Check for updates

Received: 27 January 2023 | Revised: 22 October 2023 | Accepted: 27 November 2023

DOI: 10.1111/gbi.12581

ORIGINAL ARTICLE

gebiology WILEY

Fossilized giant sulfide-oxidizing bacteria from the Devonian Hollard Mound seep deposit, Morocco

Daniel Smrzka[1,2] | **Jennifer Zwicker**[3] | **Heide Schulz-Vogt**[4] | **Crispin T. S. Little**[5,6] | **Max Rieder**[7] | **Patrick Meister**[8] | **Susanne Gier**[8] | **Jörn Peckmann**[9]

[1]Faculty of Geosciences, Universität Bremen, Bremen, Germany

[2]MARUM Center for Marine and Environmental Sciences, Bremen, Germany

[3]Institute for Mineralogy und Crystallography, Universität Wien, Wien, Austria

[4]Leibniz Institute for Baltic Sea Research Warnemünde (IOW), Rostock, Germany

[5]School of Earth and Environment, University of Leeds, Leeds, UK

[6]Life Sciences Department, Natural History Museum, London, UK

[7]Geologie Weixelberger, Pitten, Austria

[8]Department of Geology, Universität Wien, Wien, Austria

[9]Institute for Geology, Center for Earth System Research and Sustainability, Universität Hamburg, Hamburg, Germany

Correspondence
Jörn Peckmann, Institut für Geologie, Centrum für Erdsystemforschung und Nachhaltigkeit, Universität Hamburg, Hamburg 20146, Germany.
Email: joern.peckmann@uni-hamburg.de

Abstract

The giant sulfide-oxidizing bacteria are particularly prone to preservation in the rock record, and their fossils have been identified in ancient phosphorites, cherts, and carbonates. This study reports putative spherical fossils preserved in the Devonian Hollard Mound hydrocarbon-seep deposit. Based on petrographical, mineralogical, and geochemical evidence the putative microfossils are interpreted as sulfide-oxidizing bacteria similar to the present-day genus *Thiomargarita*, which is also found at modern hydrocarbon seeps. The morphology, distribution, size, and occurrence of the fossilized cells show a large degree of similarity to their modern counterparts. Some of the spherical fossils adhere to worm tubes analogous to the occurrence of modern *Thiomargarita* on the tubes of seep-dwelling siboglinid worms. Fluorapatite crystals were identified within the fossilized cell walls, suggesting the intercellular storage of phosphorus analogous to modern *Thiomargarita* cells. The preservation of large sulfide-oxidizing bacteria was probably linked to changing biogeochemical processes at the Hollard Mound seep or, alternatively, may have been favored by the sulfide-oxidizing bacteria performing nitrate-dependent sulfide oxidation—a process known to induce carbonate precipitation. The presence of sulfide-oxidizing bacteria at a Devonian hydrocarbon seep highlights the similarities of past and present chemosynthesis-based ecosystems and provides valuable insight into the antiquity of biogeochemical processes and element cycling at Phanerozoic seeps.

KEYWORDS
bacterial fossils, chemosynthesis, Hollard Mound, hydrocarbon seeps, *Thiomargarita*

1 | INTRODUCTION

The finding of well-preserved microfossils of prokaryotes has been one of the greatest challenges in historical geobiology and micropaleontology. Often, putative findings led to intense debate and the results were, at best, inconclusive (Brasier et al., 2005, 2006). The preservation potential of prokaryotes is commonly hampered by the lack of mineralized shells or skeletons, by the small body size (usually around 1 μm), and relatively low morphological complexity (rods, cocci, spirillae, filaments). For these reasons, potential prokaryotic microfossils are prone for becoming diagenetically obliterated, and if they are found, they could be contaminants from a later time period or they may represent a diagenetic artifact (Brasier et al., 2006; García-Ruiz et al., 2003). However, prokaryotic life dominated over

This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.
© 2023 The Authors. *Geobiology* published by John Wiley & Sons Ltd.

80% of Earth's history, yet its history and evolution remain poorly constrained. Finding prokaryotic microfossils contributes greatly to establish the early history of life by confirming records of major geochemical changes in Earth's evolution, and by providing absolute time points to confirm and date nodes in the phylogenetic tree of life (Battistuzzi et al., 2004).

Generally, it can be assumed that the sulfide-oxidizing bacteria developed after ca. 2 Ga, with the establishment of euxinia alongside ferruginous conditions (Canfield, 1998; Poulton et al., 2010) where sulfide could have come into contact with potential electron acceptors including molecular oxygen or nitrate. Microorganisms utilizing sulfur for metabolic processes are possibly some of the most primordial organisms on Earth (Shen & Buick, 2004). Sulfur stable isotope records suggest that microbial sulfate reduction may well have occurred in the Proterozoic (Canfield et al., 2000), and even in the Archaean (Shen et al., 2001; Ueno et al., 2008), and anomalous fractionations of the minor sulfur isotopes have allowed to constrain the antiquity of microbial sulfur metabolisms (Farquhar et al., 2007; Farquhar & Wing, 2003). Sulfur isotope data provide robust evidence for the presence of microbial communities involved in sulfur cycling, particularly reductive sulfur cycling. The taphonomy of putative microfossils can help to underpin geochemical evidence of sulfur cycling, particularly oxidative sulfur cycling by providing additional information on the organization and structure of the biosphere on ancient Earth. However, such evidence is scarce, difficult to attain with confidence, and beset with controversy (Brasier et al., 2002, 2006). Yet the morphological and metabolic peculiarities of vacuolated colorless sulfide-oxidizing bacteria are advantageous in recognizing these bacteria in ancient rocks: their unusually large cell size, commonly filamentous morphology, their capability of preserving sulfur globules within their cells set them apart from other microbial communities such as the cyanobacteria (Bailey et al., 2013). Furthermore, their size, morphology, and intracellular sulfur globules all have the potential for preservation in the fossil record and may allow a more confident identification than for other microfossils (Bailey et al., 2013).

Today, colorless sulfide-oxidizing bacteria are particularly common at marine hydrocarbon seeps, which provide a constant and reliable source of reductants (Boetius & Suess, 2004; Sibuet & Olu, 1998; Van Dover et al., 2003). The colorless sulfide-oxidizing bacteria such as the motile and non-motile marine genera of *Beggiatoa*, *Thiomargarita*, and *Thioploca* (Fossing et al., 1995; Jørgensen & Revsbach, 1983; Schulz, 2006) belong to the class of Gammaproteobacteria that have developed various morphologies and metabolisms, and can couple the biogeochemical cycles of sulfur, carbon, and nitrogen, enabling them to colonize diverse ecological niches (Gallardo, 1977; Nelson & Jannasch, 1983; Teske & Nelson, 2006). Their morphologies include spirilla, rods, cocci, and filaments, and have been considered adaptations to varying chemical and physical environmental constraints (Macalady et al., 2008; Preisler et al., 2007). In environments where reduced sulfur species come into contact with the aerobic biosphere, these bacteria exploit this redox disequilibrium by catalyzing the oxidation of hydrogen sulfide and elemental sulfur coupled to the fixation of carbon dioxide. At hydrocarbon seeps, which are dynamic environments with rapidly shifting redox boundaries, sulfide is primarily produced by the sulfate-driven anaerobic oxidation of methane (SD-AOM; Boetius et al., 2000), supplying sulfide to sulfide-oxidizing bacteria that form extensive mats covering sites of active methane and oil seepage (Grünke et al., 2012; Joye et al., 2004; Larkin & Henk, 1996; Niemann et al., 2006; Pimenov et al., 2000; Sahling et al., 2016; Von Rad et al., 1996). These bacteria form a variety of microbial mat types including *Arcobacter*, *Beggiatoa*, *Thiomargarita*, and *Thioploca* species that employ diverse strategies to inhabit ecological microniches at seeps (Grünke et al., 2011), and act as efficient benthic barriers against the diffusion of solutes from sedimentary pore waters into bottom waters (Jørgensen & Revsbach, 1983; Lavik et al., 2009; Yücel et al., 2017). The taxa *Beggiatoa*, *Thiomargarita*, and *Thioploca* have large vacuoles to store nitrate and elemental sulfur, which can be released to gain metabolic energy during periods of low nutrient availability (Jørgensen & Gallardo, 1999; Schulz & Schulz, 2005). They also store polyphosphate within their cells that can be broken down and released during times of unfavorable environmental conditions (Goldhammer et al., 2010; Schulz & Schulz, 2005). Indeed, the giant sulfide-oxidizing bacteria have been linked directly to the cycling and accumulation of phosphorus in modern upwelling zones (Schulz & Schulz, 2005), as well as to the contribution of the deposition of ancient phosphorites throughout Earth's history (Bailey et al., 2007). Their capability of coupling the cycles of sulfur, carbon, nitrogen, and phosphorus affects nutrient availability and the flux of solutes to and from seafloor sediments (Fossing et al., 1995; Huettel et al., 1996; Schulz et al., 1999).

The metabolic activity of sulfide-oxidizing bacteria at seeps has a profound influence on local macro- and microfaunal community structure, redox gradients in shallow sediments, spatial and temporal seepage variability, and even on the precipitation of authigenic minerals (Levin et al., 2003; Sahling et al., 2002; Solomon et al., 2008). Their ecological function as chemosynthetic primary producers of biomass and as nutrient cyclers makes them important members of chemosynthesis-based ecosystems at seeps (Arvidson et al., 2004; Van Dover et al., 2003). However, the record of microfossil preservation of sulfide-oxidizing bacteria in ancient seep deposits is scarce (Peckmann et al., 2004). Due to their ecological and evolutionary significance, reports on preserved remains of sulfide-oxidizing bacteria reveal critical information on the evolution of their ecology and lifestyles through geologic time.

This communication investigates putative spherical fossils of sulfide-oxidizing bacteria from the Devonian Hollard Mound seep deposit of Morocco, which had originally been interpreted to represent oil-coated gas bubbles at the ancient seep (Peckmann et al., 1999). The core facies of the Hollard Mound represents one of the oldest known seep deposits featuring abundant bivalve assemblages (Jakubowicz et al., 2022; Shapiro, 2022). We use petrographic, mineralogical, and geochemical tools to trace biogeochemical processes and reconstruct the microbial ecology of this

14724669, 2024, 1, Downloaded from https://onlinelibrary.wiley.com/doi/10.1111/gbi.12581 by Test, Wiley Online Library on [23/01/2024]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

Devonian chemosynthesis-based ecosystem. Putative microbial fossils are compared to present-day giant sulfide oxidizing bacteria of the genus *Thiomargarita* spp. in order to evaluate the biogenicity of the former. We present taphonomic evidence for the first known occurrence of sulfide-oxidizing bacteria at Paleozoic seeps and suggest mechanisms that led to their preservation.

2 | GEOLOGIC SETTING

The Hollard Mound is a well-known Paleozoic seep site that has been investigated by numerous studies (Aitken et al., 2002; Cavalazzi et al., 2007; Hryniewicz et al., 2017; Jakubowicz et al., 2015; Peckmann et al., 1999, 2005). The Hollard Mound is located within the Hamar Laghdad mountain range located to the east of the Anti-Atlas Mountains in Morocco (Figure 1a). The Hamar Laghdad range extends for roughly 8 km in East–West direction, featuring over 50 conical-shaped mounds in various shapes and sizes, referred to as Kess-Kess mud mounds (Figure 1b; Brachert et al., 1992). The Hamar Laghdad range formed as a North–South striking submarine rise that emerged as a result of volcanic activity during the earliest Devonian. This submarine rise was subsequently colonized by crinoids during a period of rapid sea level rise, which deposited almost 200 meters of crinoidal limestone on a passive continental margin up to the middle Devonian (Brachert et al., 1992; Wendt et al., 1984). These limestones are part of the Kess-Kess Formation (Brachert et al., 1992), consisting of bioclastic wackestones and packstones featuring massive bioherms and tabulate and rugose coral assemblages (Berkowski, 2006; Brachert et al., 1992). The carbonate mud mounds forming the uppermost part of the thick-bedded limestone of the Kess-Kess Formation have been interpreted as being formed along faults where hydrothermal fluids migrated to the seafloor (Belka, 1998; Mounji et al., 1998); an interpretation supported by the presence of numerous synsedimentary Neptunian dykes penetrating tens of meters into the Kess-Kess Formation (Brachert et al., 1992).

