

REVIEW

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 syndepositional 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.

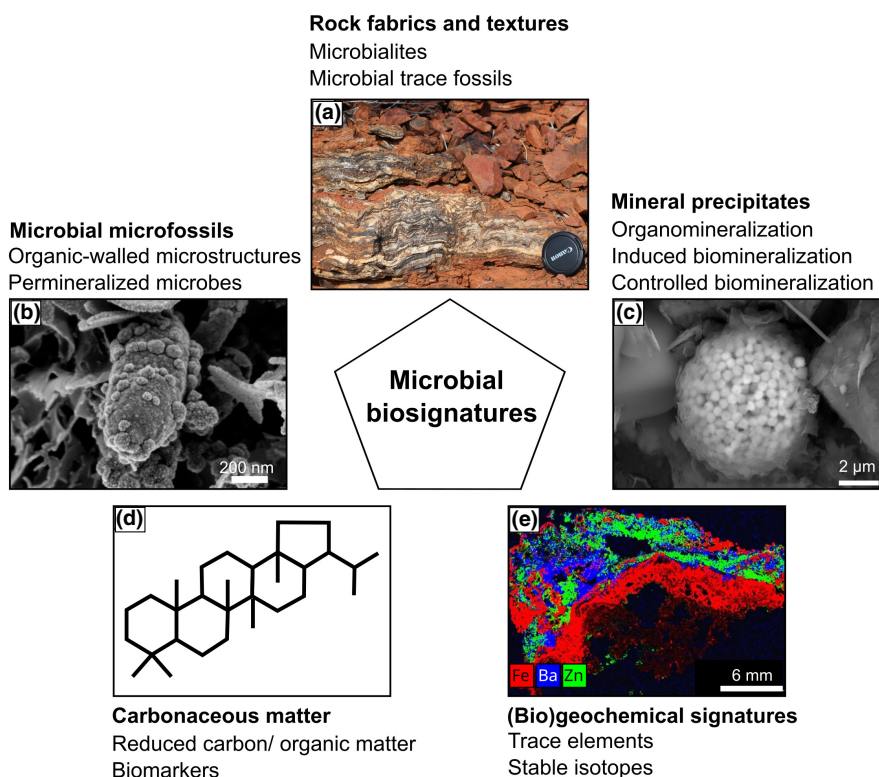
The identification and interpretation of microbial biosignatures in the geological record are challenging. For one, this is because Earth's oldest rocks may preserve primary features that resemble diagnostic biosignatures but have an abiotic origin (i.e., pseudo-biosignatures) (e.g., Brasier et al., 2002; Lowe, 1994; McCollom & Seewald, 2007; McLoughlin et al., 2008; McMahan, 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: μ XRF 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).



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 physicochemical 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 syngenecity* 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-Carbone, 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 syn-depositional 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 re-organization 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., $\delta^{13}\text{C}^*$ signatures in carbonaceous matter, thermal maturity consistent with the metamorphic grade of the host rock) can help establish the syngenecity and biogenicity of organic microstructures (Javaux et al., 2010; Lepot et al., 2013; Sforza 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 (Ohfuiji & 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; Ohfuiji & 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.

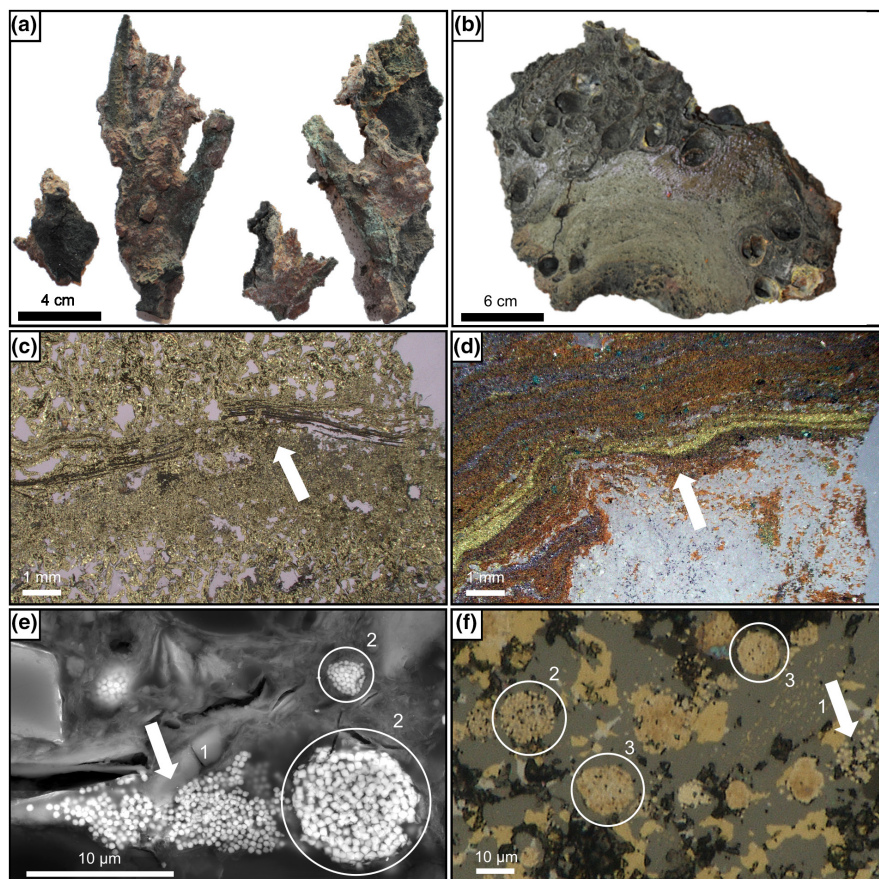
3.3.2 | Controlled biomineralization

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 *Allochroamatium*, *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-Keptra 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 derivatives 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;

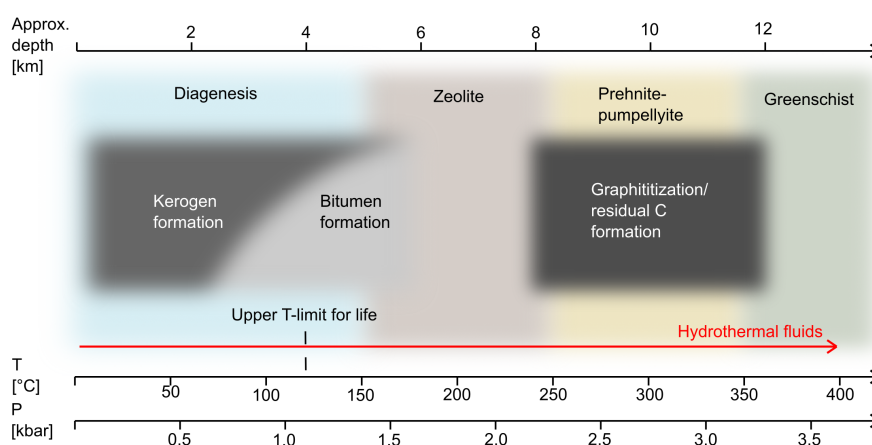


FIGURE 3 Temperature and pressure conditions relevant to the preservation of biosignatures in hydrothermal deposits. The increase in temperature (30°C/km) and pressure (0.27 kbar/km) as a function of depth are given for continental crust since the geothermal gradient is highly variable in the oceanic 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 [FeCO₃] (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 δ¹³C signatures consistent with a biogenic origin (e.g., -30‰; van Zuilen et al., 2002). Graphite may also precipitate from reactions of abiotic CO₂ and CH₄ 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 (¹²C and ¹³C, respectively) for carbon fixation. Consequently, biological organic matter is

isotopically depleted relative to the inorganic carbon pool, as expressed in negative $\delta^{13}\text{C}_{\text{Org}}$ 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 $\delta^{13}\text{C}$ 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 $\delta^{13}\text{C}_{\text{Org}}$ signatures (ca. -20% to -50% ; Blumenberg et al., 2007; Jaeschke et al., 2014; Konn et al., 2009). However, $\delta^{13}\text{C}_{\text{Org}}$ values consistent with photo- or chemoautotrophic C fixation do not provide stand-alone evidence for microbial carbon cycling. Similar $\delta^{13}\text{C}_{\text{Org}}$ 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 $\delta^{13}\text{C}_{\text{Org}}$ and $\delta^{13}\text{C}_{\text{inorg}}$ (30% to -36% ; McCollom & Seewald, 2006). Therefore, a consistent offset between $\delta^{13}\text{C}_{\text{Org}}$ and $\delta^{13}\text{C}_{\text{inorg}}$ 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 $^{34}\text{S}/^{32}\text{S}$ because the $^{34}\text{S}/^{32}\text{S}$ of sulfide species can be fractionated during microbial sulfur cycling by more than -70% (Jørgensen et al., 2019). In contrast, the $\delta^{34}\text{S}$ 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 $100\text{ }^\circ\text{C}$ yielded $\delta^{34}\text{S}$ 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 $\delta^{34}\text{S}$ 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 $\delta^{34}\text{S}$, $\Delta^{33}\text{S}^*$, and $\Delta^{36}\text{S}$ (i.e., quadruple sulfur isotopes) on Paleoproterozoic 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 ($\delta^{56}\text{Fe} > 0$) and depleted $\text{Fe}^{2+}_{\text{aq}}$ ($\delta^{56}\text{Fe} < 0$) (Johnson et al., 2020). Substantial $\delta^{56}\text{Fe}$ 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 $\text{Fe}^{2+}_{\text{aq}}$. Also, the dissimilatory reduction in Fe(III) minerals releases $\text{Fe}^{2+}_{\text{aq}}$ depleted in ^{56}Fe by up to $\sim 3\%$ (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 ($300\text{--}450\text{ }^\circ\text{C}$; Pokrovski et al., 2021). Experimental work demonstrates that biogenic magnetite formation by MTB is associated with a mass-independent fractionation* of Fe-isotopes ($\Delta^{57}\text{Fe} = 0.23$; 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).

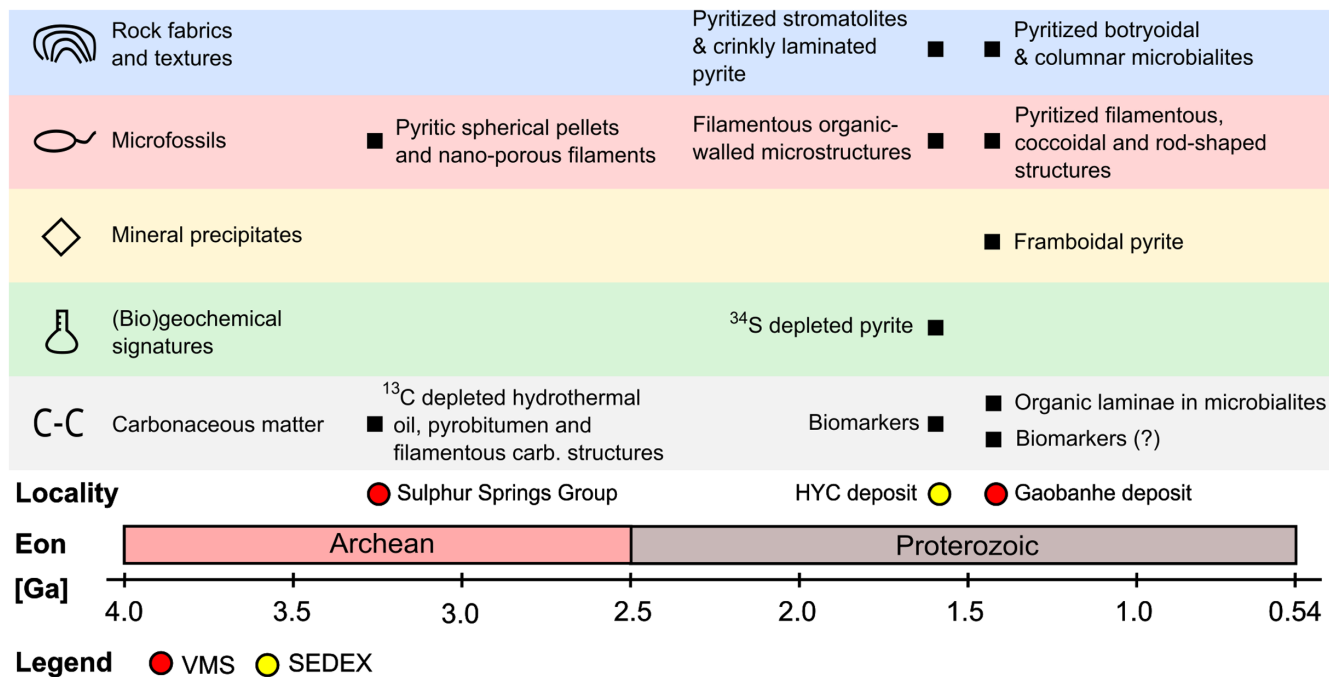


FIGURE 4 Reported microbial biosignatures in Precambrian VMS and SEDEX deposits through geologic time. See the main text for references.

