate reduction at 100 °C yielded $\delta^{34}S$ fractionation ranges of up to ca. 20‰ (Kiyosu & Krouse, 1990; Machel et al., 1995). Similar fractionation factors occur during isotopic exchange between aqueous sulfate and sulfide (Ohmoto & Lasaga, 1982; Ono, 2008). Therefore, only fractionation ranges exceeding ca. 20‰ can be considered robust signals of microbial sulfur cycling in hydrothermal sulfide systems (e.g., −48.0‰ to 23.1‰: Slack et al., 2019; see also Eldridge et al., 1993; Lode et al., 2017; Nozaki et al., 2020; Present et al., 2017; Taylor, 2004; Velasco-Acebes et al., 2019).

Compared to Phanerozoic hydrothermal sulfide deposits, the range of $\delta^{34}S$ values in Archean records seems to be diminished (−3‰ to 3‰: Golding et al., 2011; Huston et al., 2001; Wacey et al., 2014). This may point to a purely abiotic sulfide source or microbial sulfur cycling at low sulfate concentrations, as expected for Archean environments (Shen et al., 2001). Indeed, the combined analysis of $\delta^{34}S$, $\Delta^{33}S^*$, and $\Delta^{36}S$ (i.e., quadruple sulfur isotopes) on Paleoarchean pyrites and barites suggests that microbial sulfur cycling was established as early as ca. 3.5 Ga (Baumgartner, Caruso, et al., 2020; Philippot et al., 2007; Shen et al., 2001; Shen et al., 2009; Ueno et al., 2008; Wacey, Kilburn, et al., 2011; but see Liu et al., 2021; Watanabe et al., 2009). Therefore, applying quadruple sulfur isotopes provides a powerful tool to elucidate microbial sulfur cycling in ancient hydrothermal systems, where traditional approaches can prove challenging.

Fe is widespread in hydrothermal sulfide environments; hence, stable Fe isotopes (^{54}Fe, ^{56}Fe) potentially provide further evidence for geobiological processes in such settings. Fe isotopes are fractionated during partial oxidation and reduction in Fe, producing isotopically enriched Fe(III) minerals ($\delta^{56}Fe > 0$) and depleted Fe^{2+}_{aq} ($\delta^{56}Fe < 0$) (Johnson et al., 2020). Substantial $\delta^{56}Fe$ variation in natural Fe sulfide minerals (−4‰ to +4‰) may indicate intense redox cycling and potentially additional stable Fe isotope fractionation linked to pyrite precipitation (e.g., Decraene et al., 2021; Mansor & Fantle, 2019). Micro-organisms commonly control redox cycling in the environment and might also influence the degree of this fractionation. For instance, Fe oxidation experiments with anoxygenic phototrophs (Croal et al., 2004), nitrate-reducing Fe(II)-oxidizing bacteria (Kappler et al., 2010), and cyanobacteria (Swanner et al., 2017) revealed that the produced Fe oxides are enriched in ^{56}Fe by 1.5‰ to 3‰ relative to Fe^{2+}_{aq}. Also, the dissimilatory reduction in Fe(III) minerals releases Fe^{2+}_{aq} depleted in ^{56}Fe by up to ~3‰ (Beard et al., 1999; Chanda et al., 2021; Crosby et al., 2005; Fortney et al., 2016). However, these ranges are similar to those reached by abiotic redox cycling (Johnson et al., 2020; Toner et al., 2016), equilibrium precipitation of Fe minerals in hydrothermal environments (Rouxel et al., 2004, 2018), and isotopic exchange reactions between fluids and pyrite at high temperatures (300–450°C: Pokrovski et al., 2021). Experimental work demonstrates that biogenic magnetite formation by MTB is associated with a mass-independent fractionation* of Fe-isotopes ($\Delta^{57}Fe = 0.23$: Amor et al., 2016). However, magnetofossils in the environment do not seem to preserve this isotopic fingerprint (Havas et al., 2021). For these reasons, microbial Fe cycling can currently not be tracked in the geological record based on Fe isotope signatures alone.