The Hollard Mound has been interpreted as a carbonate deposit that formed an apparently large elevated structure during a repeating transgressive period in the middle Devonian (Peckmann et al., 1999; Walliser, 1991). The core facies of the Hollard Mound differs from other parts of the mound in that it exhibits a conspicuous faunal assemblage including a low diversity but high abundance assemblage of large bivalves, as well as unusually low $\delta^{13}C$ values of authigenic carbonates, which have led Peckmann et al. (1999) to interpret the Hollard Mound core facies as being derived from microbial activity related to the seepage of hydrocarbon-rich fluids.

FIGURE 1 (a) Location of the Hollard Mound (yellow star) in the eastern part of Hamar Laghdad in the eastern Anti-Atlas of southeastern Morocco. (b) Geological map of the study area showing the Hamar Laghdad as part of Devonian outcrops among pre-Devonian, Carboniferous, and Cretaceous to Tertiary deposits.

14724669, 2024, 1, Downloaded from https://onlinelibrary.wiley.com/doi/10.1111/gbi.12581 by Test, Wiley Online Library on [23/01/2024]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

Subsequent investigations have supported a microbial origin of sedimentary fabrics (Cavalazzi et al., 2007; Peckmann et al., 2005), and have further characterized its seep-endemic megafaunal inventory (Hryniewicz et al., 2017).

3 | MATERIALS AND METHODS

Rock samples that were collected from the Hollard Mound core facies are described in detail in Peckmann et al. (1999, 2005). Some of these samples were cut into smaller slabs using a rock saw, and small, standard-size thin sections (2.8 to 4.8 cm) of 25 to 30 μm thickness and larger thin sections (10 to 15 cm) of approximately 50 μm thickness were prepared for petrographic observations (Table S1). Thin-section microscopy was conducted on a Leica DM4500 P polarization microscope, and photomicrographs were taken with Leica DFC 420 and DFC 450C cameras, using the Leica Application Suite 3.2.0 and 4.4.0 software.

Scanning electron microscopy (SEM) was conducted on a conventional tungsten filament SEM (FEI Inspect S), a Field-Emission-Gun with an integrated Focused Ion Beam (FEI QuantaTM 3D FEG), and an energy dispersive X-ray detection unit (EDAX Apollo XV) at the Institute for Geology at the University of Vienna. Data were processed using the EDAX TEAM™ V3.1.1 software. Powdered sample material was treated with 25% acetic acid prior to powder X-ray diffraction (XRD) analyses in order to detect non-carbonate minerals in the samples. After washing three times, the residues were subsequently analyzed using a Panalytical PW 3040/60 X'Pert PRO diffractometer (CuKa radiation, 40 kV, 40 mA, step size 0.0167.5 s per step). X-ray diffraction patterns were interpreted using the Panalytical software "X'Pert High score plus". Raman spectroscopy was conducted on a polished thin section using a Renishaw InVia Raman spectroscope in high confocality mode at the Institute for Mineralogy, University of Bremen. A Renishaw RL532C class 3B continuous wave laser (532 nm wavelength) was used, operating with an exposure time of 10 seconds, 10% laser power (24 mW), and grating was set at 1800 L mm^{-1}. The spectroscope was coupled to a WiRE© 5.5 (Renishaw plc) software for laser and camera control, as well as for raw data processing. The spectra were truncated below 150 cm^{-1} (due to Rayleigh contribution), background subtracted, noise filtered, and maximum peaks fitted to each spectrum. The Renishaw library was used as database for spectrum matching. The area (integrated intensity), intensity (height), center position, and full width at half maximum (FWHM) were determined using the Fityk 1.3.1.© (Wojdyr, 2010) non-linear curve fitting and data analysis software. Peaks were identified and fitted employing a Pseudo Voigt function, which is a convolution of Lorentzian and Gaussian functions. Formation temperature was estimated from two spectra using equations put forward by Kouketsu et al. (2014).

Focused ion beam transmission electron microscopy (FIB-TEM) was performed at the Department of Solid-State Body Physics of the University of Bremen on a small thin section. The thin section was sputter-coated with gold prior to FIB-TEM analyses. The sample was prepared for TEM by FIB lift-out using a FEI Nova NanoLab 200 dual-beam scanning electron microscope. An additional Pt protective layer was not applied in order to keep the amount of Pt low as the Pt(M) and the P(K) peaks partially overlap in subsequent energy-dispersive X-ray spectroscopy (EDXS). The sample was analyzed by scanning TEM (STEM) in a Thermo Fisher Spectra 300 TEM at an acceleration voltage of 300 kV. EDXS was performed in STEM mode using a Thermo Fisher Super-X detector. The Thermo Fisher Velox software was used for EDXS data analyses.

Sediment cores containing *Thiomargarita* cells were collected during the RV Merian expedition MSM105 at station MSM105_110-4 (station name: N25025, position: 24° 59.99′ S, 014° 23.01′ E, depth: 138 m). The sediment cores were stored at 10°C with occasional aeration until sampled for *Thiomargarita* cells. Photomicrographs of samples containing the cells were taken with a Discovery V8 Zeiss stereomicroscope and an Axio Lab.A1 Zeiss compound microscope coupled to an AxioCam 105 color camera (Carl Zeiss MicroImaging GmbH, Jena). The AxioVision software (Carl Zeiss Imaging Solutions GmbH, Jena) was used for image analyses and camera control.

4 | RESULTS

4.1 | Thin section petrography—Hollard Mound carbonates and colorless sulfide-oxidizing bacteria

Thin section petrography of the Hollard Mound seep carbonates reveals that the rocks are mostly composed of banded and botryoidal cement that forms centimeter-thick bands (Figure 2a,b). Only few areas are filled by microcrystalline calcite, and the innermost void space is filled by later-stage equant calcite spar (Figure 2a,b). The studied Hollard Mound carbonates contain abundant fossilized worm tubes (Figure 2b), which are described in detail in Peckmann et al. (2005). The banded and botryoidal cements, as well as the exterior of the worm tubes, are covered with layers of dense clusters of spheres that appear dark brownish to black in thin section (Figure 2c,d). These layers are present in direct proximity to the exterior walls of tube worms (Figure 2c), or aligned in irregular layers that can reach several centimeters in length (Figure 2a,b,d). The spheres show various sizes between 50 and 200 μm in diameter and can be easily recognized due to their dark outer rim (Figures 3 and 4; Figure S1). These dark walls are of varying thickness and show either sharp, thin, well-defined boundaries to the surrounding authigenic carbonate or are present as thicker, diffuse seams of structurally highly ordered organic matter as identified by Raman spectroscopy (Figure 5). Spheres occur as single isolated specimens, or form clusters of several specimens (Figure 3). They are commonly present in pairs (Figures 3b,c and 4b–d). Some spheres show small indentations in their walls (Figure 4a).

14724669, 2024, 1, Downloaded from https://onlinelibrary.wiley.com/doi/10.1111/gbi.12581 by Test, Wiley Online Library on [23/01/2024]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

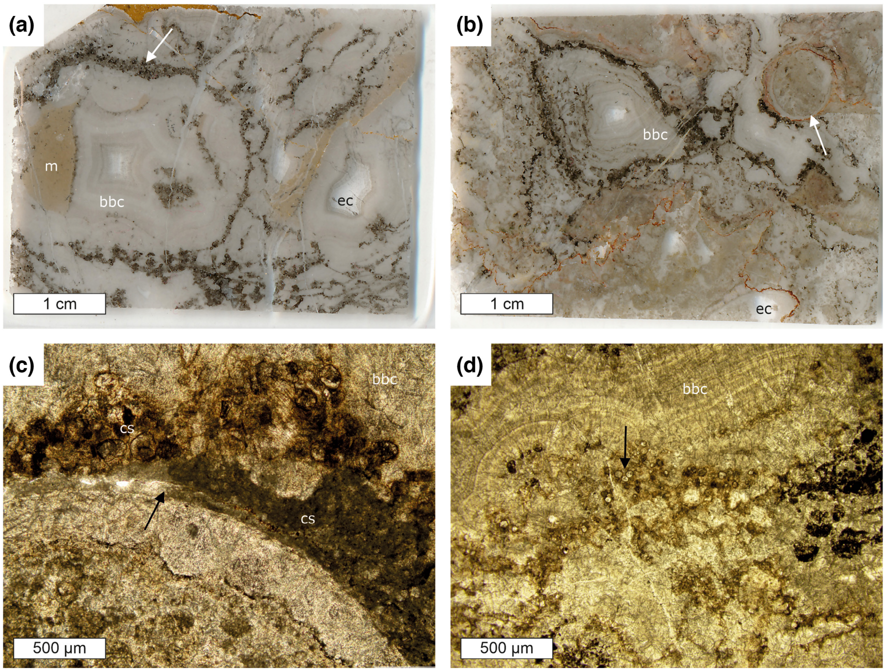

FIGURE 2 Thin section scans and photomicrographs (plane-polarized light) of the Hollard Mound seep carbonates; m = micrite, bbc = banded and botryoidal cement, eq = equant calcite, cs = carbonate spheres. (a) Thin section scan showing micrite, abundant banded and botryoidal cement, and equant calcite. White arrow denoting bands of spheres aligned along banded and botryoidal cement. (b) Thin section scan showing banded and botryoidal cement and equant calcite spar, as well as a worm tube denoted by the white arrow. (c) Thin section micrograph showing aggregates of spheres attached to the wall of a worm tube (denoted by black arrow). (d) Thin section micrograph showing an aggregate of spheres (denoted by black arrow) within banded and botryoidal cement.

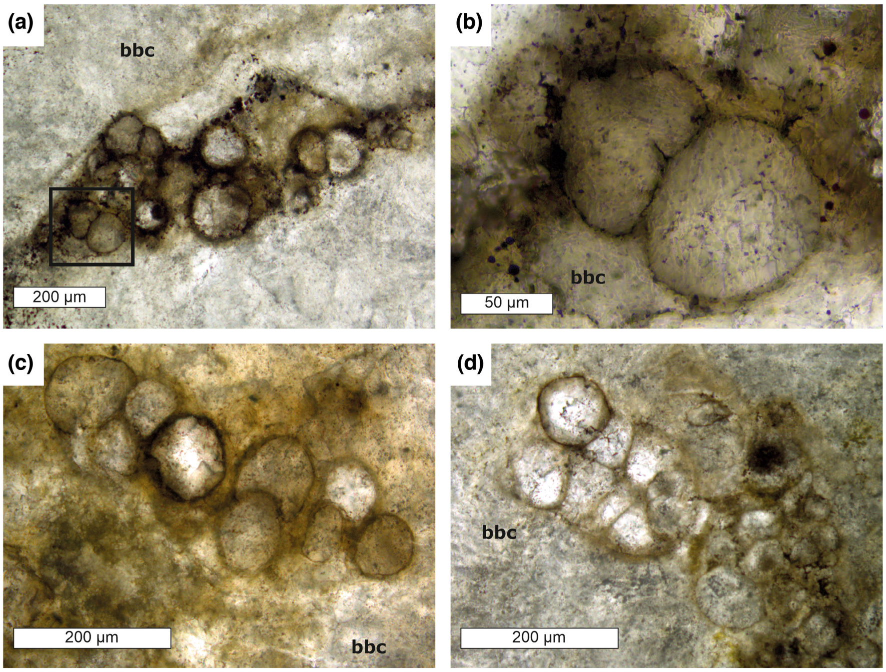

FIGURE 3 Thin section photomicrographs of Hollard Mound carbonates, plane polarized light; bbc = banded and botryoidal cement. (a) A cluster of spheres within banded and botryoidal cement. (b) Close-up image of the black rectangle in (a) showing two spheres in close proximity. (c) Cluster of spheres. (d) Larger cluster of spheres attached to each other.