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 subsurface 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 $\delta^{13}\text{C}_{\text{org}}$ values between -29.1‰ and -36.9‰, in line with a biological origin (Rasmussen & Buick, 2000). Notably, filamentous ¹³C-depleted carbonaceous structures ($\delta^{13}\text{C}_{\text{org}} = -26.8\text{‰}$ 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 $\delta^{34}\text{S}$ 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 $\delta^{13}\text{C}_{\text{Org}}$ 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.

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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):

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

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

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

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., $^{56}\text{Fe}/^{54}\text{Fe}$ vs. $^{57}\text{Fe}/^{54}\text{Fe}$). 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., $\Delta^{57}\text{Fe}$).

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):

$$K^{i,\text{Fe}} = \frac{c_{\text{Mag}}^i / c_{\text{Sol}}^i}{c_{\text{Mag}}^{\text{Fe}} / c_{\text{Sol}}^{\text{Fe}}}$$

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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REFERENCES

- Addadi, L., & Weiner, S. (1985). Interactions between acidic proteins and crystals: Stereochemical requirements in biomineralization. *Proceedings of the National Academy of Sciences of the United States of America*, 82, 4110–4114.

- Akai, J., Iida, A., Akai, K., & Chiba, A. (1997). Mn and Fe minerals of possible biogenic origin from two Precambrian stromatolites in Western Australia. *Journal of the Geological Society of Japan*, 105, 484–488.
- Alleon, J., Bernard, S., Le Guillou, C., Daval, D., Skouri-Panet, F., Pont, S., Delbes, L., & Robert, F. (2016). Early entombment within silica minimizes the molecular degradation of microorganisms during advanced diagenesis. *Chemical Geology*, 437, 98–108.
- Alleon, J., Bernard, S., Le Guillou, C., Marin-Carbonne, J., Pont, S., Beyssac, O., McKeegan, K. D., & Robert, F. (2016). Molecular preservation of 1.88 Ga Gunflint organic microfossils as a function of temperature and mineralogy. *Nature Communications*, 7, 11977.
- Allwood, A. C., Grotzinger, J. P., Knoll, A. H., Burch, I. W., Anderson, M. S., Coleman, M. L., & Kanik, I. (2009). Controls on development and diversity of Early Archean stromatolites. *Proceedings of the National Academy of Sciences of the United States of America*, 106, 9548–9555.
- Allwood, A. C., Rosing, M. T., Flannery, D. T., Hurowitz, J. A., & Heirweh, C. M. (2018). Reassessing evidence of life in 3,700-million-year-old rocks of Greenland. *Nature*, 563, 241–244.
- Amor, M., Busigny, V., Durand-Dubief, M., Tharaud, M., Ona-Nguema, G., Gélabert, A., Alphandéry, E., Menguy, N., Benedetti, M. F., Chebbi, I., & Guyot, F. (2015). Chemical signature of magnetotactic bacteria. *Proceedings of the National Academy of Sciences of the United States of America*, 112, 1699–1703.
- Amor, M., Busigny, V., Louvat, P., Gélabert, A., Cartigny, P., Durand-Dubief, M., Ona-Nguema, G., Alphandéry, E., Chebbi, I., & Guyot, F. (2016). Mass-dependent and -independent signature of Fe isotopes in magnetotactic bacteria. *Science*, 352, 705–708.
- Amor, M., Mathon, F. P., Monteil, C. L., Busigny, V., & Lefevre, C. T. (2020). Iron-biomineralizing organelle in magnetotactic bacteria: Function, synthesis and preservation in ancient rock samples. *Environmental Microbiology*, 22, 3611–3632.
- Andrews, G. F. (1988). The selective adsorption of Thiobacilli to dislocation sites on pyrite surfaces. *Biotechnology and Bioengineering*, 31, 378–381.
- Arp, G., Reimer, A., & Reitner, J. (2001). Photosynthesis-induced biofilm calcification and calcium concentrations in Phanerozoic oceans. *Science*, 292, 1701–1704.
- Arp, G., Reimer, A., & Reitner, J. (2003). Microbialite formation in seawater of increased alkalinity, Satonda Crater Lake, Indonesia. *Journal of Sedimentary Research*, 73, 105–127.
- Bai, F., Chang, L., Pei, Z., Harrison, R. J., & Winklhofer, M. (2022). Magnetic biosignatures of magnetosomal greigite from micromagnetic calculation. *Geophysical Research Letters*, 49, e2022GL098437.
- Baumgartner, R. J., Caruso, S., Fiorentini, M. L., Van Kranendonk, M. J., Martin, L., Jeon, H., Pagès, A., & Wacey, D. (2020). Sulfidation of 3.48 billion-year-old stromatolites of the dresser formation, Pilbara Craton: Constraints from in-situ sulfur isotope analysis of pyrite. *Chemical Geology*, 538, 119488.
- Baumgartner, R. J., Hu, S., Van Kranendonk, M. J., & Verrall, M. (2022). Taphonomy of microorganisms and microbial microtextures at sulfidic hydrothermal vents: A case study from the Roman ruins black smokers, Eastern Manus Basin. *Geobiology*, 20, 479–497.
- Baumgartner, R. J., Van Kranendonk, M. J., Pagès, A., Fiorentini, M. L., Wacey, D., & Ryan, C. (2020). Accumulation of transition metals and metalloids in sulfidized stromatolites of the 3.48 billion-year-old dresser formation, Pilbara Craton. *Precambrian Research*, 337, 105534.
- Baumgartner, R. J., Van Kranendonk, M. J., Wacey, D., Fiorentini, M. L., Saunders, M., Caruso, S., Pages, A., Homann, M., & Guagliardo, P. (2019). Nano-porous pyrite and organic matter in 3.5-billion-year-old stromatolites record primordial life. *Geology*, 47, 1039–1043.
- Beard, B. L., Johnson, C. M., Cox, L., Sun, H., Nealson, K. H., & Aguilar, C. (1999). Iron isotope biosignatures. *Science*, 285, 1889–1892.
- Bell, E. A., Boehnke, P., Harrison, T. M., & Mao, W. L. (2015). Potentially biogenic carbon preserved in a 4.1 billion-year-old zircon. *Proceedings of the National Academy of Sciences of the United States of America*, 112, 14518–14521.
- Bell, M. S. (2007). Experimental shock decomposition of siderite and the origin of magnetite in Martian meteorite ALH 84001. *Meteoritics & Planetary Science*, 42, 935–949.
- Bendt, G., Saddeler, S., & Schulz, S. (2019). Sulfidation of magnetite nanoparticles – Following the polysulfide pathway. *European Journal of Inorganic Chemistry*, 2019, 602–608.
- Benzerara, K., Bolzoni, R., Monteil, C., Beyssac, O., Forni, O., Alonso, B., Asta, M. P., & Lefevre, C. (2020). The gammaproteobacterium *Achromatium* forms intracellular amorphous calcium carbonate and not (crystalline) calcite. *Geobiology*, 19, 199–213.
- Bernard, S., & Papineau, D. (2014). Graphitic carbons and biosignatures. *Elements*, 10, 435–440.
- Berner, R. A. (1970). Sedimentary pyrite formation. *American Journal of Science*, 268, 1–23.
- Berner, R. A. (1984). Sedimentary pyrite formation: An update. *Geochimica et Cosmochimica Acta*, 48, 605–615.
- Berner, Z. A., Puchelt, H., Nöltner, T., & Kramar, U. (2013). Pyrite geochemistry in the Toarcian Posidonia shale of south-West Germany: Evidence for contrasting trace-element patterns of diagenetic and syngenetic pyrites: Pyrite element geochemistry. *Sedimentology*, 60, 548–573.
- Beveridge, T. J. (1989). Role of cellular design in bacterial metal accumulation and mineralization. *Annual Review of Microbiology*, 43, 147–171.
- Black, M. (1933). The algal sedimentation of Andros Island Bahamas. *Philosophical Transactions of the Royal Society B: Biological Sciences*, 222, 165–192.
- Blumenberg, M., Seifert, R., Buschmann, B., Kiel, S., & Thiel, V. (2012). Biomarkers reveal diverse microbial communities in Black smoker sulfides from turtle pits (mid-Atlantic ridge, recent) and Yaman Kasy (Russia, Silurian). *Geomicrobiology Journal*, 29, 66–75.
- Blumenberg, M., Seifert, R., Petersen, S., & Michaelis, W. (2007). Biosignatures present in a hydrothermal massive sulfide from the mid-Atlantic ridge. *Geobiology*, 5, 435–450.
- Böttcher, M. E., Thamdrup, B., & Vennemann, T. W. (2001). Oxygen and sulfur isotope fractionation during anaerobic bacterial disproportionation of elemental sulfur. *Geochimica et Cosmochimica Acta*, 65, 1601–1609.
- Brasier, M., Green, O., Lindsay, J., McLoughlin, N., Steele, A., & Stoakes, C. (2005). Critical testing of Earth's oldest putative fossil assemblage from the ~3.5Ga Apex chert, Chinaman Creek, Western Australia. *Precambrian Research*, 140, 55–102.
- Brasier, M., McLoughlin, N., Green, O., & Wacey, D. (2006). A fresh look at the fossil evidence for early Archaean cellular life. *Philosophical Transactions of the Royal Society B: Biological Sciences*, 361, 887–902.
- Brasier, M. D., Green, O. R., Jephcoat, A. P., Kleppe, A. K., Van Kranendonk, M. J., Lindsay, J. F., Steele, A., & Grassineau, N. V. (2002). Questioning the evidence for Earth's oldest fossils. *Nature*, 416, 76–81.
- Brauhart, C. W., Groves, D. I., & Morant, P. (1998). Regional alteration systems associated with volcanogenic massive sulfide mineralization at Panorama, Pilbara, Western Australia. *Economic Geology*, 93, 292–302.
- Brearley, A. J. (2003). Magnetite in ALH 84001: An origin by shock-induced thermal decomposition of iron carbonate. *Meteoritics & Planetary Science*, 38, 849–870.
- Breier, J. A., Toner, B. M., Fakra, S. C., Marcus, M. A., White, S. N., Thurnherr, A. M., & German, C. R. (2012). Sulfur, sulfides, oxides and organic matter aggregated in submarine hydrothermal plumes at 9°50'N East Pacific rise. *Geochimica et Cosmochimica Acta*, 88, 216–236.