4 | THE PRECAMBRIAN RECORD

While there are many Precambrian VMS and SEDEX deposits, only three localities have been investigated for potential biosignatures in detail: the ca. 3.2 Ga Sulphur Springs Group (Pilbara, Western Australia), the ca. 1.64 Ga Here's Your Chance (H.Y.C.) deposit in Northern Australia, and the ca. 1.43 Ga Gaobanhe massive sulfide deposit in Northern China (Figure 4).
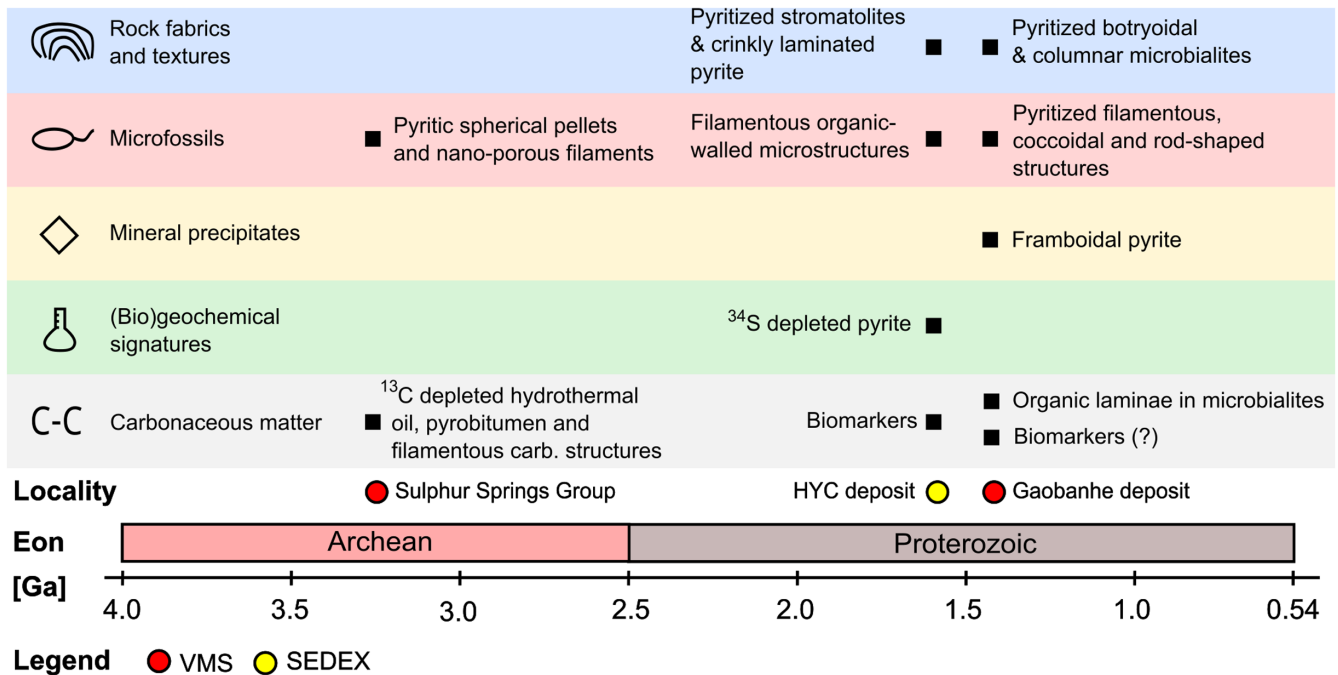
Rock fabrics and textures		Pyritized stromatolites & crinkly laminated pyrite ■	■ Pyritized botryoidal & columnar microbialites
Microfossils	■ Pyritic spherical pellets and nano-porous filaments	Filamentous organic-walled microstructures ■	■ Pyritized filamentous, coccoidal and rod-shaped structures
Mineral precipitates			■ Framboidal pyrite
(Bio)geochemical signatures		^{34}S depleted pyrite ■	
C-C Carbonaceous matter	■ ^{13}C depleted hydrothermal oil, pyrobitumen and filamentous carb. structures	Biomarkers ■	■ Organic laminae in microbialites ■ Biomarkers (?)
Locality	● Sulphur Springs Group	HYC deposit ○	● Gaobanhe deposit

Eon	Archean	Proterozoic

[Ga] 4.0 — 3.5 — 3.0 — 2.5 — 2.0 — 1.5 — 1.0 — 0.54

Legend ● VMS ○ SEDEX

FIGURE 4 Reported microbial biosignatures in Precambrian VMS and SEDEX deposits through geologic time. See the main text for references.