4.2 | Mineralogy and electron microscopy

X-ray diffraction samples were obtained from areas with abundant spheres. The non-carbonate fractions after carbonate dissolution reveal a dominance of silicate minerals including quartz, illite, and albite (Figure 6). The presence of fluorapatite and of pyrite is confirmed by XRD analysis. Spheres can be identified during scanning electron microscopy (SEM) by micron-scale porosity present in walls (Figure 7a). Within these pores, a high backscatter mineral of tens to hundreds of nanometers in size was observed (Figure 7b,c) and identified as

14724669, 2024, 1, Downloaded from https://onlinelibrary.wiley.com/doi/10.1111/gbi.12581 by Test, Wiley Online Library on [23/01/2024]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

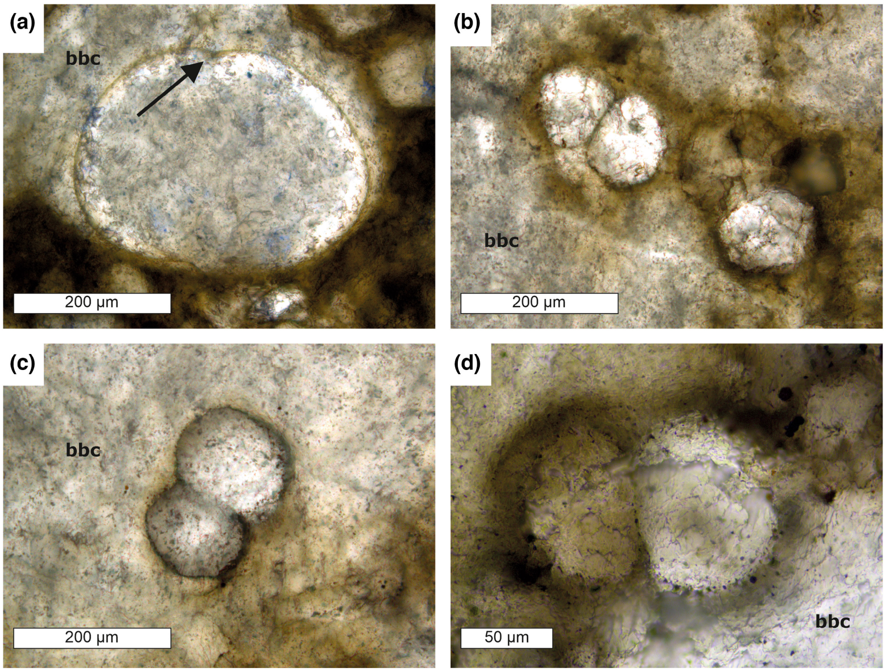

FIGURE 4 Thin section photomicrographs of Hollard Mound carbonates, plane polarized light; bbc = banded and botryoidal cement. (a) Single large sphere featuring a small indentation denoted by the black arrow. (b) Paired spheres. (c) Pair of spheres with well-identifiable walls. (d) Pair of spheres with less well identifiable walls.

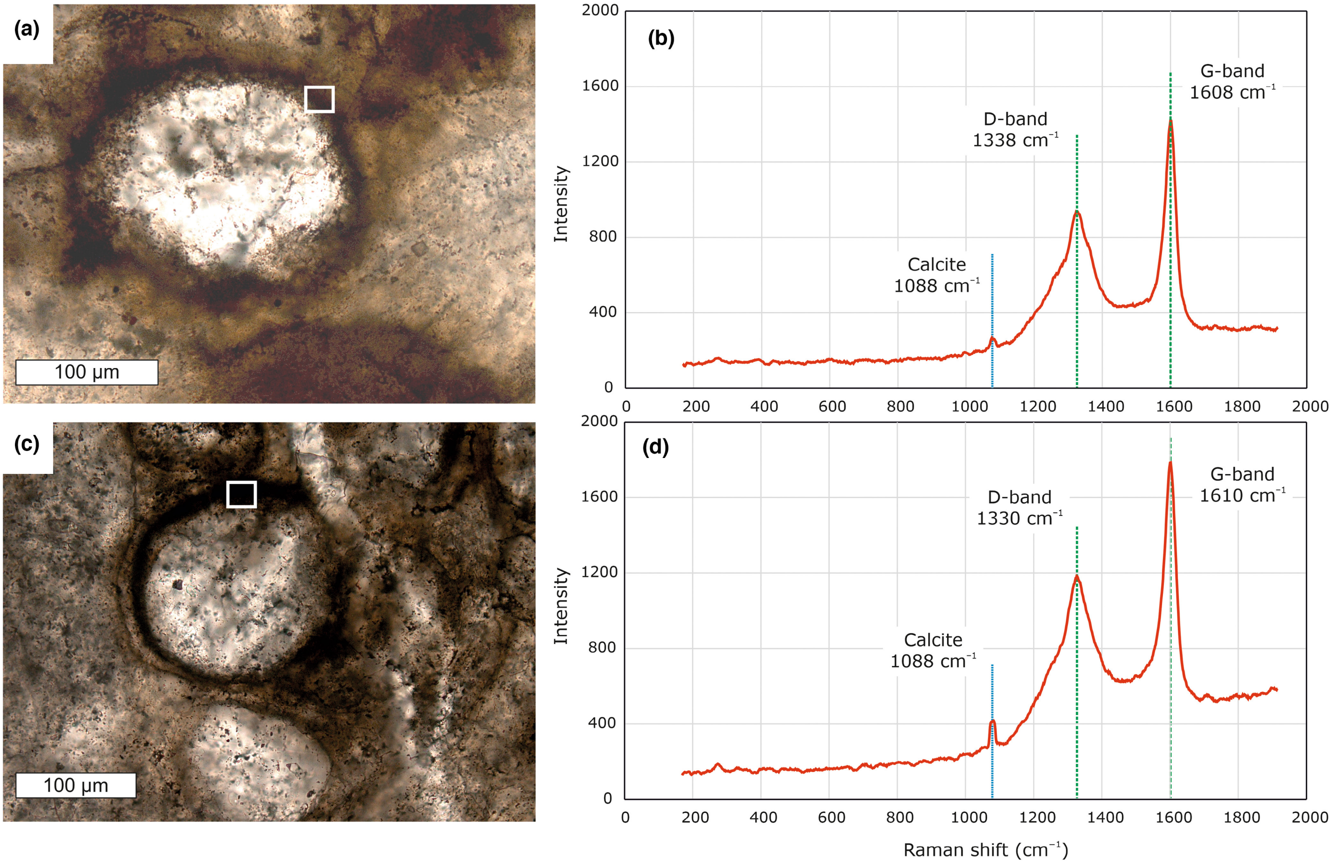

FIGURE 5 Photomicrographs and Raman spectra of dark material within the putative cell walls. (a, c) Carbonate sphere encircled by dark, diffuse material, (b, d) Raman spectra of the corresponding areas highlighted by the white rectangles in (a, c).

calcium fluorapatite containing phosphorus, calcium, as well as minor amounts of fluorine (Figure 7d,e). A closer SEM investigation of the spheres and the distribution of calcium fluorapatite in the samples shows that: (1) calcium fluorapatite is preserved only in a few individual spheres, and (2) only occurs within the porous walls of the spheres. Raman spectra of the dark, diffuse material surrounding the

14724669, 2024, 1, Downloaded from https://onlinelibrary.wiley.com/doi/10.1111/gbi.12581 by Test, Wiley Online Library on [23/01/2024]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

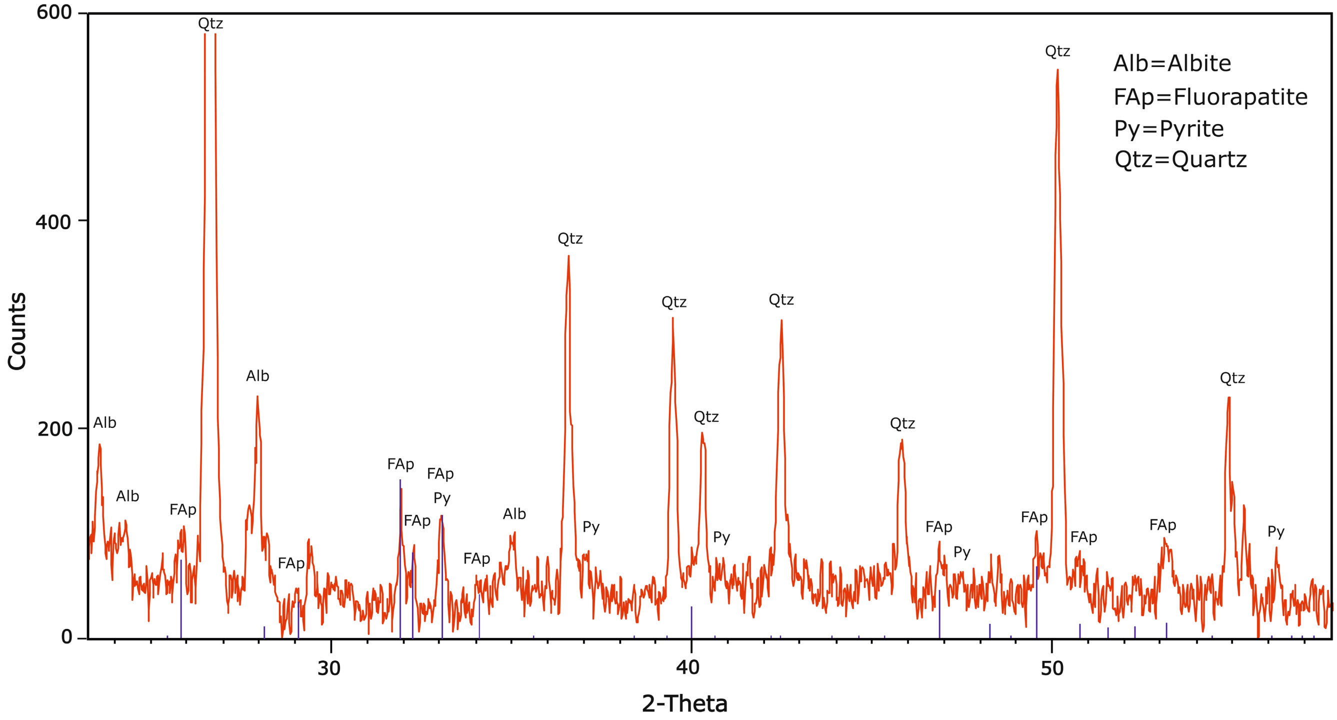

FIGURE 6 X-ray diffraction pattern of a Hollard Mound carbonate sample with spheres after decalcification showing peaks for quartz, albite, and pyrite. Fluorapatite peaks are highlighted in blue.

spheres showed several peaks at 154, 282, 1087, ca. 1330, and ca. 1600 cm^{-1} (Figure 5). The first three peak positions were matched to calcite using the Renishaw database (material index no. 305). The two last peaks are indicative of structurally ordered carbonaceous or organic matter, showing characteristic peak positions at ca. 1330 cm^{-1} and ca. 1600 cm^{-1} (Kwiecinska et al., 2017). Estimated formation temperatures from the two spectra using FWHM values from D1 and D2 (i.e. G) bands (cf. Kouketsu et al., 2014) are 145°C and 162°C, and 142°C and 227°C for the spectra shown in Figure 5a,b, respectively. For FIB-TEM analyses, an area with abundant spheres containing calcium fluorapatite was selected (Figure 8a,b). The 15-μm-long sample foil was cut through a calcium fluorapatite grain residing in the wall of the sphere for TEM analyses (Figure 8c). STEM imaging illustrates the distribution and dimensions of calcium fluorapatite grains residing in the wall of the sphere, showing that these grains are several microns in diameter (Figure 8d). Elemental distributions of carbon and phosphorus within the sample foil show a clear depletion of carbon and enrichment of phosphorus within the calcium fluorapatite grain (Figure 8e,f), as well as no significant further distribution of phosphorus on either side of the sphere wall (Figure 8f).

4.3 | Colorless sulfide-oxidizing bacteria from the Namibian shelf

Microscopy of *Thiomargarita* spp. clusters reveals large cells over 100 μm in diameter (Figure 9). The inner part of the cells exhibits white, sulfur inclusions (Figure 9a,c,d), whereas the outer part of the cells is surrounded by a diffuse mucus sheath. The cells occur in isolation (Figure 9a), as well as in clusters of two cells (Figure 9b,c), and in groups of several cells (Figure 9d). These groups are commonly connected by a layer of mucus that covers all individual cells (Figure 9d).