- Buick, R. (1990). Microfossil recognition in Archean rocks: An appraisal of spheroids and filaments from a 3500 M.Y. old Chert-barite unit at north pole, Western Australia. *PALAIOS*, 5, 441–459.
- Buick, R., Dunlop, J. S. R., & Groves, D. I. (1981). Stromatolite recognition in ancient rocks: An appraisal of irregularly laminated structures in an Early Archean chert-barite unit from north pole, Western Australia. *Alcheringa*, 5, 161–181.
- Bull, S. W. (1998). Sedimentology of the Palaeoproterozoic Barney Creek formation in DDH BMR McArthur 2, southern McArthur basin, northern territory. *Australian Journal of Earth Sciences*, 45, 21–31.
- Burne, R. V., & Moore, L. S. (1987). Microbialites: Organosedimentary deposits of benthic microbial communities. *PALAIOS*, 2, 241–254.
- Cameron, V., House, C. H., & Brantley, S. L. (2012). A first analysis of metallome biosignatures of hyperthermophilic archaea. *Archaea*, 2012, 1–12.
- Campbell, K. A. (2006). Hydrocarbon seep and hydrothermal vent paleoenvironments and paleontology: Past developments and future research directions. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 232, 362–407.
- Canfield, D. E., & Berner, R. A. (1987). Dissolution and pyritization of magnetite in anoxic marine sediments. *Geochimica et Cosmochimica Acta*, 51, 645–659.
- Canfield, D. E., & Thamdrup, B. (1994). The production of ^{34}S -depleted sulfide during bacterial disproportionation of elemental sulfur. *Science*, 266, 1973–1975.
- Cavalazzi, B., Lemelle, L., Simionovici, A., Cady, S. L., Russell, M. J., Bailo, E., Canteri, R., Enrico, E., Manceau, A., Maris, A., Salomé, M., Thomassot, E., Bouden, N., Tucoulou, R., & Hofmann, A. (2021). Cellular remains in a ~3.42-billion-year-old seafloor hydrothermal environment. *Science Advances*, 7, eabf3963.
- Chanda, P., Amenabar, M. J., Boyd, E. S., Beard, B. L., & Johnson, C. M. (2021). Stable Fe isotope fractionation during dissimilatory Fe(III) reduction by a thermoacidophile in acidic hydrothermal environments. *Geochimica et Cosmochimica Acta*, 292, 427–451.
- Chang, S. B. R., & Kirschvink, J. L. (1989). Magnetofossils, the magnetization of sediments, and the evolution of magnetite biomineralization. *Annual Review of Earth and Planetary Sciences*, 17, 169–195.
- Chang, S.-B. R., Stolz, J. F., & Kirschvink, J. L. (1989). Biogenic magnetite in Stromatolites. II. Occurrence in ancient sedimentary environments. *Precambrian Research*, 43, 305–315.
- Chaudhuri, S. K., Lack, J. G., & Coates, J. D. (2001). Biogenic magnetite formation through anaerobic biooxidation of Fe(II). *Applied and Environmental Microbiology*, 67, 2844–2848.
- Chen, J., Walter, M. R., Logan, G. A., Hinman, M. C., & Summons, R. E. (2003). The Paleoproterozoic McArthur River (HYC) Pb/Zn/Ag deposit of northern Australia: Organic geochemistry and ore genesis. *Earth and Planetary Science Letters*, 210, 467–479.
- Cosmidis, J., & Benzerara, K. (2022). Why do microbes make minerals? *Comptes Rendus Géoscience*, 354, 1–39.
- Cosmidis, J., Nims, C. W., Diercks, D., & Templeton, A. S. (2019). Formation and stabilization of elemental sulfur through organomineralization. *Geochimica et Cosmochimica Acta*, 247, 59–82.
- Cosmidis, J., & Templeton, A. S. (2016). Self-assembly of biomorphic carbon/sulfur microstructures in sulfidic environments. *Nature Communications*, 7, 12812.
- Crick, I. H. (1992). Petrological and maturation characteristics of organic matter from the Middle Proterozoic McArthur Basin, Australia. *Australian Journal of Earth Sciences*, 39, 501–519.
- Criouet, I., Viennet, J.-C., Jacquemot, P., Jaber, M., & Bernard, S. (2021). Abiotic formation of organic biomorphs under diagenetic conditions. *Geochemical Perspectives Letters*, 16, 40–46.
- Croal, L. R., Johnson, C. M., Beard, B. L., & Newman, D. K. (2004). Iron isotope fractionation by Fe(II)-oxidizing photoautotrophic bacteria. *Geochimica et Cosmochimica Acta*, 68, 1227–1242.
- Cron, B., Henri, P., Chan, C. S., Macalady, J. L., & Cosmidis, J. (2019). Elemental sulfur formation by *Sulfuricum kujense* is mediated by extracellular organic compounds. *Frontiers in Microbiology*, 10, 2710.
- Crosby, H. A., Johnson, C. M., Roden, E. E., & Beard, B. L. (2005). Coupled Fe(II)–Fe(III) electron and atom exchange as a mechanism for Fe isotope fractionation during dissimilatory iron oxide reduction. *Environmental Science & Technology*, 39, 6698–6704.
- Dahl, C. (2020). Bacterial intracellular sulphur globules. In D. Jendrossek (Ed.), *Bacterial organelles and organelle-like inclusions, microbiology monographs* (pp. 19–51). Springer International Publishing.
- Deamer, D., & Damer, B. (2017). Can life begin on Enceladus? A perspective from hydrothermal chemistry. *Astrobiology*, 17, 834–839.
- Decraene, M.-N., Marin-Carbonne, J., Thomazo, C., Olivier, N., Philippot, P., Strauss, H., & Deloule, E. (2021). Intense biogeochemical iron cycling revealed in Neoproterozoic micropyrates from stromatolites. *Geochimica et Cosmochimica Acta*, 312, 299–320.
- Delacour, A., Früh-Green, G. L., Bernasconi, S. M., Schaeffer, P., & Kelley, D. S. (2008). Carbon geochemistry of serpentinites in the lost city hydrothermal system (30°N, MAR). *Geochimica et Cosmochimica Acta*, 72, 3681–3702.
- Delarue, F., Robert, F., Sugitani, K., Tartèse, R., Duhamel, R., & Derenne, S. (2017). Investigation of the geochemical preservation of ca. 3.0 Ga permineralized and encapsulated microfossils by nanoscale secondary ion mass spectrometry. *Astrobiology*, 17, 1192–1202.
- Dellwig, O., Böttcher, M. E., Lipinski, M., & Brumsack, H.-J. (2002). Trace metals in Holocene coastal peats and their relation to pyrite formation (NW Germany). *Chemical Geology*, 182, 423–442.
- Dodd, M. S., Papineau, D., Grenne, T., Slack, J. F., Rittner, M., Pirajno, F., O'Neil, J., & Little, C. T. S. (2017). Evidence for early life in Earth's oldest hydrothermal vent precipitates. *Nature*, 543, 60–64.
- Donald, R., & Southam, G. (1999). Low temperature anaerobic bacterial diagenesis of ferrous monosulfide to pyrite. *Geochimica et Cosmochimica Acta*, 63, 2019–2023.
- Duck, L. J., Glikson, M., Golding, S. D., & Webb, R. E. (2007). Microbial remains and other carbonaceous forms from the 3.24 Ga Sulphur Springs black smoker deposit, Western Australia. *Precambrian Research*, 154, 205–220.
- Duda, J.-P., Thiel, V., Bauersachs, T., Mißbach, H., Reinhardt, M., Schäfer, N., Van Kranendonk, M. J., & Reitner, J. (2018). Ideas and perspectives: Hydrothermally driven redistribution and sequestration of early Archean biomass – The “hydrothermal pump hypothesis.”. *Biogeosciences*, 15, 1535–1548.
- Duda, J.-P., Van Kranendonk, M. J., Thiel, V., Ionescu, D., Strauss, H., Schäfer, N., & Reitner, J. (2016). A rare glimpse of Paleoproterozoic life: Geobiology of an exceptionally preserved microbial mat facies from the 3.4 Ga Strelley Pool formation, Western Australia. *PLoS One*, 11, e0147629.
- Dupraz, C., Reid, R. P., Braissant, O., Decho, A. W., Norman, R. S., & Visscher, P. T. (2009). Processes of carbonate precipitation in modern microbial mats. *Earth-Science Reviews*, 96, 141–162.
- Durand, B. (1980). Sedimentary organic matter and kerogen. Definition and quantitative importance of kerogen. In B. Durand (Ed.), *Kerogen* (pp. 13–34). Éditions Technip.
- Eglinton, G., Scott, P. M., Belsky, T., Burlingame, A. L., & Calvin, M. (1964). Hydrocarbons of biological origin from a one-billion-year-old sediment. *Science*, 145, 263–264.
- Ehrlich, H., Bailey, E., Wysokowski, M., & Jesionowski, T. (2021). Forced biomineralization: A review. *Biomimetics*, 6, 46.
- Eigenbrode, J. L., & Freeman, K. H. (2006). Late Archean rise of aerobic microbial ecosystems. *Proceedings of the National Academy of Sciences of the United States of America*, 103, 15759–15764.
- Eldridge, C. S., Williams, N., & Walshe, J. L. (1993). Sulfur isotope variability in sediment-hosted massive sulfide deposits as determined using the ion microprobe SHRIMP; II, a study of the H.Y.C. Deposit at McArthur River, Northern Territory, Australia. *Economic Geology*, 88, 1–26.

- Fallick, A. E., Ashton, J. H., Boyce, A. J., Ellam, R. M., & Russell, M. J. (2001). Bacteria were responsible for the magnitude of the world-class hydrothermal base metal sulfide orebody at Navan, Ireland. *Economic Geology*, *96*, 885–890.
- Farrimond, P., Love, G. D., Bishop, A. N., Innes, H. E., Watson, D. F., & Snape, C. E. (2003). Evidence for the rapid incorporation of hopanoids into kerogen. *Geochimica et Cosmochimica Acta*, *67*, 1383–1394.
- Ferris, F. G., Fyfe, W. S., & Beveridge, T. J. (1987). Bacteria as nucleation sites for authigenic minerals in a metal-contaminated lake sediment. *Chemical Geology*, *63*, 225–232.
- Flemming, H.-C., & Wuertz, S. (2019). Bacteria and archaea on Earth and their abundance in biofilms. *Nature Reviews Microbiology*, *17*, 247–260.
- Foley, N., Ayuso, R. A., & Li, R. S. (2001). Remnant colloform pyrite at the haile gold deposit, South Carolina: A textural key to genesis. *Economic Geology*, *96*, 891–902.
- Fortney, N. W., He, S., Converse, B. J., Beard, B. L., Johnson, C. M., Boyd, E. S., & Roden, E. E. (2016). Microbial Fe(III) oxide reduction potential in chocolate pots hot spring, Yellowstone National Park. *Geobiology*, *14*, 255–275.
- Fowler, A. D., & L'Heureux, I. (1996). Self-organized banded sphalerite and branching galena in the pine point ore deposit, Northwest Territories. *The Canadian Mineralogist*, *34*, 1211–1222.
- Fraústo da Silva, J. J. R., & Williams, R. J. P. (2001). *The biological chemistry of the elements – the inorganic chemistry of life*. Oxford University Press.
- French, K. L., Birdwell, J. E., & Vanden Berg, M. D. (2020). Biomarker similarities between the saline lacustrine Eocene Green River and the Paleoproterozoic Barney Creek formations. *Geochimica et Cosmochimica Acta*, *274*, 228–245.
- Gao, B., Zhang, L., Jin, X., Li, W., Bai, Y., & Sakyi, P. A. (2020). Re-Os geochronology and trace element characteristics of the hydrothermally reworked pyrite of the Gaobanhe sediment-hosted polymetal pyrite deposit in Northern China and its geological significance. *Journal of Geochemical Exploration*, *215*, 106561.
- Gao, S., Huang, F., Wang, Y., & Gao, W. (2016). A review of research progress in the genesis of colloform pyrite and its environmental indications. *Acta Geologica Sinica*, *90*, 1353–1369.
- García-Ruiz, J. M., Hyde, S. T., Carnerup, A. M., Christy, A. G., Van Kranendonk, M. J., & Welham, N. J. (2003). Self-assembled silica-carbonate structures and detection of ancient microfossils. *Science*, *302*, 1194–1197.
- Georgieva, M. N., Little, C. T. S., Bailey, R. J., Ball, A. D., & Glover, A. G. (2018). Microbial-tubeworm associations in a 440 million year old hydrothermal vent community. *Proceedings of the Royal Society B: Biological Sciences*, *285*, 20182004.
- Georgieva, M. N., Little, C. T. S., Maslennikov, V. V., Glover, A. G., Ayupova, N. R., & Herrington, R. J. (2021). The history of life at hydrothermal vents. *Earth-Science Reviews*, *217*, 103602.
- Glikson, M., Duck, L. J., Golding, S. D., Hofmann, A., Bolhar, R., Webb, R., Baiano, J. C. F., & Sly, L. I. (2008). Microbial remains in some earliest Earth rocks: Comparison with a potential modern analogue. *Precambrian Research*, *164*, 187–200.
- Golding, S. D., Duck, L. J., Young, E., Baublys, K. A., Glikson, M., & Kamber, B. S. (2011). Earliest seafloor hydrothermal systems on Earth: Comparison with modern analogues. In S. D. Golding & M. Glikson (Eds.), *Earliest life on Earth: Habitats, environments and methods of detection* (pp. 15–49). Springer.
- Golubic, S., Friedmann, I., & Schneider, J. (1981). The Lithobiontic ecological niche, with special reference to microorganisms. *Journal of Sedimentary Petrology*, *31*, 475–478.
- Golubic, S., & Hofmann, H. J. (1976). Comparison of Holocene and mid-Precambrian Entophysalidaceae (Cyanophyta) in stromatolitic algal mats: Cell division and degradation. *Journal of Paleontology*, *50*, 1074–1082.
- Gong, J., Myers, K. D., Munoz-Saez, C., Homann, M., Rouillard, J., Wirth, R., Schreiber, A., & van, Z. M. A. (2020). Formation and preservation of microbial palisade fabric in silica deposits from El Tatio, Chile. *Astrobiology*, *20*, 500–524.
- Greenwood, P. F., Brocks, J. J., Grice, K., Schwark, L., Jaraula, C. M. B., Dick, J. M., & Evans, K. A. (2013). Organic geochemistry and mineralogy. I. Characterisation of organic matter associated with metal deposits. *Ore Geology Reviews*, *50*, 1–27.
- Gregory, D. D., Large, R. R., Halpin, J. A., Baturina, E. L., Lyons, T. W., Wu, S., Danyushevsky, L., Sack, P. J., Chappaz, A., Maslennikov, V. V., & Bull, S. W. (2015). Trace element content of sedimentary pyrite in Black shales. *Economic Geology*, *110*, 1389–1410.
- Grey, K., & Awramik, S. (2020). *Handbook for the study and description of microbialites*. Geological Survey of Western Australia Bulletin. Geological Survey of Western Australia.
- Grey, K., & Sugitani, K. (2009). Palynology of Archean microfossils (c. 3.0Ga) from the Mount Grant area, Pilbara Craton, Western Australia: Further evidence of biogenicity. *Precambrian Research*, *173*, 60–69.
- Grosch, E. G., & McLoughlin, N. (2014). Reassessing the biogenicity of Earth's oldest trace fossil with implications for biosignatures in the search for early life. *Proceedings of the National Academy of Sciences of the United States of America*, *111*, 8380–8385.
- Grotzinger, J. P., & Rothman, D. H. (1996). An abiotic model for stromatolite morphogenesis. *Nature*, *383*, 423–425.
- Habicht, K. S., & Canfield, D. E. (1997). Sulfur isotope fractionation during bacterial sulfate reduction in organic-rich sediments. *Geochimica et Cosmochimica Acta*, *61*, 5351–5361.
- Halama, M., Swanner, E. D., Konhauser, K. O., & Kappler, A. (2016). Evaluation of siderite and magnetite formation in BIFs by pressure-temperature experiments of Fe(III) minerals and microbial biomass. *Earth and Planetary Science Letters*, *450*, 243–253.
- Han, X., Tomaszewski, E. J., Schoenberg, R., Konhauser, K. O., Amor, M., Pan, Y., Warter, V., Kappler, A., & Byrne, J. M. (2021). Using Zn and Ni behavior during magnetite precipitation in banded iron formations to determine its biological or abiotic origin. *Earth and Planetary Science Letters*, *568*, 117052.
- Hannington, M. D. (2014). Volcanogenic massive sulfide deposits. In *Treatise on Geochemistry* (pp. 463–488). Elsevier.
- Hannington, M. D., Galley, A. G., Herzig, P. M., & Petersen, S. (1998). Comparison of the TAG mound and stockwork complex with Cyprus-type massive sulfide deposits. In P. M. Herzig, S. E. Humphris, D. J. Miller, & R. A. Zierenberg (Eds.), *Proceedings of the ocean drilling program, scientific results*. Ocean Drilling Program.
- Havas, R., Savian, J. F., & Busigny, V. (2021). Iron isotope signature of magnetofossils and oceanic biogeochemical changes through the middle Eocene climatic optimum. *Geochimica et Cosmochimica Acta*, *311*, 332–352.
- Hayes, J. M. (2001). Fractionation of the isotopes of carbon and hydrogen in biosynthetic processes. In J. W. Valley & D. R. Cole (Eds.), *Stable Isotope Geochemistry, Reviews in Mineralogy and Geochemistry* (pp. 225–277). Mineralogical Society of America, Geochemical Society.
- Hayes, J. M., & Waldbauer, J. R. (2006). The carbon cycle and associated redox processes through time. *Philosophical Transactions of the Royal Society B: Biological Sciences*, *361*, 931–950.
- Heijlen, W., Appel, P. W. U., Frezzotti, M.-L., Horsewell, A., & Touret, J. L. R. (2006). Metamorphic fluid flow in the northeastern part of the 3.8–3.7 Ga Isua Greenstone Belt (SW Greenland): A re-evaluation of fluid inclusion evidence for early Archean seafloor-hydrothermal systems. *Geochimica et Cosmochimica Acta*, *70*, 3075–3095.
- Hickman-Lewis, K., Cavalazzi, B., Sorieul, S., Gautret, P., Foucher, F., Whitehouse, M. J., Jeon, H., Georgelin, T., Cockell, C. S., & Westall, F. (2020). Metallomics in deep time and the influence of ocean chemistry on the metabolic landscapes of Earth's earliest ecosystems. *Scientific Reports*, *10*, 4965.