4.1 | Sulphur Springs Group

The ca. 3.2 Ga Sulphur Springs Group (Pilbara, Western Australia) contains the Earth's oldest recognized VMS deposits and formed in a setting comparable to modern-day volcanic back-arc basins in a water depth of ca. 1000 m (Brauhart et al., 1998; Huston et al., 2019; Vearncombe et al., 1995). Based on its geological setting, mineralogy, and locally occurring mineral textures (dendritic, botryoidal, and colloform sulfide), the upper part of the Sulphur Springs deposit has been interpreted as analog to modern black smoker systems (Vearncombe et al., 1995). The ore mineralization consists mainly of pyrite, sphalerite, chalcopyrite, and galena (Brauhart et al., 1998; Huston et al., 2019), which is consistent with recent hydrothermal sulfide systems and modern VMS deposits (Hannington, 2014). Notably, primary mineral phases and textures have not been obscured by metamorphism (low-grade prehnite-pumpellyite facies*) (Vearncombe et al., 1995; Figure 3).

Spherical sulfide minerals in the Sulphur Springs Group were tentatively interpreted as mineralized bacteria (Vearncombe et al., 1995). Notably, colloform chert in the Sulphur Springs deposit contains pyritic filaments interpreted as microfossils of thermophilic, S-cycling prokaryotes living in the subseafloor of a hydrothermal system (Rasmussen, 2000). Their occurrence in paragenetically early chert suggests that the filaments predate the main phase of VMS mineralization and are more likely associated with low-temperature hydrothermal activity (<110°C), consistent with the presence of microbial life (Rasmussen, 2000). These pyrite filaments exhibit a nano-porous texture and are associated with nitrogen-enriched organic matter, which is consistent with

a biological origin, but could also be explained by abiotic crystal growth and the localized adsorption of organic matter (Wacey et al., 2014). Hydrothermally generated oil encapsulated in fluid inclusions and pyrobitumen associated with sulfide minerals in the Sulphur Springs deposits display $\delta^{13}C_{org}$ values between −29.1‰ and −36.9‰, in line with a biological origin (Rasmussen & Buick, 2000). Notably, filamentous ^{13}C-depleted carbonaceous structures ($\delta^{13}C_{org}$ = −26.8‰ to −34.0‰) resembling microbial remains have also been observed in black shales directly overlying the VMS deposit (Duck et al., 2007). In summary, the Sulphur Springs deposit represents a prime target in the search for biosignatures of early life in deep-sea hydrothermal environments. However, the biological origin of the reported filamentous microfossils remains to be further scrutinized.

4.2 | McArthur (Here's Your Chance; HYC) deposit

The HYC deposit (Northern Territory, Australia) is an unmetamorphosed SEDEX Pb-Zn deposit that occurs within the ca. 1.64 Ga Barney Creek Formation (Logan et al., 2001; Page & Sweet, 1998). The depositional environment of Barney Creek Formation was variably interpreted as a restricted deep marine setting (Bull, 1998; Jackson et al., 2000) or a saline lacustrine system (Crick, 1992; French et al., 2020). Ore mineralization in the deposit consists of pyrite, sphalerite, and galena precipitated from an oxidized hydrothermal brine rich in sulfate (Large et al., 1998; Logan, 1979).

Black chert in the HYC deposit contains μm-scale filamentous and spheroidal structures interpreted as microfossils (Oehler &

Logan, 1977). Moreover, microdigitate and columnar stromatolites with pyritic and siliceous mineralogy, as well as crinkly laminae composed of pyrite, were reported from the deposit (McGoldrick, 1999). The $\delta^{34}S$ signatures of −13‰ to +15‰ in early diagenetic sulfides suggest that microbial sulfur metabolism was involved in mineral formation (Eldridge et al., 1993). Organic matter in the HYC deposit has experienced significant hydrothermal alteration but still encodes information of ore genetic and geobiological significance (Chen et al., 2003; Greenwood et al., 2013; Holman, Greenwood, et al., 2014; Holman, Grice, et al., 2014; Logan et al., 2001; Williford et al., 2011). Preserved organic biosignatures include $\delta^{13}C_{Org}$ characteristics and biomarkers, among others indicating the presence of sulfate-reducing and sulfide-oxidizing bacteria in the environment (Holman, Grice, et al., 2014; Logan et al., 2001). In summary, the HYC deposit provides rare clues on microbial sulfur cycling in Precambrian hydrothermal sulfide systems.