5 | DISCUSSION

5.1 | Colorless sulfide-oxidizing bacteria—*Thiomargarita* fossils—Identification and criteria for biogenicity

While demonstrating the biogenicity of putative prokaryotic microfossils is challenging, criteria have been proposed by several researchers to make such interpretations more consistent: Cloud (1976) proposed that "a given microstructure can be considered demonstrably biogenic only if some of its representatives display a level of cellular, microstructural, or biogeochemical differentiation comparable with that of living organisms and implying a similarity of function and continuity of evolution between them." Further criteria that have been put forward are that the respective microstructures should (1) be similar in size to modern bacteria, (2) occur isolated as well as in groups or colonies, (3) be derived from well-preserved host rocks, (4) exhibit structurally identifiable cell walls, and (5) show variable preservation throughout the sample (Buick, 1990; Schopf et al., 2007; Westall, 1999). The core facies of the Hollard Mound has been identified as a hydrocarbon-seep

14724669, 2024, 1, Downloaded from https://onlinelibrary.wiley.com/doi/10.1111/gbi.12581 by Test, Wiley Online Library on [23/01/2024]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

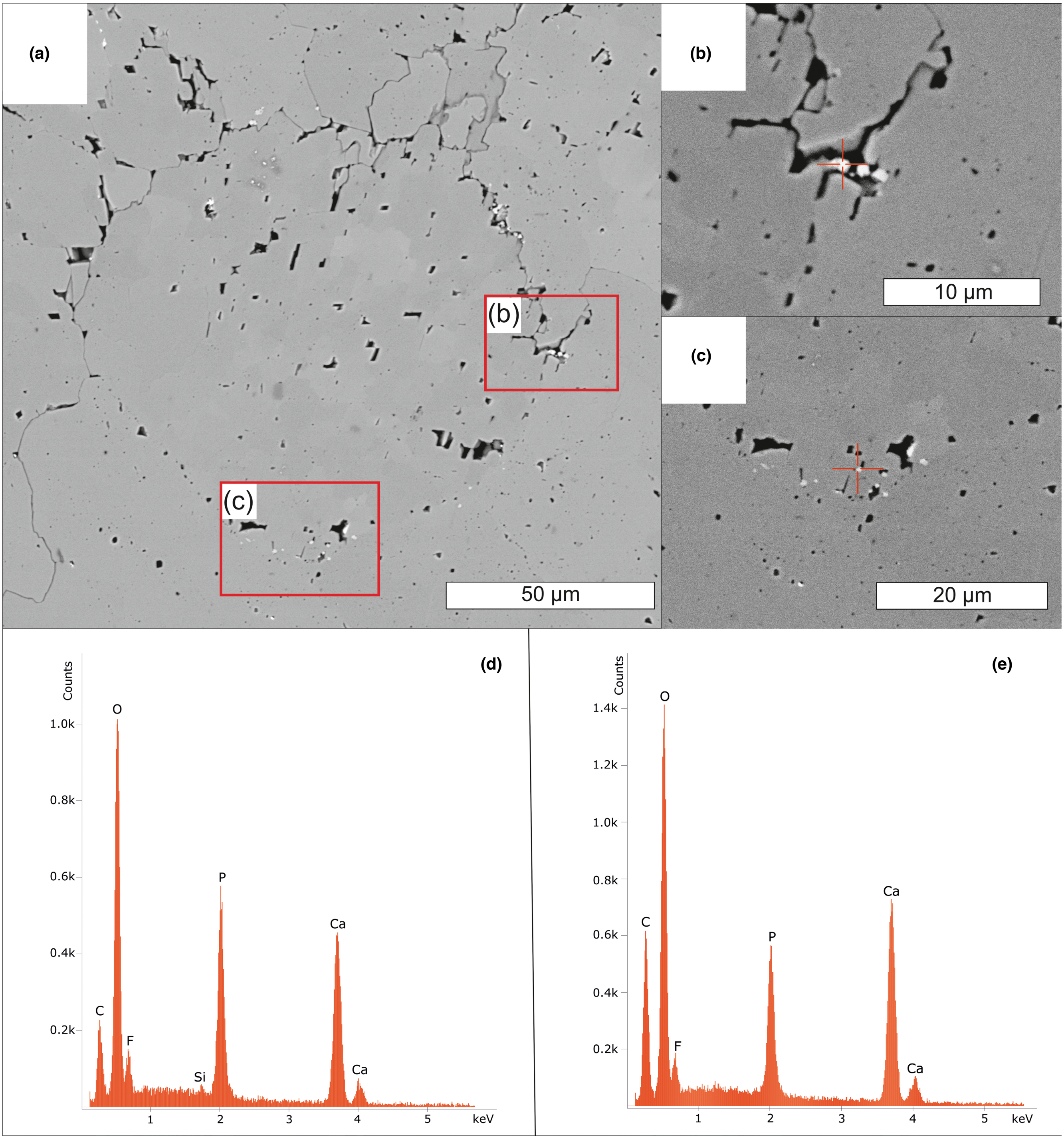

FIGURE 7 Scanning electron microscope imaging of Hollard Mound carbonate. (a) Electron backscatter image of a single sphere showing high backscatter minerals at sphere walls. (b) Details of (a) showing high backscatter minerals at higher magnification. (c) Detail of (a) showing high backscatter minerals at higher magnification. (d) Energy dispersive spectra of high backscatter minerals with peaks in phosphorus, calcium, oxygen, and subordinate fluorine.

deposit by a paragenetic sequence typical for seep carbonates, carbonate phase-specific stable isotope signatures, and by a high-abundance but low-diversity assemblage of bivalves and the presence of dense clusters of worm tubes (Hryniewicz et al., 2017; Peckmann et al., 1999, 2005). The microbial consortia that inhabit hydrocarbon seeps today includes anaerobic methanotrophic archaea and sulfate-reducing bacteria mediating SD-AOM (Boetius et al., 2000; Knittel et al., 2005; Orphan et al., 2002). Apart from these key players involved in methane consumption, seeps are also inhabited by a variety of bacteria that oxidize sulfide produced during SD-AOM (Girnth et al., 2011; Grünke et al., 2011; Larkin & Henk, 1996). The large colorless sulfide-oxidizing bacteria *Thioploca*,

14724669, 2024, 1, Downloaded from https://onlinelibrary.wiley.com/doi/10.1111/gbi.12581 by Test, Wiley Online Library on [23/01/2024]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

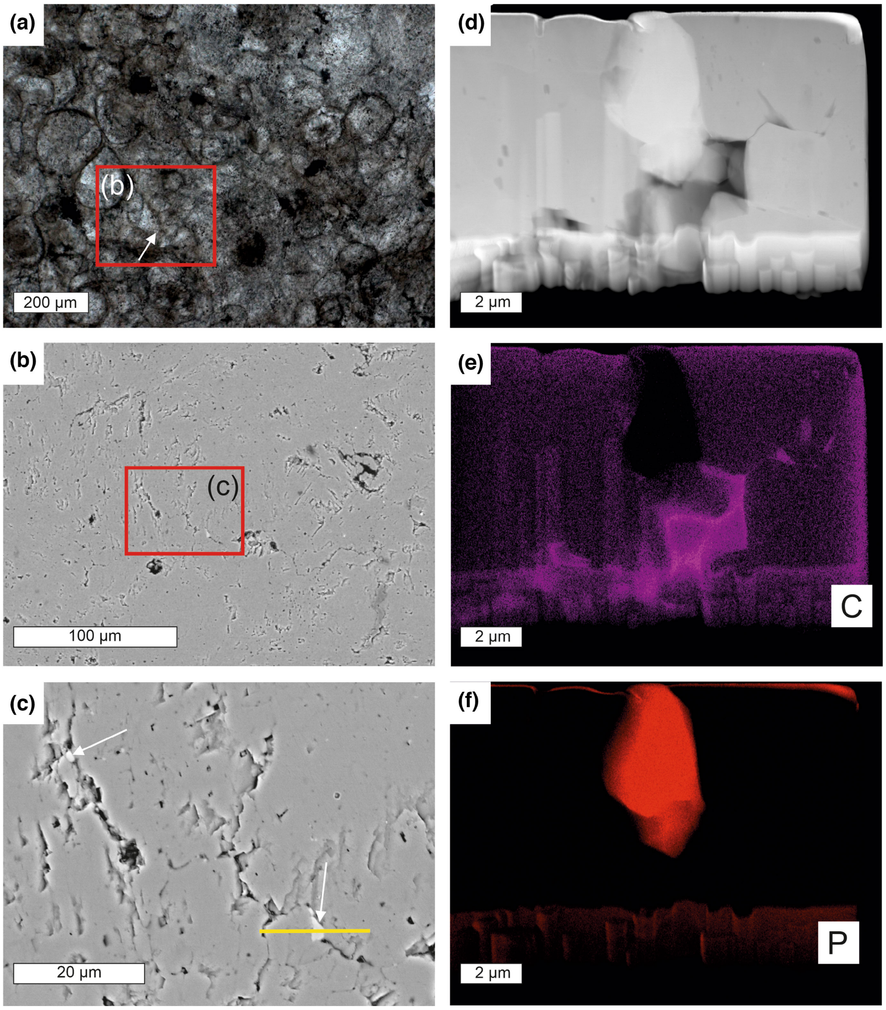

FIGURE 8 Photomicrograph, scanning electron microscope, and transmission electron microscope imaging of Hollard Mound carbonates. (a) Photomicrograph (plane-polarized light) showing abundant spheres clumped together; white arrow denotes individual sphere. (b) Magnified section denoted by the red rectangle in (a) in electron backscatter imaging mode showing the walls of spheres. (c) Magnified electron backscatter image of the red rectangle in (b) showing a close-up view of the spheres and high backscatter minerals identified as calcium fluorapatite (denoted by the white arrows); yellow line delineates the position of the focused ion beam foil. (d) High-angular-annular dark field scanning transmission microscope image of the focused ion beam foil. (e) Energy dispersive spectra imaging of carbon distribution in the sample shown in (d). (f) Energy dispersive spectra imaging of phosphorus distribution in the sample shown in (e).

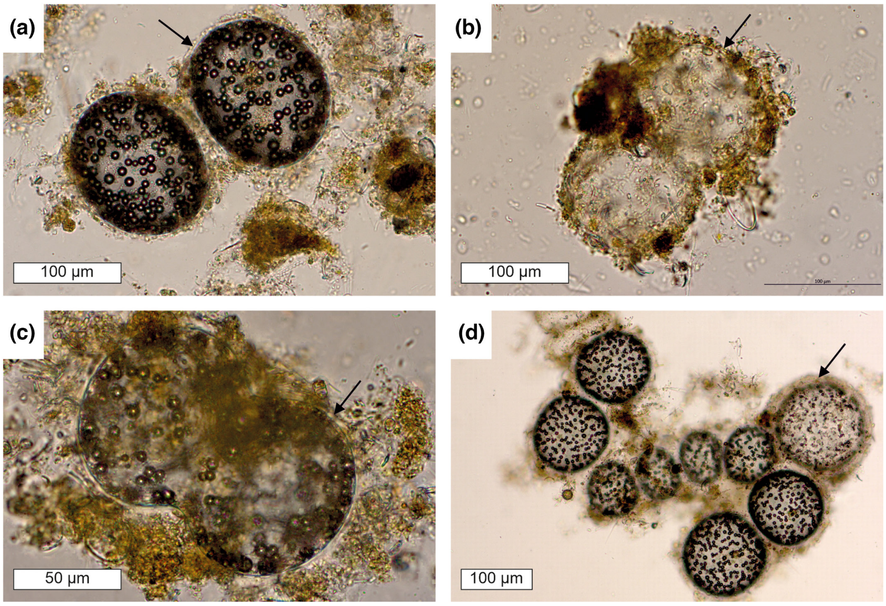

FIGURE 9 Photomicrographs of *Thiomargarita* cells. (a) A pair of two cells with large sulfur inclusions surrounded by a common sheath. (b) A pair of cells without sulfur inclusions; the cells recently divided. (c) A single *Thiomargarita* cell in division. (d) A clump of cells with different diameters surrounded by a common sheath.

Beggiatoa, and *Thiomargarita* are keystone members of the microbial communities at seeps, where they commonly form thick bacterial mats on the seafloor (Grünke et al., 2011; Mills et al., 2004; Zopfi et al., 2001). *Thiomargarita* exhibit the largest cell sizes of this group, forming dense clusters of cells within bacterial mats at seeps (Grünke et al., 2011; Schulz, 2006). The shape, size, and distribution

14724669, 2024, 1, Downloaded from https://onlinelibrary.wiley.com/doi/10.1111/gbi.12581 by Test, Wiley Online Library on [23/01/2024]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

of *Thiomargarita* at modern seeps raises the question if the spheres observed in the Hollard Mound seep deposit could be the fossilized remains of *Thiomargarita*-like cells preserved in the Devonian seep limestone.