- Hoefs, J. (2021). *Stable isotope geochemistry*. Springer textbooks in earth sciences, geography and environment. Springer International Publishing.
- Hofmann, A. (2011). Archaean hydrothermal Systems in the Barberton Greenstone belt and their significance as a habitat for early life. In S. D. Golding & M. Glikson (Eds.), *Earliest life on earth: Habitats, environments and methods of detection* (pp. 51–78). Springer.
- Holm, N. G., & Charlou, J. L. (2001). Initial indications of abiotic formation of hydrocarbons in the rainbow ultramafic hydrothermal system, mid-Atlantic ridge. *Earth and Planetary Science Letters*, *191*, 8.
- Holman, A. I., Greenwood, P. F., Brocks, J. J., & Grice, K. (2014). Effects of sulfide minerals on aromatic maturity parameters: Laboratory investigation using micro-scale sealed vessel pyrolysis. *Organic Geochemistry*, *76*, 270–277.
- Holman, A. I., Grice, K., Jaraula, C. M. B., & Schimmelmann, A. (2014). Bitumen II from the Paleoproterozoic Here's your chance Pb/Zn/Ag deposit: Implications for the analysis of depositional environment and thermal maturity of hydrothermally-altered sediments. *Geochimica et Cosmochimica Acta*, *139*, 98–109.
- Horita, J., & Berndt, M. E. (1999). Abiogenic methane formation and isotopic fractionation under hydrothermal conditions. *Science*, *285*, 1055–1057.
- Hoshino, Y., Flannery, D. T., Walter, M. R., & George, S. C. (2014). Hydrocarbons preserved in a ~2.7 Ga outcrop sample from the Fortescue Group, Pilbara Craton, Western Australia. *Geobiology*, *13*, 99–111.
- Houghton, J. L., Shanks, W. C., & Seyfried, W. E. (2004). Massive sulfide deposition and trace element remobilization in the Middle Valley sediment-hosted hydrothermal system, northern Juan de Fuca Ridge. *Geochimica et Cosmochimica Acta*, *68*, 2863–2873.
- Huber, C., & Wächtershäuser, G. (1997). Activated acetic acid by carbon fixation on (Fe, Ni)S under primordial conditions. *Science*, *276*, 245–247.
- Huerta-Díaz, M. A., Delgadillo-Hinojosa, F., Siqueiros-Valencia, A., Valdivieso-Ojeda, J., Reimer, J. J., & Segovia-Zavala, J. A. (2012). Millimeter-scale resolution of trace metal distributions in microbial mats from a hypersaline environment in Baja California, Mexico. *Geobiology*, *10*, 531–547.
- Huston, D. L., Brauhart, C. W., Driehage, S. L., Davidson, G. J., & Groves, D. I. (2001). Metal leaching and inorganic sulfate reduction in volcanic-hosted massive sulfide mineral systems: Evidence from the paleo-Archean panorama district, Western Australia. *Geology*, *29*, 687.
- Huston, D. L., Pirajno, F., Morant, P., Cummins, B., Baker, D., & Mernagh, T. P. (2019). Paleoproterozoic mineral deposits of the Pilbara Craton: Genesis, tectonic environment, and comparisons with younger deposits. In *Earth's oldest rocks* (pp. 519–551). Elsevier.
- Ionescu, D., Zoccarato, L., Zaduryan, A., Schorn, S., Bizic, M., Pinnow, S., Cypionka, H., & Grossart, H.-P. (2020). Heterozygous, polyploid, Giant bacterium, achromatium, possesses an identical functional inventory worldwide across drastically different ecosystems. *Molecular Biology and Evolution*, *38*, 1040–1059.
- Ivarsson, M., Drake, H., Neubeck, A., Snoeyenbos-West, O., Belivanova, V., & Bengtson, S. (2021). Introducing palaeolithobiology. *GFF*, *143*, 305–319.
- Jackson, M. J., Scott, D. L., & Rawlings, D. J. (2000). Stratigraphic framework for the Leichhardt and Calvert Superbasins: Review and correlations of the pre- 1700 Ma successions between Mt Isa and McArthur River. *Australian Journal of Earth Sciences*, *47*, 381–403.
- Jaeschke, A., Eickmann, B., Lang, S. Q., Bernasconi, S. M., Strauss, H., & Früh-Green, G. L. (2014). Biosignatures in chimney structures and sediment from the Loki's Castle low-temperature hydrothermal vent field at the Arctic Mid-Ocean Ridge. *Extremophiles*, *18*, 545–560.
- Javaux, E. J. (2019). Challenges in evidencing the earliest traces of life. *Nature*, *572*, 451–460.
- Javaux, E. J., Knoll, A. H., & Walter, M. (2003). Recognizing and interpreting the fossils of early eukaryotes. *Origins of Life and Evolution of the Biosphere*, *33*, 75–94.
- Javaux, E. J., & Lepot, K. (2018). The Paleoproterozoic fossil record: Implications for the evolution of the biosphere during Earth's middle-age. *Earth-Science Reviews*, *176*, 68–86.
- Javaux, E. J., Marshall, C. P., & Bekker, A. (2010). Organic-walled microfossils in 3.2-billion-year-old shallow-marine siliciclastic deposits. *Nature*, *463*, 934–938.
- Johnson, C., Beard, B., & Weyer, S. (2020). *Iron geochemistry: An isotopic perspective*. *Advances in isotope geochemistry*. Springer International Publishing.
- Johnson, T. E., Brown, M., Kaus, B. J. P., & VanTongeren, J. A. (2014). Delamination and recycling of Archaean crust caused by gravitational instabilities. *Nature Geoscience*, *7*, 47–52.
- Jones, B., & Renaut, R. W. (2007). Microstructural changes accompanying the opal-A to opal-CT transition: New evidence from the siliceous sinters of Geysir, Haukadalur, Iceland. *Sedimentology*, *54*, 921–948.
- Jørgensen, B. B., Findlay, A. J., & Pellerin, A. (2019). The biogeochemical sulfur cycle of marine sediments. *Frontiers in Microbiology*, *10*, 849.
- Kalkowsky, E. (1908). Oolith und Stromatolith im norddeutschen Buntsandstein. *Zeitschrift der Deutschen Geologischen Gesellschaft*, *60*, 68–125.
- Kappler, A., Bryce, C., Mansor, M., Lueder, U., Byrne, J. M., & Swanner, E. D. (2021). An evolving view on biogeochemical cycling of iron. *Nature Reviews Microbiology*, *19*, 360–374.
- Kappler, A., Johnson, C. M., Crosby, H. A., Beard, B. L., & Newman, D. K. (2010). Evidence for equilibrium iron isotope fractionation by nitrate-reducing iron(II)-oxidizing bacteria. *Geochimica et Cosmochimica Acta*, *74*, 2826–2842.
- Kappler, A., Pasquero, C., Konhauser, K. O., & Newman, D. K. (2005). Deposition of banded iron formations by anoxygenic phototrophic Fe(II)-oxidizing bacteria. *Geology*, *33*, 865–868.
- Kashefi, K., & Lovley, D. R. (2003). Extending the upper temperature limit for life. *Science*, *301*, 934.
- Kelley, D. S., Baross, J. A., & Delaney, J. R. (2002). Volcanoes, fluids, and life at Mid-Ocean ridge spreading centers. *Annual Review of Earth and Planetary Sciences*, *30*, 385–491.
- Kesler, S. E., Gesink, J. A., & Haynes, F. M. (1989). Evolution of mineralizing brines in the East Tennessee Mississippi Valley-type ore field. *Geology*, *17*, 466–469.
- Kirschvink, J. L., & Chang, S.-B. R. (1984). Ultrafine-grained magnetite in deep-sea sediments: Possible bacterial magnetofossils. *Geology*, *12*, 559–562.
- Kiyosu, Y., & Krouse, H. R. (1990). The role of organic acid in the abiogenic reduction of sulfate and the sulfur isotope effect. *Geochemical Journal*, *24*, 21–27.
- Knoll, A. H., & Barghoorn, E. S. (1974). Ambient pyrite in Precambrian Chert: New evidence and a theory. *Proceedings of the National Academy of Sciences of the United States of America*, *71*, 2329–2331.
- Knoll, A. H., & Barghoorn, E. S. (1977). Archean microfossils showing cell division from the Swaziland system of South Africa. *Science*, *198*, 396–398.
- Knoll, A. H., Bergmann, K. D., & Strauss, J. V. (2016). Life: The first two billion years. *Philosophical Transactions of the Royal Society B: Biological Sciences*, *371*, 20150493.
- Köhler, I., Konhauser, K. O., Papineau, D., Bekker, A., & Kappler, A. (2013). Biological carbon precursor to diagenetic siderite with spherical structures in iron formations. *Nature Communications*, *4*, 1741.
- Konhauser, K. O., Jones, B., Phoenix, V. R., Ferris, G., & Renaut, R. W. (2004). The microbial role in hot spring silicification. *AMBIO*, *33*, 552–558.
- Konn, C., Charlou, J. L., Donval, J. P., Holm, N. G., Dehairs, F., & Bouillon, S. (2009). Hydrocarbons and oxidized organic compounds in hydrothermal fluids from rainbow and lost City ultramafic-hosted vents. *Chemical Geology*, *258*, 299–314.