4.3 | Gaobanhe massive sulfide deposit

The ca. 1.43 Ga Gaobanhe massive sulfide deposit (North China) is a SEDEX deposit formed in a submerged graben* system on the North China Craton* (Kusky & Li, 2003; Li & Kusky, 2007). Hydrothermal fluid exhalation caused synsedimentary ore mineralization with an upward zonation from pyrite at the bottom to Zn–Pb-sulfide at the top (Kusky & Li, 2003). Rhenium-osmium isotope data and trace-element patterns in the Gaobanhe sulfide phases suggest local hydrothermal overprint during the Mesozoic break-up of the North China Craton (Gao et al., 2020). Nevertheless, the massive sulfide deposits contain the oldest reported morphologically preserved black smoker chimneys reported to date, offering an opportunity to study the association of ancient microbial life with these structures (Li & Kusky, 2007).

The chimney structures contain dome-shaped build-ups of concentric botryoidal and columnar sulfides interlayered with organic matter that are interpreted as microbialites (Li & Kusky, 2007). Putative pyritic microfossils within the sulfide chimneys include filamentous, coccoidal, and rod-shaped structures locally associated with framboidal pyrite (Li & Kusky, 2007). Perhaps the deposit also preserves biomarkers (Xia et al., 2008), but the provided information does not allow for adequately assessing the quality and validity of the data. Nonetheless, the Gaobanhe deposit is a promising target for studying microbial biosignatures but needs further investigation in greater detail.

5 | CONCLUDING REMARKS

Deep-sea hydrothermal sulfide systems might have been crucial for the emergence of life, making ancient deposits from such settings highly relevant to deep-time geobiology and astrobiology.

However, reconstructing life in ancient hydrothermal environments is still challenging. Perhaps the most critical problems are (i) the limited number of well-preserved records, (ii) the insufficient understanding of the formation and preservation of geologically stable microbial biosignatures in hydrothermal environments and (iii) the large number of hydrothermal processes that may produce pseudo-biosignatures. Candidate microbial biosignatures that can remain stable over geological time scales include rock fabrics and mineral textures (e.g., microbialites, framboidal pyrite), microfossils, biogenic mineral precipitates (e.g., magnetite, pyrite), as well as trace element, stable isotope (C, S, Fe) and biomarker signatures preserved in minerals and associated organic matter. So far, no stand-alone tool is available that unequivocally proves the presence of past microbial life in ancient rocks. Still, a comprehensive model combining mutually consistent biosignatures with a plausible geological scenario for their formation and preservation can result in high confidence for life detection.

Despite the general diversity of potential biosignatures, reported fingerprints of microbial life in Precambrian hydrothermal sulfides are scarce, and many of these findings are still controversially discussed. Of these examples, the HYC deposit currently provides the most comprehensive record because it contains a diverse set of morphologic, textural, and (bio)geochemical biosignatures. Detailed petrographic studies that involve analytical imaging techniques and geochemical approaches will be essential for identifying features that may be indicative of past microbial life and hence might serve as biosignatures in the future. Equally important are continued experimental efforts to understand the formation and geological stability of (pseudo)biosignatures, allowing to build a more solid framework for the unambiguous identification of microbial fingerprints in ancient hydrothermal deposits. This, in turn, is vital to understanding the emergence of life on Earth and the search for life elsewhere in the universe.

DATA AVAILABILITY STATEMENT

Data are available upon request.

GLOSSARY

Allochthonous: Rocks, sediment, mineral particles, or organic matter which did not form at the place of deposition but away from their current location.

Craton: Precambrian cores of modern continents; characterized by high crustal thickness and structural rigidity that prevented their subduction and enabled their long-term preservation.