The size, morphology, and spatial arrangement of the Hollard Mound spheres argue for bacterial cells that are similar to some of the giant marine sulfide-oxidizing bacteria found at hydrocarbon seeps today. Specifically, most *Thiomargarita* cells are 100 to several hundred microns in size and may occur either as individual cells, commonly as clusters of several overlapping individual cells, as well as closely attached cells forming chains of several centimeters in length (Salman et al., 2011, 2013; Schulz, 2006; Schulz et al., 1999). The putative fossilized bacteria of the Hollard Mound seep deposit are likewise arranged in chains and clusters of individual cells that resemble their modern equivalents (cf. Figure 9). Typical in situ cell diameter distributions among *Thiomargarita* populations from modern organic-rich sediments and seep environments are on the order of 100 to 400 μm (Figure 9; Bailey et al., 2017; Girnth et al., 2011; Kalanetra et al., 2005; Salman et al., 2013; Schulz et al., 1999), which is in a similar size range distribution as the Hollard Mound spheres (Figures 3–5). Microfossils of similar morphology reported from Devonian limestones include calcispheres and radiolarian tests. Calcispheres have been described as spherical bodies with a hollow central chamber enveloped by calcareous walls, which are typically ornamented with extended radial spines (Kazmierczak & Kremer, 2005). Devonian calcispheres are within a similar size range (120 to 180 μm) than the fossilized cells, but are characterized by a wall thickness ranging from 20 to 25 microns (Berkyova & Munnecke, 2010, see their Figure 3j–l). These walls are composed of two dark micritic rims with different degrees of micritization. Devonian radiolarians are also in a similar size range to the fossilized cells, ranging between several tens to over 100 microns in diameter. They exhibit distinct outer shell ornamentations that distinguish them from calcispheres and other microfossils such as foraminifera (Antoshikna et al., 2014). This outer shell framework may be either preserved or replaced by micritic envelopes of several tens of microns in thickness (Afanasieva & Amon, 2011). The main feature that distinguishes the fossilized *Thiomargarita* cells from calcispheres or radiolarians is the lack of a siliceous or micritized outer rim, as well as the lack of a skeletal framework. Instead, they are enveloped by a layer of structurally-ordered organic material (Figure 5).

The reproductive cycle of *Thiomargarita* produces cell morphologies, beginning with bud formation followed by reductive division and cell dimorphism (Bailey et al., 2011). During the initiation of cell division, cells show distinct indentations as well as typical spatial arrangements of two or more (quadruple) cells close to each other (Figure 9; Bailey et al., 2011; Kalanetra et al., 2005; Salman et al., 2013). Symmetric reductive cell division is commonly observed that results in symmetrically arranged duplets of cells, as well as cube-like aggregates of four to eight or even more cells (Salman et al., 2013; Bailey et al., 2017). These cell morphologies produced by reductive division of *Thiomargarita* are similar to those observed in the Hollard Mound seep carbonates. Analogous to the sequence of morphological change during reductive division observed for *Thiomargarita* (cf. Kalanetra et al., 2005; Salman et al., 2013), these division stages occur in the Hollard Mound spheres, whereby symmetrical division resulting in two cells of similar size in immediate proximity is a common arrangement (Figures 3b, and 4b–d), and are similar in size and morphology to *Thiomargarita* cells from present-day organic-rich sediments (Figure 9b,c). Some of the putative cells are arranged in clusters of four that show two sets of cells, where those opposite each other are of different size (Figure 3c). This spatial arrangement as tetrad clusters is also observed for *Thiomargarita* cells during symmetric cell division; either one cell in a chain of three cells divides and the others do not, or one cell divides into two cells of different size that further divide into daughter cells of equal size (Salman et al., 2013).

Modern *Thiomargarita* have thick mucus sheaths surrounding the cell (Schulz et al., 1999), which either manifests as a diffuse, dark to black organic material or finely dispersed filaments reaching from the cell exterior (Figure 9; Bailey et al., 2017). These mucilaginous sheaths also surround colonial cell aggregates, as well as chains of individual cells (Kalanetra et al., 2005; Salman et al., 2013). This organic material is usually most dense along the edges where two or more individual cells are attached, as well as during initiation of reductive cell division (Figure 9b,d). By analogy, the putative fossilized cells from Hollard Mound show similar dark rims of a brownish to black coloration composed of organic matter (Figures 3a,c and 5) where the cell walls are composed of multiple fine sheaths as also observed for *Thiomargarita* cells (Figure 9; Bailey et al., 2017; Salman et al., 2011). The double-layer cell walls that can be observed using cell staining (cf. Bailey et al., 2017), corresponds to some examples of larger cells in the Hollard Mound seep deposit. The Hollard Mound *Thiomargarita*-like fossils display a wall morphology that is typical for other fossilized cell material reported from the rock record (Javaux et al., 2003, 2004; Sugitani et al., 2015) and constitutes a critical diagnostic feature identifying microfossils as the remains of large prokaryotes. The putative Hollard Mound sulfide-oxidizing bacteria form dense aggregates and chains that commonly encircle and cover worm tubes (Figure 2c; cf. Peckmann et al., 2005), similar to sulfide-oxidizing bacteria today adhering to the tubes of seep-dwelling siboglinids (Grünke et al., 2012; Kalanetra et al., 2005).

5.2 | Preservation and taphonomy

The degree of diagenetic alteration of the host rock determines the quality of preservation of microfossils. The $\delta^{13}C$ and $\delta^{18}O$ values of Hollard Mound carbonate cements, ranging between −25‰ and −10‰ and between −12‰ and 0‰, respectively (Peckmann et al., 2005), have been interpreted to reflect the oxidation of thermogenic methane at a seafloor seep as well as burial diagenesis having caused moderate neomorphism of carbonate cements (Aitken et al., 2002). Negative cerium anomalies in shale-normalized rare earth element patterns in some of the carbonate phases may indicate temporally limited exposure of the anoxic sediment to

14724669, 2024, 1, Downloaded from https://onlinelibrary.wiley.com/doi/10.1111/gbi.12581 by Test, Wiley Online Library on [23/01/2024]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

oxygenated seawater during carbonate precipitation, and that the geochemical signatures of the Hollard Mound carbonates were not erased by burial diagenetic processes (Jakubowicz et al., 2015). Temperature estimations calculated from Raman spectra of organic matter between 140°C and 230°C suggest that the samples were not metamorphosed, thus explaining the high degree of preservation of the putative microfossils. Our petrographic observations here and those of previous studies (e.g., Cavalazzi et al., 2007; Peckmann et al., 1999) in combination with the identification of structurally ordered organic matter (Figure 5) confirm that the degree of preservation of the Hollard Mound carbonates allows for a geochemical reconstruction of environmental conditions, as well as for the identification of bona fide microfossils.

Due to their abundance in modern upwelling zones at the sites of phosphogenesis, the involvement of giant sulfide-oxidizing bacteria has been invoked in cases of microfossil-bearing ancient phosphorites (Czaja et al., 2016; Hiatt et al., 2015; Lepland et al., 2013). Some of these examples, such as putative fossilized *Thiomargarita* cells reported from the Neoproterozoic Doushantuo Formation (Bailey et al., 2007), are of similar morphology and size as the Hollard Mound microfossils. Cunningham et al. (2012) demonstrated pathways for the preservation of *Thiomargarita* cells, concluding that while internally stored sulfur globules should not be preserved within the center of the cell, the multi-layered sheaths exhibit the highest resistance toward decay, and thus highest potential for preservation. These results agree with our observations on the Hollard Mound microfossils. While there is little to no internal structure preserved within the cells, their outer structure is preserved by a well-defined, brownish-to-black rim that make them distinct and clearly identifiable from the carbonate cement in which they were preserved (Figures 3 and 4). This pattern of preservation is a criterion for biogenicity (Buick, 1990), while also agreeing with observations derived from experimental taphonomy (Cunningham et al., 2012). This selective preservation is further supported by the identified Raman peaks at ca. 1330 and ca. 1600 cm^{-1} within the brownish-to-black rim. These peaks can be assigned to the D and G peak positions characteristic of structurally ordered organic material (Liu et al., 2013). Given the higher degree of cell wall preservation, it is likely that organic material in the cell walls was preserved during early diagenesis and later transformed to structurally-ordered organic matter in the course of burial diagenesis as outlined above.

Although sulfide-oxidizing bacteria are common at modern seeps, identifiable fossilized bacterial remains are scarce in ancient seep deposits. This scarcity is likely due to the taphonomic requirements for preservation, where preservation requires a fast shift from oxic or suboxic conditions to anoxic conditions allowing for SD-AOM-driven carbonate precipitation (Peckmann et al., 2004). In seep environments the preservation or destruction of cellular material is in part controlled by the balance between carbonate-dissolving and carbonate precipitating reactions: hydrogen sulfide oxidation with molecular oxygen, which triggers carbonate dissolution, must be rapidly overcome by SD-AOM, which triggers carbonate precipitation, entombing and preserving cells of sulfide-oxidizing bacteria by carbonate minerals. This scenario implies that the preservation of fossils of sulfide-oxidizing bacteria in seep deposits depends on a delicate biogeochemical switch that leads to the fossilization of bacterial cells. Interestingly, carbonate precipitation has been shown to favor fossilization of cells at seeps where nitrate-dependent sulfide oxidation—a process mediated by giant sulfide-oxidizing bacteria (Fossing et al., 1995)—is dominant, leading to the preservation of filamentous *Thioploca* cells (Himmler et al., 2018). By analogy to the model of preservation of *Thioploca* filaments, a genus closely related to *Thiomargarita* (Teske & Nelson, 2006), a rapid change of redox conditions may not have been necessary for fossilization if the Hollard Mound *Thiomargarita*-like bacteria performed nitrate-dependent sulfide oxidation.

It seems that the large sulfide-oxidizing bacteria are particularly prone to preservation in the rock record including Neoarchean and Proterozoic sedimentary rocks (e.g., Bailey et al., 2007, 2013; Czaja et al., 2016; Georgieva et al., 2022) simply due to their large cell size and the amount and composition of mucilaginous sheath and cell wall material capable of withstanding decay (cf. Cunningham et al., 2012). The process of cell entombment by mineralization must proceed rapidly after the cessation of microbial activity before microbial decay can take effect, after which cells have a large potential of preservation as microfossils in sedimentary rocks (Bailey et al., 2009). These requirements for preservation are especially met at hydrocarbon seeps, where rapidly forming authigenic minerals have been shown to preserve bacterial fossils with great textural detail (Himmler et al., 2018; Peckmann et al., 2004; Stevens et al., 2015), as well as preserving organic walled worm tubes (Georgieva et al., 2019).

5.3 | Paleoecology at the Hollard Mound seep and evolutionary implications

The ecological evolution of sulfide-oxidizing bacteria is linked to the antiquity of oxygenic photosynthesis, microbial sulfate reduction, and, possibly, to the nitrogen cycle. Microbial cycling of sulfur and nitrogen has been traced back as far as 3.5 and 3.2 Ga, respectively (Shen et al., 2009; Stüecken et al., 2015; Ueno et al., 2008), predating the oldest known seep deposits (Jakubowicz et al., 2017; Peng et al., 2022). Most of the oldest microbial fossils related to sulfur cycling have been interpreted as being phototrophs (Javaux & Lepot, 2018; Lepot, 2020; Wacey et al., 2011 and references therein), and are therefore ecologically unrelated to seep ecosystems of the deep sea. Nitrate-dependent sulfide oxidation, as mediated by the giant sulfide-oxidizing bacteria at seeps today, would have been efficiently inhibited by ferruginous conditions in Archaean oceans (Bekker et al., 2010; Canfield et al., 2018), keeping sulfide and nitrate separated from each other. This would suggest that these bacteria would have emerged prior or during the Great Oxidation Event (cf. Czaja et al., 2016), possibly alongside the development of increased diversity of other microorganisms such as cyanobacteria (Schirrmeister et al., 2013). Some of the oldest evidence for the presence of large sulfide-oxidizing bacteria stems from

14724669, 2024, 1, Downloaded from https://onlinelibrary.wiley.com/doi/10.1111/gbi.12581 by Test, Wiley Online Library on [23/01/2024]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

ancient phosphorites and phosphate-rich sedimentary rocks (Bailey et al., 2007; Lepland et al., 2013), where these bacteria apparently contributed to phosphogenesis by facilitating the precipitation of authigenic phosphate minerals (Goldhammer et al., 2010; Schulz & Schulz, 2005). *Thiomargarita*, but also *Beggiatoa* and *Thioploca*, are common at methane and oil seeps today (Joye et al., 2004; Mills et al., 2004; Niemann et al., 2006; Sahling et al., 2016), where abundant dissolved sulfide is produced by the sulfate-driven oxidation of methane and oil (Boetius & Suess, 2004; Joye et al., 2004; Smrzka et al., 2019). However, hydrocarbon seepage and hotspots of phosphogenesis do not typically coincide, even though both environments provide habitats for the large sulfide-oxidizing bacteria. Also in the fossil record, a convergence of seepage and phosphogenesis seems to be rare. Zwicker et al. (2021) suggested that giant sulfide-oxidizing bacteria facilitated phosphorus accumulation and carbonate fluorapatite precipitation at a Cretaceous seep. Similarly, Lepland et al. (2013) suggested a link between sulfide-oxidizing bacteria and phosphogenesis for a Paleoproterozoic oil field system fueled by volcanic intrusions within organic carbon-rich mudstones, which apparently represented a main source of phosphorus (Kipp et al., 2020).