- Konn, C., Charlou, J. L., Holm, N. G., & Mousis, O. (2015). The production of methane, hydrogen, and organic compounds in ultramafic-hosted hydrothermal vents of the mid-Atlantic ridge. *Astrobiology*, 15, 381–399.
- Kopp, R. E., & Kirschvink, J. L. (2008). The identification and biogeochemical interpretation of fossil magnetotactic bacteria. *Earth Science Reviews*, 86, 42–61.
- Kotopoulou, E., Godelitsas, A., Göttlicher, J., Steininger, R., Price, R., Fike, D. A., Amend, J. P., Gilhooly, W. P., Druschell, G., Nomikou, P., Gamaletsos, P. N., & Lozios, S. (2022). Metastable iron (mono)sulfides in the shallow-sea hydrothermal sediments of Milos, Greece. *ACS Earth and Space Chemistry*, 6, 920–931.
- Kucha, H., Schroll, E., & Stumpf, E. F. (2005). Fossil sulphate-reducing bacteria in the Bleiberg lead-zinc deposit, Austria. *Mineralium Deposita*, 40, 123–126.
- Kusky, T. M., & Li, J. (2003). Paleoproterozoic tectonic evolution of the North China craton. *Journal of Asian Earth Sciences*, 22, 383–397.
- Labrenz, M., Druschel, G. K., Thomsen-Ebert, T., Gilbert, B., Welch, S. A., Kemner, K. M., Logan, G. A., Summons, R. E., De Stasio, G., Bond, P. L., Lai, B., Kelly, S. D., & Banfield, J. F. (2000). Formation of sphalerite (ZnS) deposits in natural biofilms of sulfate-reducing bacteria. *Science*, 290, 1744–1747.
- Lam, K. P., Hitchcock, A. P., Obst, M., Lawrence, J. R., Swerhone, G. D. W., Leppard, G. G., Tyliczszak, T., Karunakaran, C., Wang, J., Kaznatcheev, K., Bazylinski, D. A., & Lins, U. (2010). Characterizing magnetism of individual magnetosomes by X-ray magnetic circular dichroism in a scanning transmission X-ray microscope. *Chemical Geology*, 270, 110–116.
- Large, R. R., Bull, S. W., Cooke, D. R., & McGoldrick, P. J. (1998). A genetic model for the H.Y.C. Deposit, Australia; based on regional sedimentology, geochemistry, and sulfide-sediment relationships. *Economic Geology*, 93, 1345–1368.
- Lepland, A., Arrhenius, G., & Cornell, D. (2002). Apatite in early Archean Isua supracrustal rocks, southern West Greenland: Its origin, association with graphite and potential as a biomarker. *Precambrian Research*, 118, 221–241.
- Lepland, A., Van Zuilen, M., & Philippot, P. (2011). Fluid-deposited graphite and its geobiological implications in early Archean gneiss from Akilia, Greenland. *Geobiology*, 9, 2–9.
- Lepot, K. (2020). Signatures of early microbial life from the Archean (4 to 2.5 Ga) eon. *Earth-Science Reviews*, 209, 103296.
- Lepot, K., Benzerara, K., & Philippot, P. (2011). Biogenic versus metamorphic origins of diverse microtubes in 2.7Gyr old volcanic ashes: Multi-scale investigations. *Earth and Planetary Science Letters*, 312, 37–47.
- Lepot, K., Williford, K. H., Ushikubo, T., Sugitani, K., Mimura, K., Spicuzza, M. J., & Valley, J. W. (2013). Texture-specific isotopic compositions in 3.4Gyr old organic matter support selective preservation in cell-like structures. *Geochimica et Cosmochimica Acta*, 112, 66–86.
- Li, J., & Kusky, T. M. (2007). World's largest known Precambrian fossil black smoker chimneys and associated microbial vent communities, North China: Implications for early life. *Gondwana Research*, 12, 84–100.
- Liermann, L. J., Hausrath, E. M., Anbar, A. D., & Brantley, S. L. (2007). Assimilatory and dissimilatory processes of microorganisms affecting metals in the environment. *Journal of Analytical Atomic Spectrometry*, 22, 867.
- Lin, W., Paterson, G. A., Zhu, Q., Wang, Y., Kopylova, E., Li, Y., Knight, R., Bazylinski, D. A., Zhu, R., Kirschvink, J. L., & Pan, Y. (2017). Origin of microbial biomineralization and magnetotaxis during the Archean. *Proceedings of the National Academy of Sciences of the United States of America*, 114, 2171–2176.
- Little, C. T. S., Glynn, S. E. J., & Mills, R. A. (2004). Four-hundred-and-ninety-million-year record of bacteriogenic iron oxide precipitation at sea-floor hydrothermal vents. *Geomicrobiology Journal*, 21, 415–429.
- Little, C. T. S., Herrington, R. J., Maslennikov, V. V., & Zaykov, V. V. (1998). The fossil record of hydrothermal vent communities. In R. A. Mills & K. Harrison (Eds.), *Modern ocean floor processes and the geological record* (pp. 259–270). Geological Society Special Publications.
- Little, C. T. S., Johannessen, K. C., Bengtson, S., Chan, C. S., Ivarsson, M., Slack, J. F., Broman, C., Thorseth, I. H., Grenne, T., Rouxel, O. J., & Bekker, A. (2021). A late Paleoproterozoic (1.74 Ga) deep-sea, low-temperature, iron-oxidizing microbial hydrothermal vent community from Arizona, USA. *Geobiology*, 19, 228–249.
- Liu, L., Ireland, T. R., & Holden, P. (2021). SHRIMP 4-S isotope systematics of two pyrite generations in the 3.49 Ga Dresser Formation. *Geochemical Perspectives Letters*, 17, 45–49.
- Liu, W., Zhang, X., & Wang, W. (2020). Microbial imprints on sulfide minerals in submarine hydrothermal deposits of the East Pacific rise. *Journal of Geophysical Research Biogeosciences*, 125, e2020JG005736.
- Lode, S., Piercey, S. J., Layne, G. D., Piercey, G., & Cloutier, J. (2017). Multiple sulphur and lead sources recorded in hydrothermal exhalites associated with the Lemarchant volcanogenic massive sulphide deposit, central Newfoundland, Canada. *Mineralium Deposita*, 52, 105–128.
- Logan, G. A., Hinman, M. C., Walter, M. R., & Summons, R. E. (2001). Biogeochemistry of the 1640 Ma McArthur River (HYC) lead-zinc ore and host sediments, Northern Territory, Australia. *Geochimica et Cosmochimica Acta*, 65, 2317–2336.
- Logan, R. G. (1979). *The Geology and Mineralogical Zoning of the H.Y.C. Ag-Pb-Zn Deposit, McArthur River, Northern Territory, Australia*. Master thesis.
- Lovley, D. R., Stolzt, J. F., & Phillips, E. J. P. (1987). Anaerobic production of magnetite by a dissimilatory iron-reducing microorganism. *Nature*, 330, 252–254.
- Lowe, D. R. (1994). Abiological origin of described stromatolites older than 3.2 Ga. *Geology*, 22, 387–390.
- Lowenstam, H. (1981). Minerals formed by organisms. *Science*, 211, 1126–1131.
- Luque, F. J., Crespo-Feo, E., Barrenechea, J. F., & Ortega, L. (2012). Carbon isotopes of graphite: Implications on fluid history. *Geoscience Frontiers*, 3, 197–207.
- Machel, H. G., Krouse, H. R., & Sassen, R. (1995). Products and distinguishing criteria of bacterial and thermochemical sulfate reduction. *Applied Geochemistry*, 10, 373–389.
- MacLeod, F. S., Kindler, G., Lun Wong, H., Chen, R. P., & Burns, B. (2019). Asgard archaea: Diversity, function, and evolutionary implications in a range of microbiomes. *AIMS Microbiology*, 5, 48–61.
- Manning-Berg, A., Wood, R., Williford, K., Czaja, A., & Kah, L. (2019). The taphonomy of proterozoic microbial mats and implications for early diagenetic silicification. *Geosciences*, 9, 40.
- Manning-Berg, A. R., & Kah, L. C. (2017). Proterozoic microbial mats and their constraints on environments of silicification. *Geobiology*, 15, 469–483.
- Mansor, M., Berti, D., Hochella, M. F., Murayama, M., & Xu, J. (2019). Phase, morphology, elemental composition, and formation mechanisms of biogenic and abiogenic Fe–Cu-sulfide nanoparticles: A comparative study on their occurrences under anoxic conditions. *American Mineralogist*, 104, 703–717.
- Mansor, M., & Fantle, M. S. (2019). A novel framework for interpreting pyrite-based Fe isotope records of the past. *Geochimica et Cosmochimica Acta*, 253, 39–62.
- Mansor, M., & Xu, J. (2020). Benefits at the nanoscale: A review of nanoparticle-enabled processes favouring microbial growth and functionality. *Environmental Microbiology*, 22, 3633–3649.
- Marin-Carbonne, J., Remusat, L., Sforza, M. C., Thomazo, C., Cartigny, P., & Philippot, P. (2018). Sulfur isotope's signal of nanopyrates enclosed in 2.7 Ga stromatolitic organic remains reveal microbial sulfate reduction. *Geobiology*, 16, 121–138.