δ−/Δ-notation: Deviation of an isotopic ratio in a sample from a corresponding isotopic ratio in a reference material in ‰, e.g., for stable sulfur isotopes (Marin-Carbonne et al., 2018):

$$\delta^{3i}S = \left(\frac{\left(\frac{S3i}{S32} \right)_{sample}}{\left(\frac{S3i}{S32} \right)_{standard}} - 1 \right) \times 1000$$

$$\Delta S33 = \delta S - 1000 \times 33 \left(\left(1 - \frac{\delta S34}{1000} \right) - 1 \right)$$

$$\Delta S36 = \delta S - 1000 \times 36 \left(\left(1 - \frac{\delta S34}{1000} \right) - 1 \right)$$

For more information on stable isotope systematics and commonly used reference materials, readers are referred to Hoefs (2021).

Diagenesis: Transformation of sediments into sedimentary rocks through progressive lithification. Diagenetic processes commence immediately after the deposition of the primary sediments and proceed through burial. Diagenesis is poorly defined concerning temperatures, but 150°C is commonly taken as an upper limit.

Endogeneity: Occurring within the analyzed rock or mineral.

Fabric: Components, structural elements, and their geometry within a rock. Commonly used terms to describe fabrics of microbial sediments and microbialites include domal, columnar, layered, laminated, clotted, colloform, botryoidal, fenestral, microdigitate, and peloidal. For examples with images, readers are referred to Grey and Awramik (2020).

Facies (sedimentary): Characteristics of sediments and sedimentary rocks that can be linked to the original depositional environment. Not be confused with metamorphic facies (see below).

Graben: Linear depression of the Earth's continental crust caused by tectonic faulting due to crustal extension.

LUCA: Last Universal Common Ancestor; a hypothetical unicellular organism representing the phylogenetically youngest predecessor of all modern domains of life (bacteria, archaea, eukaryotes).

Mass-dependent (isotope) fractionation: Describes the relative change in the abundance of single isotopes of an element proportional to their mass. The degree of fractionation follows a linear function with a slope governed by the mass differences of the investigated isotope ratios (m_3–m_1 vs. m_2–m_1), as commonly demonstrated in a three-isotope plot (e.g., $^{56}Fe/^{54}Fe$ vs. $^{57}Fe/^{54}Fe$). The magnitude of fractionation increases with the relative mass difference between isotopes.

Mass-independent (isotope) fractionation: A deviation from the linear function of the mass-dependent fractionation that is expressed through the relative difference Δ from this line (e.g., $\Delta^{57}Fe$).

Metamorphism: Pressure- and/or heat-induced structural and mineralogical transformation of rocks. This transformation commonly includes the deformation of the precursor rock (protolith), coarsening of mineral crystals, and the formation of new minerals from the breakdown of existing, no longer stable minerals. Metamorphism does not include chemical changes to the protolith (i.e., it is "isochemical").

Metamorphic facies: Characteristic assemblage of minerals formed during metamorphic alteration of a primary rock (protolith).

Metasomatism: Chemical alteration of a precursor rock (protolith) in exchange with hydrothermal fluids.

Partition coefficient: Ratio K of the concentration c of an element i in a mineral to the concentration of the same element in solution, normalized to a reference element, e.g., element i in magnetite, normalized to Fe (Amor et al., 2015):

$$K^{i,Fe} = \frac{c^i_{Mag} / c^i_{Sol}}{c^{Fe}_{Mag} / c^{Fe}_{Sol}}$$

Permineralization: Non-destructive replacement of original materials by secondary minerals. Permineralization is typically related to fluids and can account for the detailed preservation of delicate primary features in fossils.

Serpentinization: Hydrothermal alteration of olivine and pyroxene minerals in rocks, yielding serpentine, magnetite, and brucite as well as highly alkaline fluids (pH 9–11) rich in H_2.

Syngenicity: Having formed at the same time as the host rock.

Synsedimentary: Having occurred during sediment deposition.

Taphonomy: The study of how organisms and biogenic materials are altered and/or preserved in the fossil record.

Texture: Morphological features of individual mineral particles within sediment or rock, such as particle size, shape, and organization.

Ultramafic: Rocks that primarily consist of Fe- and Mg-rich minerals (e.g., olivine, pyroxene). Important examples are peridotite (the rock that constitutes Earth's upper mantle) and komatiite (a volcanic rock that was a widespread constituent of the Archean crust).

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