The Hollard Mound is one of the oldest known seep deposits to date and the oldest seep deposit with identifiable cellular remains of large sulfide-oxidizing bacteria, following the argumentation above. Apart from the similarities in size and morphology to their modern counterparts, the presence of calcium fluorapatite in fossilized cells is further evidence for the assignment of the Hollard Mound microfossils to the colorless sulfide-oxidizing bacteria. Sulfide-oxidizing bacteria are capable of storing polyphosphate within their cells that can be released under sulfidic conditions, thus providing a source of phosphorus for the precipitation of phosphate minerals (Goldhammer et al., 2010; Holmkvist et al., 2010; Schulz & Schulz, 2005; Sievert et al., 2007). Scanning electron microscope examination shows that the distribution of calcium fluorapatite is not random, but is concentrated along former cell walls (Figure 7a–c). Upon closer examination, calcium fluorapatite crystals are several µm in size and are situated directly within voids that delineate the walls of the fossilized bacteria (Figures 7a and 8b–e). The apparent absence of carbon (Figure 8e) and the presence of phosphorus (Figure 8f) in these minerals is in agreement with mineralogical identification of calcium fluorapatite (cf. Figure 6). The size and distribution of calcium fluorapatite in the samples argues for authigenic formation in the direct vicinity of the cell walls, possibly related to metabolic activity. The presence of authigenic phosphate minerals, which are rare at seeps (Peckmann et al., 2005; Zwicker et al., 2021), would probably have required the local release of (poly)phosphate or similar phosphorus compounds as observed in organic- and phosphate-rich sediments today. Although sulfide-oxidizing bacteria are capable of precipitating authigenic phosphate minerals, their abundance alone is apparently insufficient to enable phosphogenesis in seep environments, which requires additional phosphorus sources as well as efficient mechanisms to prevent cycling and loss of dissolved phosphorus from sediments to bottom waters. Such additional sources could either be thick bacterial mats with abundant organic matter combined with a mechanism that prevents phosphorus from escaping the pore waters (Zwicker et al., 2021), or an abundance of organic material in the host sediments that provides sufficient phosphorus for phosphogenesis (Glenn et al., 1994; Schenau et al., 2000). Neither of these two requirements were met at the Hollard Mound seep since neither the carbonates, their fossil inventory, nor the host rock are phosphatized, and no other phosphate minerals could be identified apart from those within the fossilized cell walls.

The similarity of the Hollard Mound paleoecosystem to present-day ecosystems at seeps with abundant giant sulfide-oxidizing bacteria suggests that hydrocarbon seeps experienced few changes in physicochemical environments and micro- and macrofaunal ecology throughout the Phanerozoic. Although the macrofaunal composition at seeps has changed over time, most ancient seep deposits exhibit characteristic faunal assemblages with high degrees of endemism (Campbell & Bottjer, 1995; Kiel & Dando, 2009; Kiel & Peckmann, 2019; Van Dover et al., 2002). Annelid tubeworms, which are common invertebrates inhabiting hydrocarbon seeps today (Hilário et al., 2011), have been identified in ancient seep ecosystems since the Paleozoic with little morphological or ecological change (Georgieva et al., 2019; Little & Vrijenhoek, 2003; Vinn et al., 2013). The presence of fossilized sulfide-oxidizing bacteria adhering to worm tubes in the Hollard Mound seep deposit suggests that some aspects of chemosynthesis-based ecosystems at seeps remained largely unchanged for hundreds of millions of years. Similar conclusions have been drawn from fossilized microbial assemblages in anoxic subseafloor environments from the 1.8 Ga Duck Creek and the 2.3 Ga Turee Creek formations (Schopf et al., 2015). These Proterozoic ecosystems harbored non-phototrophic sulfide-oxidizing bacteria, reflecting little to no ecological or morphological change over a period of more than one billion years, demonstrating that chemosynthesis-based ecosystems may enter phases of long-lasting evolutionary stasis (Georgieva et al., 2022; Schopf et al., 2015). Although this notion does not hold true for most of the seep-endemic megafaunal invertebrate communities (Kiel & Peckmann, 2019), the Hollard Mound deposit provides evidence that chemosynthesis-based ecosystems have the potential to cope with macrofaunal evolutionary change and still function in a similar fashion despite changes in the phylogenetic affiliation of most of its metazoan members.

6 | CONCLUSIONS

This study provides evidence for the presence of giant sulfur-oxidizing bacteria at a Devonian hydrocarbon seep. The size and morphology of spheres present within the authigenic carbonate are similar to modern-day sulfide-oxidizing bacteria of the genus *Thiomargarita*. Their distribution in the vicinity of worm tubes, with many spheres adhering to external tube surfaces, resembles the coexistence of sulfide-oxidizing bacteria with siboglinid tubeworms living at modern hydrocarbon seeps. Although preservation

14724669, 2024, 1, Downloaded from https://onlinelibrary.wiley.com/doi/10.1111/gbi.12581 by Test, Wiley Online Library on [23/01/2024]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

of bacterial fossils is generally rare in ancient seep deposits, the colorless sulfide-oxidizing bacteria are particularly prone to preservation due to their large size. In addition, rapid changes in biogeochemical reactions that trigger carbonate precipitation may promote the preservation of microbial fossils or, alternatively, fossilization may be favored by carbonate formation induced by nitrate-driven sulfide oxidation performed by sulfide-oxidizing bacteria. The occurrence of calcium fluorapatite within the cell walls of the putative bacterial fossils suggests that the spherical microorganisms accumulated phosphate in their cells, analogous to modern colorless sulfide-oxidizing bacteria. These observations demonstrate that large sulfide-oxidizing bacteria have existed at seeps since the Paleozoic, and suggest that some aspects of the ecology of chemosynthesis-based ecosystems remained largely unchanged for millions of years.

ACKNOWLEDGMENTS

We thank Claudia Beybel for preparing high-quality polished thin sections, Dieter Mader for assistance in cathodoluminescence petrography, Tim Grieb (University of Bremen) for FIB-TEM analyses, and Marcos Toro (University of Bremen) for assistance in Raman spectroscopy. Insightful comments by three anonymous reviewers and editor Jake Bailey helped to improve this article. We acknowledge financial support from the Open Access Publication Fund of Universität Hamburg. Open Access funding enabled and organized by Projekt DEAL.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

ORCID

Jörn Peckmann https://orcid.org/0000-0002-8572-0060

REFERENCES

Afanasieva, M. S., & Amon, E. O. (2011). Devonian radiolarians of Russia. *Palaeontological Journal*, *45*, 1313–1532. https://doi.org/10.1134/S0031030111110013

Aitken, S. A., Collom, C. J., Henderson, C. M., & Johnston, P. A. (2002). Stratigraphy, paleoecology, and origin of lower Devonian (Emsian) carbonate mud buildups, Hamar Laghdad, eastern Anti-Atlas, Morocco, Africa. *Bulletin of Canadian Petroleum Geology*, *50*, 217–243.

Antoshikna, A. I., Ponomarenko, E. S., & Kaneva, N. A. (2014). Fenestral limestones: Specific features of late Devonian seas in the Timan – Northern Ural region. *Lithology of Mineral Resources*, *49*, 461–472. https://doi.org/10.1134/S0024490214060029

Arvidson, R. S., Morse, J. W., & Joye, S. B. (2004). The sulfur biogeochemistry of chemosynthetic cold seep communities, Gulf of Mexico, USA. *Marine Chemistry*, *87*, 97–119. https://doi.org/10.1016/j.marchem.2003.11.004

Bailey, J. V., Corsetti, F. A., Greene, S. E., Crosby, C. H., Liu, P., & Orphan, V. J. (2013). Filamentous sulfur bacteria preserved in modern and ancient phosphatic sediments: Implications for the role of oxygen and bacteria in phosphogenesis. *Geobiology*, *11*, 397–405. https://doi.org/10.1111/gbi.12046

Bailey, J. V., Flood, E. B., Ricci, E., & Delherbe, N. (2017). Imaging of cellular oxidoreductase activity suggests mixotrophic metabolisms in *Thiomargarita* spp. *mBio*, *8*, e01263-17. https://doi.org/10.1128/mBio.01263-17

Bailey, J. V., Joye, S. B., Kalanetra, K. M., Flood, B. E., & Corsetti, F. A. (2007). Evidence of giant sulphur bacteria in Neoproterozoic phosphorites. *Nature*, *445*, 198–201. https://doi.org/10.1038/nature05457

Bailey, J. V., Orphan, V. J., Joye, S. B., & Corsetti, F. A. (2009). Chemotrophic microbial mats and their potential for preservation in the rock record. *Astrobiology*, *9*, 843–859. https://doi.org/10.1089/ast.2008.0314

Bailey, J. V., Salman, V., Rouse, G. W., Schulz-Vogt, H. N., Levin, L. A., & Orphon, V. J. (2011). Dimorphism in methane seep-dwelling ecotypes of the largest known bacteria. *The ISME Journal*, *5*, 1926–1935.

Battistuzzi, F. U., Feijao, A., & Hedges, S. B. (2004). A genomic timescale of prokaryote evolution: Insights into the origin of methanogenesis, phototrophy, and the colonization of land. *BMC Evolutionary Biology*, *4*, 1–14.

Bekker, A., Slack, J. F., Planavsky, N. J., Krapez, B., Hofmann, A., Konhauser, K. O., & Rouxel, O. J. (2010). Iron formation: The sedimentary product of a complex interplay among mantle, tectonic, oceanic, and biospheric processes. *Economic Geology*, *105*, 467–508.

Belka, Z. (1998). Early Devonian Kess-Kess carbonate mud mounds of the eastern anti-atlas (Morocco), and their relation to submarine hydrothermal venting. *Journal of Sedimentary Research*, *68*, 368–377.

Berkowski, B. (2006). Vent and mound rugose coral associations from the middle Devonian of Hamar Laghdad (Anti-Atlas, Morocco). *Geobios*, *39*, 155–170. https://doi.org/10.1016/j.geobios.2004.11.003

Berkyova, B., & Munnecke, A. (2010). "Calcispheres" as a source of lime mud and peloids – Evidence from the early middle Devonian of the Prague Basin, The Czech Republic. *Bulletin of Geosciences*, *85*, 585–602.

Boetius, A., Ravenschlag, K., Schubert, C. J., Rickert, D., Widdel, F., Gieseke, A., Amann, R., Jørgensen, B. B., Witte, U., & Pfannkuche, O. (2000). A marine microbial consortium apparently mediating anaerobic oxidation of methane. *Nature*, *407*, 623–626. https://doi.org/10.1038/35036572

Boetius, A., & Suess, E. (2004). Hydrate ridge: A natural laboratory for the study of microbial life fueled by methane from near-surface gas hydrates. *Chemical Geology*, *205*, 291–310. https://doi.org/10.1016/j.chemgeo.2003.12.034

Brachert, T. C., Buggisch, W., Flügel, E., Hüssner, H. M., Joachimski, M. M., Tourneur, F., & Walliser, O. H. (1992). Controls of mud mound formation: The early Devonian Kess-Kess carbonates of the Hamar Laghdad, Antiatlas, Morocco. *Geologische Rundschau*, *81*, 15–44. https://doi.org/10.1007/BF01764537

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. https://doi.org/10.1038/416076a

Brasier, M. D., Green, O. R., Lindsay, J. F., McLoughlin, N., Steele, A., & Stoakes, C. (2005). Critical testing of Earth's oldest putative fossil assemblage from the ~3.5 Ga Apex chert, Chinaman Creek, Western Australia. *Precambrian Research*, *140*, 55–102. https://doi.org/10.1016/j.precamres.2005.06.008

Brasier, M. D., 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 of London B Biological Sciences*, *361*, 887–902. https://doi.org/10.1098/rstb.2006.1835

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.