- Marlow, J., Peckmann, J., & Orphan, V. (2015). Autoendoliths: A distinct type of rock-hosted microbial life. *Geobiology*, 13, 303–307.
- Marshall, C. P., Love, G. D., Snape, C. E., Hill, A. C., Allwood, A. C., Walter, M. R., Van Kranendonk, M. J., Bowden, S. A., Sylva, S. P., & Summons, R. E. (2007). Structural characterization of kerogen in 3.4Ga Archaean cherts from the Pilbara Craton, Western Australia. *Precambrian Research*, 155, 1–23.
- Maslennikov, V. V., Maslennikova, S. P., Large, R. R., Danyushevsky, L. V., Herrington, R. J., Ayupova, N. R., Zaykov, V. V., Lein, A. Y., Tseluyko, A. S., Melekestseva, I. Y., & Tessalina, S. G. (2017). Chimneys in Paleozoic massive sulfide mounds of the Urals VMS deposits: Mineral and trace element comparison with modern black, grey, white and clear smokers. *Ore Geology Reviews*, 85, 64–106.
- McCullom, T., & Seewald, J. (2006). Carbon isotope composition of organic compounds produced by abiotic synthesis under hydrothermal conditions. *Earth and Planetary Science Letters*, 243, 74–84.
- McCullom, T. M. (2003). Formation of meteorite hydrocarbons from thermal decomposition of siderite (FeCO₃). *Geochimica et Cosmochimica Acta*, 67, 311–317.
- McCullom, T. M. (2013). Laboratory simulations of abiotic hydrocarbon formation in Earth's deep subsurface. *Reviews in Mineralogy and Geochemistry*, 75, 467–494.
- McCullom, T. M., & Donaldson, C. (2019). Experimental constraints on abiotic formation of tubules and other proposed biological structures in subsurface volcanic glass. *Astrobiology*, 19, 53–63.
- McCullom, T. M., Ritter, G., & Simoneit, B. R. T. (1999). Lipid synthesis under hydrothermal conditions by Fischer-Tropsch-type reactions. *Origins of Life and Evolution of the Biosphere*, 29, 153–166.
- McCullom, T. M., & Seewald, J. S. (2007). Abiotic synthesis of organic compounds in deep-sea hydrothermal environments. *Chemical Reviews*, 107, 382–401.
- McGoldrick, P. (1999). Northern Australian “Sedex” Zn–Pb deposits: Microbial oases in Proterozoic seas. In C. J. Stanley (Ed.), *Mineral deposits: Processes to processing*. A.A. Balkema.
- McKay, D. S., Gibson, E. K., Thomas-Keperta, K. L., Vali, H., Romanek, C. S., Clemett, S. J., Chillier, X. D. F., Maechling, C. R., & Zare, R. N. (1996). Search for past life on Mars: Possible relic biogenic activity in Martian meteorite ALH84001. *Science*, 273, 924–930.
- McLoughlin, N., Brasier, M. D., Wacey, D., Green, O. R., & Perry, R. S. (2007). On Biogenicity criteria for endolithic microborings on early Earth and beyond. *Astrobiology*, 7, 10–26.
- McLoughlin, N., Wilson, L. A., & Brasier, M. D. (2008). Growth of synthetic stromatolites and wrinkle structures in the absence of microbes – Implications for the early fossil record. *Geobiology*, 6, 95–105.
- McMahon, S. (2019). Earth's earliest and deepest purported fossils may be iron-mineralized chemical gardens. *Proceedings of the Royal Society B: Biological Sciences*, 286, 20192410.
- Ménez, B., Pisapia, C., Andreani, M., Jamme, F., Vanbellingen, Q. P., Brunelle, A., Richard, L., Dumas, P., & Réfrégiers, M. (2018). Abiotic synthesis of amino acids in the recesses of the oceanic lithosphere. *Nature*, 564, 59–63.
- Milesi, V., Guyot, F., Brunet, F., Richard, L., Recham, N., Benedetti, M., Dairou, J., & Prinzhofer, A. (2015). Formation of CO₂, H₂ and condensed carbon from siderite dissolution in the 200–300°C range and at 50MPa. *Geochimica et Cosmochimica Acta*, 154, 201–211.
- Milesi, V., McCullom, T. M., & Guyot, F. (2016). Thermodynamic constraints on the formation of condensed carbon from serpentinization fluids. *Geochimica et Cosmochimica Acta*, 189, 391–403.
- Miot, J., Benzerara, K., Morin, G., Kappler, A., Bernard, S., Obst, M., Féraud, C., Skouri-Panet, F., Guigner, J.-M., Posth, N., Galvez, M., Brown, G. E., & Guyot, F. (2009). Iron biomineralization by anaerobic neutrophilic iron-oxidizing bacteria. *Geochimica et Cosmochimica Acta*, 73, 696–711.
- Mißbach, H., Duda, J.-P., van den Kerkhof, A. M., Lüders, V., Pack, A., Reitner, J., & Thiel, V. (2021). Ingredients for microbial life preserved in 3.5 billion-year-old fluid inclusions. *Nature Communications*, 12, 1101.
- Mißbach, H., Schmidt, B. C., Duda, J.-P., Lünsdorf, N. K., Goetz, W., & Thiel, V. (2018). Assessing the diversity of lipids formed via Fischer-Tropsch-type reactions. *Organic Geochemistry*, 119, 110–121.
- Moeller, K., Schoenberg, R., Grenne, T., Thorseth, I. H., Drost, K., & Pedersen, R. B. (2014). Comparison of iron isotope variations in modern and Ordovician siliceous Fe oxyhydroxide deposits. *Geochimica et Cosmochimica Acta*, 126, 422–440.
- Mojzsis, S. J., Arrhenius, G., McKeegan, K. D., Harrison, T. M., Nutman, A. P., & Friend, C. R. L. (1996). Evidence for life on Earth before 3,800 million years ago. *Nature*, 384, 55–59.
- Monecke, T., Kempe, U., & Go, J. (2002). Genetic significance of the trace element content in metamorphic and hydrothermal quartz: A reconnaissance study. *Earth and Planetary Science Letters*, 202, 709–724.
- Mycke, B., Michaelis, W., & Degens, E. T. (1988). Biomarkers in sedimentary sulfides of precambrian age. *Organic Geochemistry*, 13, 619–625.
- Nims, C., Cron, B., Wetherington, M., Macalady, J., & Cosmidis, J. (2019). Low frequency Raman spectroscopy for micron-scale and in vivo characterization of elemental sulfur in microbial samples. *Scientific Reports*, 9, 7971.
- Nims, C., Lafond, J., Alleon, J., Templeton, A. S., & Cosmidis, J. (2021). Organic biomorphs may be better preserved than microorganisms in early Earth sediments. *Geology*, 49, 629–634.
- Nozaki, T., Nagase, T., Ushikubo, T., Shimizu, K., Ishibashi, J., & D/V Chikyu Expedition 909 Scientists. (2020). Microbial sulfate reduction plays an important role at the initial stage of seafloor sulfide mineralization. *Geology*, 49, 222–227.
- O'Brien, C. E., Giovannelli, D., Govenar, B., Luther, G. W., Lutz, R. A., Shank, T. M., & Vetriani, C. (2015). Microbial biofilms associated with fluid chemistry and megafaunal colonization at post-eruptive deep-sea hydrothermal vents. *Deep Sea Research Part II: Topical Studies in Oceanography*, 121, 31–40.
- Oehler, J. H., & Logan, R. G. (1977). Microfossils, cherts, and associated mineralization in the Proterozoic McArthur (H.Y.C.) lead-zinc-silver deposit. *Economic Geology*, 72, 1393–1409.
- Ohfuji, H., & Rickard, D. (2005). Experimental syntheses of framboids—A review. *Earth-Science Reviews*, 71, 147–170.
- Ohmoto, H. (1996). Formation of volcanogenic massive sulfide deposits: The Kuroko perspective. *Ore Geology Reviews*, 10, 135–177.
- Ohmoto, H., & Lasaga, A. C. (1982). Kinetics of reactions between aqueous sulfates and sulfides in hydrothermal systems. *Geochimica et Cosmochimica Acta*, 46, 1727–1745.
- Ono, S. (2008). Multiple-sulphur isotope biosignatures. *Space Science Reviews*, 135, 203–220.
- Ortega, L., Millward, D., Luque, F. J., Barrenechea, J. F., Beyssac, O., Huizenga, J.-M., Rodas, M., & Clarke, S. M. (2010). The graphite deposit at Borrowdale (UK): A catastrophic mineralizing event associated with Ordovician magmatism. *Geochimica et Cosmochimica Acta*, 74, 2429–2449.
- Page, R. W., & Sweet, I. P. (1998). Geochronology of basin phases in the western Mt Isa Inlier, and correlation with the McArthur Basin. *Australian Journal of Earth Sciences*, 45, 219–232.
- Papineau, D., De Gregorio, B. T., Cody, G. D., Fries, M. D., Mojzsis, S. J., Steele, A., Stroud, R. M., & Fogel, M. L. (2010). Ancient graphite in the Eoarchean quartz–pyroxene rocks from Akilia in southern West Greenland I: Petrographic and spectroscopic characterization. *Geochimica et Cosmochimica Acta*, 74, 5862–5883.
- Papineau, D., De Gregorio, B. T., Cody, G. D., O'Neil, J., Steele, A., Stroud, R. M., & Fogel, M. L. (2011). Young poorly crystalline graphite in the >3.8-Gyr-old Nuvvuagittuq banded iron formation. *Nature Geoscience*, 4, 376–379.

- Papineau, D., De Gregorio, B. T., Stroud, R. M., Steele, A., Pecoits, E., Konhauser, K., Wang, J., & Fogel, M. L. (2010). Ancient graphite in the Eoarchean quartz-pyroxene rocks from Akilia in southern West Greenland II: Isotopic and chemical compositions and comparison with Paleoproterozoic banded iron formations. *Geochimica et Cosmochimica Acta*, 74, 5884–5905.
- Papineau, D., She, Z., Dodd, M. S., Iacoviello, F., Slack, J. F., Hauri, E., Shearing, P., & Little, C. T. S. (2022). Metabolically diverse primordial microbial communities in Earth's oldest seafloor-hydrothermal jasper. *Science Advances*, 8, eabm2296.
- Park, Y., & Faivre, D. (2022). Diversity of microbial metal sulfide biomineralization. *ChemPlusChem*, 87, e2021004.
- Peter, J. M., & Scott, S. D. (1988). Mineralogy, composition, and fluid-inclusion microthermometry of seafloor hydrothermal deposits in the southern trough of Guaymas Basin, Gulf of California. *Canadian Mineralogist*, 26, 567–587.
- Peters, K. E., Walters, C. C., & Moldowan, J. M. (2005a). *The biomarker guide - Volume 1: Biomarkers and isotopes in the environment and human history* (2nd ed.). Cambridge University Press.
- Peters, K. E., Walters, C. C., & Moldowan, J. M. (2005b). *The biomarker guide - Volume 2: Biomarkers and isotopes in petroleum exploration and earth history* (2nd ed.). Cambridge University Press.
- Petrash, D. A., Robbins, L. J., Shapiro, R. S., Mojzsis, S. J., & Konhauser, K. O. (2016). Chemical and textural overprinting of ancient stromatolites: Timing, processes, and implications for their use as paleoenvironmental proxies. *Precambrian Research*, 278, 145–160.
- Philippot, P., Van Zuilen, M., Lepot, K., Thomazo, C., Farquhar, J., & Van Kranendonk, M. J. (2007). Early Archaean microorganisms preferred elemental sulfur, not sulfate. *Science*, 317, 1534–1537.
- Picard, A., Gartman, A., Clarke, D. R., & Girguis, P. R. (2018). Sulfate-reducing bacteria influence the nucleation and growth of mackinawite and greigite. *Geochimica et Cosmochimica Acta*, 220, 367–384.
- Picard, A., Gartman, A., Cosmidis, J., Obst, M., Vidoudez, C., Clarke, D. R., & Girguis, P. R. (2019). Authigenic metastable iron sulfide minerals preserve microbial organic carbon in anoxic environments. *Chemical Geology*, 530, 119343.
- Picard, A., Gartman, A., & Girguis, P. R. (2016). What do we really know about the role of microorganisms in iron sulfide mineral formation? *Frontiers in Earth Science*, 4, 68.
- Picard, A., Gartman, A., & Girguis, P. R. (2021). Interactions between iron sulfide minerals and organic carbon: Implications for biosignature preservation and detection. *Astrobiology*, 21, 587–604.
- Pinti, D. L., Mineau, R., & Clement, V. (2009). Hydrothermal alteration and microfossil artefacts of the 3,465-million-year-old apex chert. *Nature Geoscience*, 2, 640–643.
- Pirajno, F. (2010). *Hydrothermal processes and mineral systems*. Springer.
- Pokrovski, G. S., Blanchard, M., Saunier, G., & Poitrasson, F. (2021). Mechanisms and rates of pyrite formation from hydrothermal fluid revealed by iron isotopes. *Geochimica et Cosmochimica Acta*, 304, 281–304.
- Popa, R., Kinkle, B. K., & Badescu, A. (2004). Pyrite Framboids as biomarkers for iron-sulfur systems. *Geomicrobiology Journal*, 21, 193–206.
- Posth, N. R., Canfield, D. E., & Kappler, A. (2014). Biogenic Fe(III) minerals: From formation to diagenesis and preservation in the rock record. *Earth-Science Reviews*, 135, 103–121.
- Posth, N. R., Köhler, I. D., Swanner, E., Schröder, C., Wellmann, E., Binder, B., Konhauser, K. O., Neumann, U., Berthold, C., Nowak, M., & Kappler, A. (2013). Simulating Precambrian banded iron formation diagenesis. *Chemical Geology*, 362, 66–73.
- Poulton, S. W., Krom, M. D., & Raiswell, R. (2004). A revised scheme for the reactivity of iron (oxyhydr)oxide minerals towards dissolved sulfide. *Geochimica et Cosmochimica Acta*, 68, 3703–3715.
- Prange, A., Chauvistré, R., Modrow, H., Hormes, J., Trüper, H. G., & Dahl, C. (2002). Quantitative speciation of sulfur in bacterial sulfur globules: X-ray absorption spectroscopy reveals at least three different species of sulfur. *Microbiology*, 148, 267–276.
- Present, T. M., Bergmann, K. D., Myers, C., Slotznick, S. P., Creveling, J. R., Zieg, J., Fischer, W. W., Knoll, A. H., & Grotzinger, J. P. (2017). Pyrite-walled tube structures in a Mesoproterozoic sediment-hosted metal sulfide deposit. *Geological Society of America Bulletin*, 130, 598–616.
- Proskurowski, G., Lilley, M. D., Seewald, J. S., Fruh-Green, G. L., Olson, E. J., Lupton, J. E., Sylva, S. P., & Kelley, D. S. (2008). Abiogenic hydrocarbon production at lost City hydrothermal field. *Science*, 319, 604–607.
- Qian, G., Brugger, J., Skinner, W. M., Chen, G., & Pring, A. (2010). An experimental study of the mechanism of the replacement of magnetite by pyrite up to 300°C. *Geochimica et Cosmochimica Acta*, 74, 5610–5630.
- Qian, G., Brugger, J., Testemale, D., Skinner, W., & Pring, A. (2013). Formation of As(II)-pyrite during experimental replacement of magnetite under hydrothermal conditions. *Geochimica et Cosmochimica Acta*, 100, 1–10.
- Raiswell, R., & Plant, J. (1980). The incorporation of trace elements into pyrite during diagenesis of black shales, Yorkshire, England. *Economic Geology*, 75, 684–699.
- Rasmussen, B. (2000). Filamentous microfossils in a 3,235-million-year-old volcanogenic massive sulphide deposit. *Nature*, 405, 676–679.
- Rasmussen, B., & Buick, R. (2000). Oily old ores: Evidence for hydrothermal petroleum generation in an Archean volcanogenic massive sulfide deposit. *Geology*, 28, 731–734.
- Rasmussen, B., Fletcher, I. R., Brocks, J. J., & Kilburn, M. R. (2008). Reassessing the first appearance of eukaryotes and cyanobacteria. *Nature*, 455, 1101–1104.
- Rasmussen, B., Muhling, J. R., & Fischer, W. W. (2021). Ancient oil as a source of carbonaceous matter in 1.88-billion-year-old gunflint stromatolites and microfossils. *Astrobiology*, 21, 655–672.
- Reeves, E. P., Yoshinaga, M. Y., Pjevac, P., Goldenstein, N. I., Peplies, J., Meyerdieks, A., Amann, R., Bach, W., & Hinrichs, K.-U. (2014). Microbial lipids reveal carbon assimilation patterns on hydrothermal sulfide chimneys: Microbial lipids on hydrothermal sulfide structures. *Environmental Microbiology*, 16, 3515–3532.
- Reid, R. P., James, N. P., Macintyre, I. G., Dupraz, C. P., & Burne, R. V. (2003). Shark Bay stromatolites: Microfabrics and reinterpretation of origins. *Facies*, 49, 299–324.
- Reinhardt, M., Goetz, W., Duda, J.-P., Heim, C., Reitner, J., & Thiel, V. (2019). Organic signatures in Pleistocene cherts from Lake Magadi (Kenya), analogs for early Earth hydrothermal deposits. *Biogeosciences*, 16, 2443–2465.
- Reitner, J. (1993). Modern cryptic microbialite/metazoan facies from Lizard Island (Great Barrier Reef, Australia) formation and concepts. *Facies*, 29, 3–39.
- Reitner, J. (2011). Microbial mats. In J. Reitner & V. Thiel (Eds.), *Encyclopedia of geobiology* (pp. 606–608). Springer.
- Reitner, J., Blumenberg, M., Walliser, E.-O., Schäfer, N., & Duda, J.-P. (2015). Methane-derived carbonate conduits from the late Aptian of Salinac (Marne Bleues, Vocontian Basin, France): Petrology and biosignatures. *Marine and Petroleum Geology*, 66, 641–652.
- Reitner, J., Peckmann, J., Reimer, A., Schumann, G., & Thiel, V. (2005). Methane-derived carbonate build-ups and associated microbial communities at cold seeps on the lower Crimean shelf (Black Sea). *Facies*, 51, 66–79.
- Revan, M. K., Genç, Y., Maslennikov, V. V., Maslennikova, S. P., Large, R. R., & Danyushevsky, L. V. (2014). Mineralogy and trace-element geochemistry of sulfide minerals in hydrothermal chimneys from the Upper-Cretaceous VMS deposits of the eastern Pontide orogenic belt (NE Turkey). *Ore Geology Reviews*, 63, 129–149.
- Reysenbach, A.-L., & Cady, S. L. (2001). Microbiology of ancient and modern hydrothermal systems. *Trends in Microbiology*, 9, 79–86.