14724669, 2024, 1, Downloaded from https://onlinelibrary.wiley.com/doi/10.1111/gbi.12581 by Test, Wiley Online Library on [23/01/2024]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

Campbell, K. A., & Bottjer, D. J. (1995). Brachiopods and chemosymbiotic bivalves in Phanerozoic hydrothermal vent and cold seep environments. *Geology*, *23*, 321–324.

Canfield, D. E. (1998). A new model for Proterozoic ocean chemistry. *Nature*, *396*, 450–453.

Canfield, D. E., Habicht, K. S., & Thamdrup, B. (2000). The Archean sulfur cycle and the early history of atmospheric oxygen. *Science*, *288*, 658–661.

Canfield, D. E., Zhang, S., Wang, H., Wang, X., Zhao, W., Su, J., Bjerrum, C. J., Haxen, E. R., & Hammarlund, E. U. (2018). A Mesoproterozoic iron formation. *Proceedings of the National Academy of Science U.S.A.*, *115*, 3895–3904. https://doi.org/10.1073/pnas.1720529115

Cavalazzi, B., Barbieri, R., & Ori, G. G. (2007). Chemosynthetic microbialites in the Devonian carbonate mounds of Hamar Laghdad (Anti-Atlas, Morocco). *Sedimentary Geology*, *200*, 73–88. https://doi.org/10.1016/j.sedgeo.2007.03.002

Cloud, P. (1976). Beginnings of biospheric evolution and their biogeochemical consequences. *Paleobiology*, *2*, 351–387.

Cunningham, J. A., Thomas, C.-W., Bengston, S., Marine, F., Stampanoni, M., Turner, F. R., Bailey, J. V., Raff, R. A., Raff, E. C., & Donoghue, P. C. J. (2012). Experimental taphonomy of giant sulphur bacteria: Implications for the interpretation of the embryo-like Ediacaran Doushantuo fossils. *Proceedings of the Royal Society B*, *279*, 1857–1864.

Czaja, A. D., Beukes, N. J., & Osterhout, J. T. (2016). Sulfur-oxidizing bacteria prior to the great oxidation event from the 2.52 Ga Gamohaan formation of South Africa. *Geology*, *44*, 983–986.

Farquhar, J., Peters, M., Johnston, D. T., Strauss, H., Masterson, A., Wiechert, U., & Kaufman, A. J. (2007). Isotopic evidence for Mesoarchaean anoxia and changing atmospheric sulphur chemistry. *Nature*, *449*, 706–709. https://doi.org/10.1038/nature06202

Farquhar, J., & Wing, B. A. (2003). Multiple sulfur isotopes and the evolution of the atmosphere. *Earth and Planetary Science Letters*, *213*, 1–13. https://doi.org/10.1016/S0012-821X(03)00296-6

Fossing, H., Gallardo, V. A., Jørgensen, B. B., Hüttel, M., Nielsen, L. P., Schulz, H., Canfield, D. E., Forster, S., Glud, R. N., Gundersen, J. K., Küver, J., Ramsing, N. B., Teske, A., Thamdrup, B., & Ulloa, O. (1995). Concentration and transport of nitrate by the mat-forming sulphur bacterium *Thioploca*. *Nature*, *374*, 713–715. https://doi.org/10.1038/374713a0

Gallardo, V. A. (1977). Large benthic microbial communities in sulphide biota under Peru–Chile Subsurface Countercurrent. *Nature*, *268*, 331–332. https://doi.org/10.1038/268331a0

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., Herrington, R. J., Boyce, A. J., Zerkle, A. L., Maslennikov, V. V., EIMF, & Glover, A. G. (2022). Sulfur isotopes of hydrothermal vent fossils and insights into microbial sulfur cycling within a lower Paleozoic (Ordovician-early Silurian) vent community. *Geobiology*, *20*, 465–478.

Georgieva, M. N., Little, C. T. S., Watson, J. S., Sephton, M. A., Ball, A. D., & Glover, A. G. (2019). Identification of fossil worm tubes from Phanerozoic hydrothermal vents and cold seeps. *Journal of Systematic Palaeontology*, *17*, 287–329. https://doi.org/10.1080/14772019.2017.1412362

Girnth, A.-C., Grünke, S., Lichtschlag, A., Felden, J., Knittel, K., Wenzhöfer, F., de Beer, D., & Boetius, A. (2011). A novel, mat-forming *Thiomargarita* population associated with sulfidic fluid flow from a deep-sea mud volcano. *Environmental Microbiology*, *13*, 495–505.

Glenn, C. R., Föllmi, K. B., Riggs, S. R., Baturin, G. N., Grimm, K. A., Trappe, J., Abed, A. M., Galli-Oliver, C., Garrison, R. E., Ilyin, A. V., Jehl, C., Rohrlich, V., Sadaqah, R. M. Y., Schildowski, M., Sheldon, R. E., & Siegmund, H. (1994). Phosphorus and phosphorites: Sedimentology and environments of formation. *Eclogae Geologicae Helvetiae*, *87*, 747–788.

Goldhammer, T., Brüchert, V., Ferdelman, T. G., & Zabel, M. (2010). Microbial sequestration of phosphorus in anoxic upwelling sediments. *Nature Geoscience*, *3*, 557–561. https://doi.org/10.1038/ngeo913

Grünke, S., Felden, J., Lichtschlag, A., Girnth, A.-C., de Beer, D., Wenzhöfer, F., & Boetius, A. (2011). Niche differentiation among mat-forming, sulfide-oxidizing bacteria at cold seeps of the Nile Deep Sea fan (Eastern Mediterranean Sea). *Geobiology*, *9*, 330–348.

Grünke, S., Lichtschlag, A., de Beer, D., Felden, J., Salman, V., Ramette, A., Schulz-Vogt, H. N., & Boetius, A. (2012). Mats of psychrophilic thiotrophic bacteria associated with cold seeps of the Barents Sea. *Biogeosciences*, *9*, 2947–2960. https://doi.org/10.5194/bg-9-2947-2012

Hiatt, E. E., Pufahl, P. K., & Edwards, C. T. (2015). Sedimentary phosphate and associated fossil bacteria in a Paleoproterozoic tidal flat in the 1.85 Ga Michigamme formation, Michigan, USA. *Sedimentary Geology*, *319*, 24–39. https://doi.org/10.1016/j.sedgeo.2015.01.006

Hilário, A., Capa, M., Dahlgren, T. G., Halanych, K. M., Little, C. T. S., Thornhill, D. J., Verna, C., & Glover, A. G. (2011). New perspectives on the ecology and evolution of siboglinid tubeworms. *PLoS One*, *6*, e16309. https://doi.org/10.1371/journal.pone.0016309

Himmler, T., Smrzka, D., Zwicker, J., Kasten, S., Shapiro, R. S., Bohrmann, G., & Peckmann, J. (2018). Stromatolites below the photic zone in the northern Arabian Sea formed by calcifying chemotrophic microbial mats. *Geology*, *46*, 339–342. https://doi.org/10.1130/G39890.1

Holmkvist, L., Arning, E. T., Küster-Heins, K., Vandieken, V., Peckmann, J., Zabel, M., & Jørgensen, B. B. (2010). Phosphate geochemistry, mineralization processes, and *Thioploca* distribution in shelf sediments off Central Chile. *Marine Geology*, *277*, 61–72. https://doi.org/10.1016/j.margeo.2010.08.011

Hryniewicz, K., Jakubowicz, M., Belka, Z., Dopierskala, J., & Kaim, A. (2017). New bivalves from a middle Devonian methane seep in Morocco: The oldest record of repetitive shell morphologies among some seep bivalve molluscs. *Journal of Systematic Palaeontology*, *33*, 19–41. https://doi.org/10.1080/14772019.2015.1136900

Huettel, M., Forster, S., Klöser, S., & Fossing, H. (1996). Vertical migration in the sediment-dwelling sulfur bacteria *Thioploca* spp. in overcoming diffusion limitations. *Applied and Environmental Microbiology*, *62*, 1863–1872.

Jakubowicz, M., Berkowsi, B., Hryniewicz, K., & Belka, Z. (2022). Middle Palaeozoic of Morocco: The earliest-known methane seep metazoan ecosystem. In A. Kaim, J. K. Cochran, & N. H. Landman (Eds.), Topics in Geobiology *Ancient hydrocarbon seeps* (Vol. *53*, pp. 479–516). Springer.

Jakubowicz, M., Dopieralska, J., & Belka, Z. (2015). Tracing the composition and origin of fluids at an ancient hydrocarbon seep (Hollard mound, middle Devonian, Morocco): A Nd, REE and stable isotope study. *Geochimica et Cosmochimica Acta*, *156*, 50–74. https://doi.org/10.1016/j.gca.2015.02.027

Jakubowicz, M., Hryniewicz, K., & Belka, Z. (2017). Mass occurrence of seep-specific bivalves in the oldest-known cold seep metazoan community. *Scientific Reports*, *7*, 14292.

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. https://doi.org/10.1023/A:1023992712071

Javaux, E. J., Knoll, A. H., & Walter, M. (2004). TEM evidence for eukaryotic diversity in mid-Proterozoic oceans. *Geobiology*, *2*, 121–132. https://doi.org/10.1111/j.1472-4677.2004.00027.x

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. https://doi.org/10.1016/j.earscirev.2017.10.001

14724669, 2024, 1, Downloaded from https://onlinelibrary.wiley.com/doi/10.1111/gbi.12581 by Test, Wiley Online Library on [23/01/2024]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

Jørgensen, B. B., & Gallardo, V. A. (1999). *Thioploca* spp: Filamentous sulfur bacteria with nitrate vacuoles. *FEMS Microbiology Ecology*, *28*, 301–313. https://doi.org/10.1111/j.1574-6941.1999.tb00585.x

Jørgensen, B. B., & Revsbach, N. P. (1983). Colorless sulfur bacteria, *Beggiatoa* spp. and *Thiovulum* spp, in O_2 and H_2S microgradients. *Applied and Environmental Microbiology*, *45*, 1261–1270. https://doi.org/10.1128/aem.45.4.1261-1270.1983

Joye, S. B., Boetius, A., Orcutt, B. N., Montoya, J. P., Schulz, H. N., Erickson, M. J., & Lugo, S. K. (2004). The anaerobic oxidation of methane and sulfate reduction in sediments from Gulf of Mexico cold seeps. *Chemical Geology*, *205*, 219–238. https://doi.org/10.1016/j.chemgeo.2003.12.019

Kalanetra, K. M., Joye, S. B., Sunseri, N. R., & Nelson, D. C. (2005). Novel vacuolate sulfur bacteria from the Gulf of Mexico reproduce by reductive division in three dimensions. *Environmental Microbiology*, *7*, 1451–1460.

Kazmierczak, J., & Kremer, B. (2005). Early post-mortem calcified Devonian acritarchs as a source of calcisphere structures. *Facies*, *51*, 554–565.

Kiel, S., & Dando, P. R. (2009). Chaetopterid tubes from vent and seep sites: Implications for fossil record and evolutionary history of vent and seep annelids. *Acta Palaeontologica Polonica*, *54*, 443–448.

Kiel, S., & Peckmann, J. (2019). Resource partitioning among brachiopods and bivalves at ancient hydrocarbon seeps: A hypothesis. *PLoS One*, *14*, e0221887. https://doi.org/10.1371/journal.pone.0221887

Kipp, M. A., Lepland, A., & Buick, R. (2020). Redox fluctuations, trace metal enrichment and phosphogenesis in the ~2.0 Ga Zaonega formation. *Precambrian Research*, *343*, 105716. https://doi.org/10.1016/j.precamres.2020.105716

Knittel, K., Lösekann, T., Boetius, A., Kort, R., & Amann, R. (2005). Diversity and distribution of methanotrophic archaea at cold seeps. *Applied and Environmental Microbiology*, *71*, 467–479.