- Rickard, D. T. (1975). Kinetics and mechanism of pyrite formation at low temperatures. *American Journal of Science*, 275, 636–652.
- Riding, R. (2000). Microbial carbonates: The geological record of calcified bacterial-algal mats and biofilms. *Sedimentology*, 47, 179–214.
- Riding, R. (2011). Microbialites, stromatolites, and thrombolites. In J. Reitner & V. Thiel (Eds.), *Encyclopedia of geobiology* (pp. 635–654). Springer.
- Rojas-Chapana, J., & Tributsch, H. (2004). Interfacial activity and leaching patterns of *Leptospirillum ferrooxidans* on pyrite. *FEMS Microbiology Ecology*, 47, 19–29.
- Rouillard, J., García-Ruiz, J.-M., Gong, J., & van Zuilen, M. A. (2018). A morphogram for silica-witherite biomorphs and its application to microfossil identification in the early earth rock record. *Geobiology*, 16, 279–296.
- Rouillard, J., García-Ruiz, J. M., Kah, L., Gérard, E., Barrier, L., Nabhan, S., Gong, J., & Zuilen, M. A. (2019). Identifying microbial life in rocks: Insights from population morphometry. *Geobiology*, 18, 282–305.
- Rouxel, O., Fouquet, Y., & Ludden, J. N. (2004). Subsurface processes at the lucky strike hydrothermal field, Mid-Atlantic ridge: Evidence from sulfur, selenium, and iron isotopes. *Geochimica et Cosmochimica Acta*, 68, 2295–2311.
- Rouxel, O., Toner, B., Germain, Y., & Glazer, B. (2018). Geochemical and iron isotopic insights into hydrothermal iron oxyhydroxide deposit formation at Loihi Seamount. *Geochimica et Cosmochimica Acta*, 220, 449–482.
- Rouzaud, J.-N., Deldicque, D., Charon, É., & Pageot, J. (2015). Carbons at the heart of questions on energy and environment: A nanostructural approach. *Comptes Rendus Geoscience*, 347, 124–133.
- Rumble, D., & Hoering, T. C. (1986). Carbon isotope geochemistry of graphite vein deposits from New Hampshire, U.S.A. *Geochimica et Cosmochimica Acta*, 50, 1239–1247.
- Rushdi, A. I., & Simoneit, B. R. T. (2001). Lipid formation by aqueous Fischer-Tropsch-type synthesis over a temperature range of 100 to 400°C. *Origins of Life and Evolution of the Biosphere*, 31, 103–118.
- Russell, M. J. (1996). The generation at hot springs of sedimentary ore deposits, microbialites and life. *Ore Geology Reviews*, 10, 199–214.
- Russell, M. J., Daniel, R. M., Hall, A. J., & Sherringham, J. A. (1994). A hydrothermally precipitated catalytic iron sulphide membrane as a first step toward life. *Journal of Molecular Evolution*, 39, 231–243.
- Russell, M. J., Hall, A. J., & Martin, W. (2010). Serpentinization as a source of energy at the origin of life: Serpentinization and the emergence of life. *Geobiology*, 8, 355–371.
- Saito, M. A., Sigman, D. M., & Morel, F. M. M. (2003). The bioinorganic chemistry of the ancient ocean: the co-evolution of cyanobacterial metal requirements and biogeochemical cycles at the Archean-Proterozoic boundary? *Inorganica Chimica Acta*, 356, 308–318.
- Schad, M., Halama, M., Jakus, N., Robbins, L. J., Warchola, T. J., Tejada, J., Kirchhof, R., Lalonde, S. V., Swanner, E. D., Planavsky, N. J., Thorwarth, H., Mansor, M., Konhauser, K. O., & Kappler, A. (2021). Phosphate remobilization from banded iron formations during metamorphic mineral transformations. *Chemical Geology*, 584, 120489.
- Schidlowski, M. (2001). Carbon isotopes as biogeochemical recorders of life over 3.8 Ga of Earth history: Evolution of a concept. *Precambrian Research*, 106, 117–134.
- Schieber, J. (2002). Sedimentary pyrite: A window into the microbial past. *Geology*, 30, 531–534.
- Schiffbauer, J. D., Yin, L., Bodnar, R. J., Kaufman, A. J., Meng, F., Hu, J., Shen, B., Yuan, X., & Xiao, S. (2007). Ultrastructural and geochemical characterization of Archean–Paleoproterozoic graphite particles: Implications for recognizing traces of life in highly metamorphosed rocks. *Astrobiology*, 7, 684–704.
- Schopf, J., & Packer, B. (1987). Early Archean (3.3-billion to 3.5-billion-year-old) microfossils from Warrawoona group, Australia. *Science*, 237, 70–73.
- Schroll, E., & Rantitsch, G. (2005). Sulphur isotope patterns from the Bleiberg deposit (Eastern Alps) and their implications for genetically affiliated lead-zinc deposits. *Mineralogy and Petrology*, 84, 1–18.
- Semikhatov, M. A., Gebelein, C. D., Cloud, P., Awramik, S. M., & Benmore, W. C. (1979). Stromatolite morphogenesis—Progress and problems. *Canadian Journal of Earth Sciences*, 19, 992–1015.
- Sephton, M. A., & Gilmour, I. (2001). Compound-specific isotope analysis of the organic constituents in carbonaceous chondrites. *Mass Spectrometry Reviews*, 20, 111–120.
- Sephton, M. A., Verchovsky, A. B., Bland, P. A., Gilmour, I., Grady, M. M., & Wright, I. P. (2003). Investigating the variations in carbon and nitrogen isotopes in carbonaceous chondrites. *Geochimica et Cosmochimica Acta*, 67, 2093–2108.
- Sforna, M. C., Brunelli, D., Pisapia, C., Pasini, V., Malferrari, D., & Ménez, B. (2018). Abiotic formation of condensed carbonaceous matter in the hydrating oceanic crust. *Nature Communications*, 9, 5049.
- Sforna, M. C., Daye, M., Philippot, P., Somogyi, A., van Zuilen, M. A., Medjoubi, K., Gérard, E., Jamme, F., Dupraz, C., Braissant, O., Glunk, C., & Visscher, P. T. (2016). Patterns of metal distribution in hypersaline microbialites during early diagenesis: Implications for the fossil record. *Geobiology*, 15, 259–279.
- Sforna, M. C., van Zuilen, M. A., & Philippot, P. (2014). Structural characterization by Raman hyperspectral mapping of organic carbon in the 3.46 billion-year-old Apex chert, Western Australia. *Geochimica et Cosmochimica Acta*, 124, 18–33.
- Shen, Y., Buick, R., & Canfield, D. E. (2001). Isotopic evidence for microbial sulphate reduction in the early Archean era. *Nature*, 410, 77–81.
- Shen, Y., Farquhar, J., Masterson, A., Kaufman, A. J., & Buick, R. (2009). Evaluating the role of microbial sulfate reduction in the early Archean using quadruple isotope systematics. *Earth and Planetary Science Letters*, 279, 383–391.
- Sim, M. S., Bosak, T., & Ono, S. (2011). Large sulfur isotope fractionation does not require disproportionation. *Science*, 333, 74–77.
- Simoneit, B. R. T. (1993). Aqueous high-temperature and high-pressure organic geochemistry of hydrothermal vent systems. *Geochimica et Cosmochimica Acta*, 57, 3231–3243.
- Simoneit, B. R. T., Lein, A. Y., Peresyppkin, V. I., & Osipov, G. A. (2004). Composition and origin of hydrothermal petroleum and associated lipids in the sulfide deposits of the rainbow field (Mid-Atlantic ridge at 36°N). *Geochimica et Cosmochimica Acta*, 68, 2275–2294.
- Slack, J. F., Shanks, W. C., Ridley, W. I., Dusel-Bacon, C., DesOrmeau, J. W., Ramezani, J., & Fayek, M. (2019). Extreme sulfur isotope fractionation in the Late Devonian Dry Creek volcanogenic massive sulfide deposit, central Alaska. *Chemical Geology*, 513, 226–238.
- Southam, G., & Saunders, J. A. (2005). The geomicrobiology of ore deposits. *Economic Geology*, 100, 1067–1084.
- Spang, A., Saw, J. H., Jørgensen, S. L., Zaremba-Niedzwiedzka, K., Martijn, J., Lind, A. E., van Eijk, R., Schleper, C., Guy, L., & Ettema, T. J. G. (2015). Complex archaea that bridge the gap between prokaryotes and eukaryotes. *Nature*, 521, 173–179.
- Strauss, H. (1997). The isotopic composition of sedimentary sulfur through time. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 132, 97–118.
- Suarez-Gonzalez, P., Benito, M. I., Quijada, I. E., Mas, R., & Campos-Soto, S. (2019). Trapping and binding: A review of the factors controlling the development of fossil agglutinated microbialites and their distribution in space and time. *Earth-Science Reviews*, 194, 182–215.
- Sugitani, K., Grey, K., Allwood, A., Nagaoka, T., Mimura, K., Minami, M., Marshall, C. P., Van Kranendonk, M. J., & Walter, M. R. (2007). Diverse microstructures from Archean chert from the Mount Goldsworthy–Mount Grant area, Pilbara Craton, Western Australia: Microfossils, dubiofossils, or pseudofossils? *Precambrian Research*, 158, 228–262.

- Summons, R. E., Welander, P. V., & Gold, D. A. (2021). Lipid biomarkers: Molecular tools for illuminating the history of microbial life. *Nature Reviews Microbiology*, 20, 174–185.
- Suzuki, Y., Inagaki, F., Takai, K., Nealson, K. H., & Horikoshi, K. (2004). Microbial diversity in inactive chimney structures from Deep-Sea hydrothermal systems. *Microbial Ecology*, 47, 186–196.
- Swanner, E. D., Bayer, T., Wu, W., Hao, L., Obst, M., Sundman, A., Byrne, J. M., Michel, F. M., Kleinhanns, I. C., Kappler, A., & Schoenberg, R. (2017). Iron isotope fractionation during Fe(II) oxidation mediated by the oxygen-producing marine cyanobacterium *Synechococcus* PCC 7002. *Environmental Science & Technology*, 51, 4897–4906.
- Taylor, B. E. (2004). Biogenic and thermogenic sulfate reduction in the Sullivan Pb–Zn–Ag deposit, British Columbia (Canada): Evidence from micro-isotopic analysis of carbonate and sulfide in bedded ores. *Chemical Geology*, 204, 215–236.
- Thiel, J., Byrne, J. M., Kappler, A., Schink, B., & Pester, M. (2019). Pyrite formation from FeS and H₂S is mediated through microbial redox activity. *Proceedings of the National Academy of Sciences of the United States of America*, 116, 6897–6902.
- Thomas-Keprta, K. L., Bazylinski, D. A., Kirschvink, J. L., Clemett, S. J., McKay, D. S., Wentworth, S. J., Vali, H., Gibson, E. K., Jr., & Romanek, C. S. (2000). Elongated prismatic magnetite crystals in ALH84001 carbonate globules: Potential Martian magnetofossils. *Geochimica et Cosmochimica Acta*, 64, 4049–4081.
- Thorseth, I. H., Torsvik, T., Torsvik, V., Daae, F. L., & Pedersen, R. B. (2001). Diversity of life in ocean floor basalt. *Earth and Planetary Science Letters*, 194, 31–37.
- Toner, B. M., Lesniewski, R. A., Marlow, J. J., Briscoe, L. J., Santelli, C. M., Bach, W., Orcutt, B. N., & Edwards, K. J. (2013). Mineralogy drives bacterial biogeography of hydrothermally inactive seafloor sulfide deposits. *Geomicrobiology Journal*, 30, 313–326.
- Toner, B. M., Rouxel, O. J., Santelli, C. M., Bach, W., & Edwards, K. J. (2016). Iron transformation pathways and redox micro-environments in seafloor sulfide-mineral deposits: Spatially resolved Fe XAS and $\delta^{57}/^{54}\text{Fe}$ observations. *Frontiers in Microbiology*, 7, 648.
- Tornos, F., Velasco, F., Menor-Salván, C., Delgado, A., Slack, J. F., & Escobar, J. M. (2014). Formation of recent Pb–Ag–Au mineralization by potential sub-surface microbial activity. *Nature Communications*, 5, 4600.
- Treiman, A. H. (2003). Submicron magnetite grains and carbon compounds in Martian meteorite ALH84001: Inorganic, abiotic formation by shock and thermal metamorphism. *Astrobiology*, 3, 369–392.
- Trichet, J., & Défarge, C. (1995). Non-biologically supported organomineralization. In: *Proceedings 7th international symposium on biomineralization*, bulletin de l'Institut Océanographique de Monaco (pp. 203–236).
- Ueno, Y., Ono, S., Rumble, D., & Maruyama, S. (2008). Quadruple sulfur isotope analysis of ca. 3.5 Ga Dresser Formation: New evidence for microbial sulfate reduction in the early Archean. *Geochimica et Cosmochimica Acta*, 72, 5675–5691.
- Valdivieso-Ojeda, J. A., Huerta-Díaz, M. A., & Delgadillo-Hinojosa, F. (2014). High enrichment of molybdenum in hypersaline microbial mats of Guerrero Negro, Baja California Sur, Mexico. *Chemical Geology*, 363, 341–354.
- Van Dover, C. L. (2000). *The ecology of Deep-Sea hydrothermal vents*. Princeton University Press.
- Van Dover, C. L. (2019). Inactive sulfide ecosystems in the Deep Sea: A review. *Frontiers in Marine Science*, 6, 461.
- Van Kranendonk, M., Philippot, P., Lepot, K., Bodorkos, S., & Pirajno, F. (2008). Geological setting of Earth's oldest fossils in the ca. 3.5 Ga Dresser formation, Pilbara craton, Western Australia. *Precambrian Research*, 167, 93–124.
- Van Kranendonk, M. J. (2011). Morphology as an indicator of Biogenicity for 3.5–3.2 Ga Fossil Stromatolites from the Pilbara Craton, Western Australia. In J. Reitner, N.-V. Quéric, & G. Arp (Eds.), *Advances in stromatolite geobiology, lecture notes in earth sciences* (pp. 537–554). Springer.
- van Zuilen, M. A. (2019). The significance of carbonaceous matter to understanding life processes on early Earth. In *Earth's oldest rocks* (pp. 945–963). Elsevier.
- van Zuilen, M. A., Lepland, A., & Arrhenius, G. (2002). Reassessing the evidence for the earliest traces of life. *Nature*, 418, 627–630.
- van Zuilen, M. A., Lepland, A., Teranes, J., Finarelli, J., Wahlen, M., & Arrhenius, G. (2003). Graphite and carbonates in the 3.8 Ga old Isua Supracrustal Belt, southern West Greenland. *Precambrian Research*, 126, 331–348.
- Vandenbroucke, M., & Largeau, C. (2007). Kerogen origin, evolution and structure. *Organic Geochemistry*, 38, 719–833.
- Vearncombe, S., Barley, M. E., Groves, D. I., McNaughton, N. J., Mikucki, E. J., & Vearncombe, J. R. (1995). 3.26 Ga black smoker-type mineralization in the Strelley Belt, Pilbara Craton, Western Australia. *Journal of the Geological Society*, 152, 587–590.
- Velasco-Acebes, J., Tornos, F., Kidane, A. T., Wiedenbeck, M., Velasco, F., & Delgado, A. (2019). Isotope geochemistry tracks the maturation of submarine massive sulfide mounds (Iberian Pyrite Belt). *Mineralium Deposita*, 54, 913–934.
- Von Damm, K. L. (1995). Controls on the chemistry and temporal variability of seafloor hydrothermal fluids. In S. E. Humphris, R. A. Zierenberg, L. S. Mullineaux, & R. E. Thomson (Eds.), *Geophysical monograph series* (pp. 222–247). American Geophysical Union.
- Wacey, D., Kilburn, M. R., Saunders, M., Cliff, J., & Brasier, M. D. (2011). Microfossils of sulphur-metabolizing cells in 3.4-billion-year-old rocks of Western Australia. *Nature Geoscience*, 4, 698–702.
- Wacey, D., Noffke, N., Cliff, J., Barley, M. E., & Farquhar, J. (2015). Micro-scale quadruple sulfur isotope analysis of pyrite from the ~3480 Ma Dresser Formation: New insights into sulfur cycling on the early Earth. *Precambrian Research*, 258, 24–35.
- Wacey, D., Noffke, N., Saunders, M., Guagliardo, P., & Pyle, D. M. (2018). Volcanogenic pseudo-fossils from the ~3.48 Ga Dresser Formation, Pilbara, Western Australia. *Astrobiology*, 18, 539–555.
- Wacey, D., Saunders, M., Brasier, M. D., & Kilburn, M. R. (2011). Earliest microbially mediated pyrite oxidation in ~3.4 billion-year-old sediments. *Earth and Planetary Science Letters*, 301, 393–402.
- Wacey, D., Saunders, M., Cliff, J., Kilburn, M. R., Kong, C., Barley, M. E., & Brasier, M. D. (2014). Geochemistry and nano-structure of a putative ~3240 million-year-old black smoker biota, Sulphur Springs Group, Western Australia. *Precambrian Research*, 249, 1–12.
- Wacey, D., Saunders, M., & Kong, C. (2018). Remarkably preserved tephra from the 3430 Ma Strelley Pool Formation, Western Australia: Implications for the interpretation of Precambrian microfossils. *Earth and Planetary Science Letters*, 487, 33–43.
- Wacey, D., Saunders, M., Kong, C., Brasier, A., & Brasier, M. (2016). 3.46 Ga Apex chert 'microfossils' reinterpreted as mineral artefacts produced during phyllosilicate exfoliation. *Gondwana Research*, 36, 296–313.
- Wächtershäuser, G. (1990). Evolution of the first metabolic cycles. *Proceedings of the National Academy of Sciences of the United States of America*, 87, 200–204.
- Watanabe, Y., Farquhar, J., & Ohmoto, H. (2009). Anomalous fractionations of sulfur isotopes during thermochemical sulfate reduction. *Science*, 324, 370–373.
- Weiner, S., & Dove, P. M. (2003). An overview of biomineralization processes and the problem of the vital effect. *Reviews in Mineralogy and Geochemistry*, 54, 1–29.
- Weiss, M. C., Sousa, F. L., Mrnjavac, N., Neukirchen, S., Roettger, M., Nelson-Sathi, S., & Martin, W. F. (2016). The physiology and habitat of the last universal common ancestor. *Nature Microbiology*, 1, 16116.
- Westall, F. (2005). Life on the early Earth: A sedimentary view. *Science*, 308, 366–367.
- Westall, F., & Folk, R. L. (2003). Exogenous carbonaceous microstructures in Early Archean cherts and BIFs from the Isua Greenstone Belt: Implications for the search for life in ancient rocks. *Precambrian Research*, 126, 313–330.

- Widdel, F., Schnell, S., Heising, S., Ehrenreich, A., Assmus, B., & Schink, B. (1993). Ferrous iron oxidation by anoxygenic phototrophic bacteria. *Nature*, *362*, 834–836.
- Wilkin, R. T., & Barnes, H. L. (1997). Formation processes of framboidal pyrite. *Geochimica et Cosmochimica Acta*, *61*, 323–339.
- Williams, R. J. P., & Fraústo Da Silva, J. J. R. (2003). Evolution was chemically constrained. *Journal of Theoretical Biology*, *220*, 323–343.
- Williford, K. H., Grice, K., Logan, G. A., Chen, J., & Huston, D. (2011). The molecular and isotopic effects of hydrothermal alteration of organic matter in the Paleoproterozoic McArthur River Pb/Zn/Ag ore deposit. *Earth and Planetary Science Letters*, *301*, 382–392.
- Wilson, N. S. F., Zentilli, M., & Spiro, B. (2003). A sulfur, carbon, oxygen, and strontium isotope study of the volcanic-hosted El Soldado Manto-type copper deposit, Chile: Essential role of bacteria and petroleum. *Economic Geology*, *98*, 163–174.
- Xia, X., Lian, W., Yuan, C., Yan, F., & Yuan, J. (2008). Mineralization of a Proterozoic sulfide Black smoker chimney and thermophilous microorganisms in Eastern Hebei, China. *Acta Geologica Sinica*, *82*, 858–863.
- Xu, J., Murayama, M., Roco, C. M., Veeramani, H., Michel, F. M., Rimstidt, J. D., Winkler, C., & Hochella, M. F. (2016). Highly-defective nanocrystals of ZnS formed via dissimilatory bacterial sulfate reduction: A comparative study with their abiogenic analogues. *Geochimica et Cosmochimica Acta*, *180*, 1–14.
- Zawaski, M. J., Kelly, N. M., Orlandini OF, Nichols, C. I. O., Allwood, A. C., & Mojzsis, S. J. (2020). Reappraisal of purported ca. 3.7 Ga stromatolites from the Isua Supracrustal Belt (West Greenland) from detailed chemical and structural analysis. *Earth and Planetary Science Letters*, *545*, 116409.

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