Kouketsu, Y., Mizukami, T., Mori, H., Endo, S., Aoya, M., Hara, H., Nakamura, D., & Wallis, S. (2014). A new approach to develop the Raman carbonaceous material geothermometer for low-grade metamorphism using peak width. *Island Arc*, *23*, 33–50. https://doi.org/10.1111/iar.12057

Kwiecinska, B., Suarez-Ruiz, I., Paluszkiewicz, C., & Rodriques, S. (2010). Raman spectroscopy of selected carbonaceous materials. *International Journal of Coal Geology*, *84*, 206–212.

Larkin, J. M., & Henk, M. C. (1996). Filamentous sulfide-oxidizing bacteria at hydrocarbon seeps of the Gulf of Mexico. *Microscopy Research Techniques*, *33*, 23–31.

Lavik, G., Stührmann, T., Brüchert, V., Van der Plas, A., Mohrholz, V., Lam, P., Mußmann, M., Fuchs, B. M., Amann, R., Lass, U., & Kuypers, M. M. (2009). Detoxification of sulphidic African shelf waters by blooming chemolithotrophs. *Nature*, *457*, 581–585. https://doi.org/10.1038/nature07588

Lepland, A., Joosu, L., Kirsimäe, K., Prave, A. R., Romashkin, A. E., Crne, A. E., Martin, A. P., Fallick, A. E., Somelar, P., Üpraus, K., Mänd, K., Roberts, N. M. W., van Zuilen, M. A., Wirth, R., & Schreiber, A. (2013). Potential influence of sulphur bacteria on Palaeoproterozoic phosphogenesis. *Nature Geoscience*, *7*, 20–24. https://doi.org/10.1038/ngeo2005

Lepot, K. (2020). Signatures of early microbial life from the Archean (4 to 2.5 Ga) eon. *Earth-Science Reviews*, *209*, 103296. https://doi.org/10.1016/j.earscirev.2020.103296

Levin, L. A., Ziebis, W., Mendoza, G. F., Growney, V. A., Tryon, M. D., Brown, K. M., Mahn, C., Gieskes, J. M., & Rathburn, A. E. (2003). Spatial heterogeneity of macrofauna at northern California methane seeps: Influence of sulfide concentration and fluid flow. *Marine Ecology Progress Series*, *265*, 123–139.

Little, C. T. S., & Vrijenhoek, R. C. (2003). Are hydrothermal vent animals living fossils? *Trends in Ecology & Evolution*, *18*, 582–588. https://doi.org/10.1016/j.tree.2003.08.009

Liu, D., Xiao, X., Tian, H., Min, Y., Zhou, Q., Cheng, P., & Shen, J. (2013). Sample maturation calculated using Raman spectroscopic parameters for solid organics: Methodology and geological applications. *Chinese Science Bulletin*, *58*, 1285–1298.

Macalady, J. L., Dattagupta, S., Schaperdoth, I., Jones, D. S., Druschel, G. K., & Eastman, D. (2008). Niche differentiation among sulfur-oxidizing bacterial populations in cave waters. *The ISME Journal*, *2*, 590–601. https://doi.org/10.1038/ismej.2008.25

Mills, H. J., Martinez, R. J., Story, S., & Sobecky, P. A. (2004). Identification of members of the metabolically active microbial populations associated with *Beggiatoa* species mat communities from Gulf of Mexico cold-seep sediments. *Applied and Environmental Microbiology*, *70*, 5447–5458.

Mounji, D., Bourque, P.-A., & Savard, M. M. (1998). Hydrothermal origin of Devonian conical mounds (Kess-Kess) of Hamar Lakhdad ridge, Anti-Atlas, Morocco. *Geology*, *26*, 1123–1126.

Nelson, D. C., & Jannasch, H. W. (1983). Chemoautotrophic growth of a marine *Beggiatoa* in sulfide-gradient cultures. *Archives of Microbiology*, *136*, 262–269. https://doi.org/10.1007/BF00425214

Niemann, H., Lösekann, T., de Beer, D., Elvert, M., Nadalig, T., Knittel, K., Amann, R., Sauter, E. J., Schlüter, M., Klages, M., Foucher, J. P., & Boetius, A. (2006). Novel microbial communities of the Haakon Mosby mud volcano and their role as a methane sink. *Nature*, *443*, 854–858. https://doi.org/10.1038/nature05227

Orphan, V. J., House, C. H., Hinrichs, K.-U., McKeegan, K. D., & DeLong, E. F. (2002). Multiple archaeal groups mediate methane oxidation in anoxic cold seep sediments. *Proceedings of the National Academy of Science U.S.A.*, *99*, 7663–7668. https://doi.org/10.1073/pnas.072210299

Peckmann, J., Little, C. T. S., Gill, F., & Reitner, J. (2005). Worm tube fossils from the Hollard mound hydrocarbon-seep deposit, middle Devonian, Morocco: Palaeozoic seep-related vestimentiferans? *Palaeogeography, Palaeoclimatology, Palaeoecology*, *227*, 242–257. https://doi.org/10.1016/j.palaeo.2005.04.021

Peckmann, J., Thiel, V., Reitner, J., Taviani, M., Aharon, P., & Michaelis, W. (2004). A microbial mat of a large sulfur bacterium preserved in a Miocene methane-seep limestone. *Geomicrobiology Journal*, *21*, 247–255. https://doi.org/10.1080/01490450490438757

Peckmann, J., Walliser, O. H., Riegel, W., & Reitner, J. (1999). Signatures of hydrocarbon venting in a middle Devonian carbonate mound (Hollard mound) at the Hamar Laghdad (Antiatlas, Morocco). *Facies*, *40*, 281–296. https://doi.org/10.1007/BF02537477

Peng, Y., Bao, H., Jiang, G., Crockford, P., Feng, D., Xiao, S., Kaufman, A. J., & Wang, J. (2022). A transient peak in marine sulfate after the 635-Ma snowball earth. *Proceedings of the National Academy of Science U.S.A.*, *119*, e2117341119. https://doi.org/10.1073/pnas.2117341119

Pimenov, N. V., Savvichev, A. S., Rusanov, I. I., Lein, A. Y., & Ivanov, M. V. (2000). Microbiological processes of the carbon and sulfur cycles at cold methane seeps of the North Atlantic. *Microbiology*, *69*, 709–720. https://doi.org/10.1023/A:1026666527034

Poulton, S. W., Fralick, P. W., & Canfield, D. E. (2010). Spatial variability in oceanic redox structure 1.8 billion years ago. *Nature Geoscience*, *3*, 486–490.

Preisler, A., de Beer, D., Lichtschlag, A., Lavik, G., Boetius, A., & Jørgensen, B. B. (2007). Biological and chemical sulfide oxidation in a *Beggiatoa* inhabited marine sediment. *The ISME Journal*, *1*, 341–353. https://doi.org/10.1038/ismej.2007.50

Sahling, H., Borowski, C., Briones-Escobar, E., Gaytan-Caballero, A., Hsu, C.-W., Loher, M., MacDonald, I., Marcon, Y., Pape, T., Römer, M., Rubin-Blum, M., Schubotz, F., Smrzka, D., Wegener, G., & Bohrmann, G. (2016). Massive asphalt deposits, oil seepage, and gas venting support abundant chemosynthetic communities at the Campeche knolls, southern Gulf of Mexico. *Biogeosciences*, *13*, 4491–4512. https://doi.org/10.5194/bg-13-4491-2016

14724669, 2024, 1, Downloaded from https://onlinelibrary.wiley.com/doi/10.1111/gbi.12581 by Test, Wiley Online Library on [23/01/2024]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

Sahling, H., Rickert, D., Lee, R. W., Linke, P., & Suess, E. (2002). Macrofaunal community structure and sulfide flux at gas hydrate deposits from the Cascadia convergent margin, NE Pacific. *Marine Ecology Progress Series*, *231*, 121–138.

Salman, V., Amann, R., Girnth, A.-C., Polerecky, L., Bailey, J. V., Høgslund, S., Jessen, G., Pantoja, S., & Schulz-Vogt, H. N. (2011). A single-cell sequencing approach to the classification of large, vacuolated sulfur bacteria. *Systematic and Applied Microbiology*, *34*, 243–259. https://doi.org/10.1016/j.syapm.2011.02.001

Salman, V., Bailey, J. V., & Teske, A. (2013). Phylogenetic and morphologic complexity of giant sulphur bacteria. *Antonie Van Leeuwenhoek*, *104*, 169–186.

Schenau, S. J., Slomp, C. P., & De Lange, G. J. (2000). Phosphogenesis and active phosphorite formation in sediments from the Arabian Sea oxygen minimum zone. *Marine Geology*, *169*, 1–20. https://doi.org/10.1016/S0025-3227(00)00083-9

Schirrmeister, B. E., de Vos, J. M., Antonelli, A., & Bagheri, H. C. (2013). Evolution of multicellularity coincided with increased diversification of cyanobacteria and the great oxidation event. *Proceedings of the National Academy of Science U.S.A.*, *110*, 1791–1796. https://doi.org/10.1073/pnas.12099271

Schopf, J. W., Kudryavtsev, A. B., Czaja, A. D., & Tripathi, A. B. (2007). Evidence of Archean life: Stromatolites and microfossils. *Precambrian Research*, *158*, 141–155. https://doi.org/10.1016/j.precamres.2007.04.009

Schopf, J. W., Kudryavtsev, A. B., Walter, M. R., Van Kranendonk, M. J., Williford, K. H., Kozdon, R., Valley, J. W., Gallardo, V. A., Espinoza, C., & Flannery, D. T. (2015). Sulfur-cycling fossil bacteria from the 1.8-Ga Duck Creek formation provide promising evidence of evolution's null hypothesis. *Proceedings of the National Academy of Science U.S.A.*, *112*, 2087–2092. https://doi.org/10.1073/pnas.1419241112

Schulz, H. N. (2006). The genus *Thiomargarita*. In M. Dworkin, S. Falkow, E. Rosenberg, K.-H. Schleifer, & E. Stackebrandt (Eds.), *The prokaryotes, A handbook on the biology of bacteria: Proteobacteria: Gamma subclass* (pp. 1156–1163). Springer. https://doi.org/10.1007/0-387-30746-x_47

Schulz, H. N., Brinkhoff, T., Ferdelman, T. G., Hernández Mariné, M., Teske, A., & Jørgensen, B. B. (1999). Dense populations of a giant sulfur bacterium in Namibian shelf sediments. *Science*, *284*, 493–495.

Schulz, H. N., & Schulz, H. D. (2005). Large sulfur bacteria and the formation of phosphorite. *Science*, *307*, 416–418.

Shapiro, R. S. (2022). Microbes in modern and ancient hydrocarbon seeps. In A. Kaim, J. K. Cochran, & N. H. Landman (Eds.), Topics in Geobiology *Ancient hydrocarbon seeps* (Vol. *53*, pp. 113–122). Springer. https://doi.org/10.1007/978-3-031-05623-9_4

Shen, Y., & Buick, R. (2004). The antiquity of microbial sulfate reduction. *Earth-Science Reviews*, *64*, 243–272. https://doi.org/10.1016/S0012-8252(03)00054-0

Shen, Y., Buick, R., & Canfield, D. E. (2001). Isotopic evidence for microbial sulphate reduction in the early Archaean era. *Nature*, *401*, 77–81. https://doi.org/10.1038/35065071

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. https://doi.org/10.1016/j.epsl.2009.01.018

Sibuet, M., & Olu, K. (1998). Biogeography, biodiversity and fluid dependence of deep-sea cold-seep communities at active and passive margins. *Deep-Sea Research II Topics and Studies in Oceanography*, *45*, 517–567. https://doi.org/10.1016/S0967-0645(97)00074-X

Sievert, S. M., Keine, R. P., & Schultz-Vogt, H. N. (2007). The sulfur cycle. *Oceanography*, *20*, 117–123. https://doi.org/10.5670/oceanog.2007.55

Smrzka, D., Zwicker, J., Misch, D., Walkner, C., Gier, S., Monien, P., Bohrmann, G., & Peckmann, J. (2019). Oil seepage and carbonate formation: A case study from the southern Gulf of Mexico. *Sedimentology*, *66*, 238–2353. https://doi.org/10.1111/sed.12593

Solomon, E. A., Kastner, M., Jannasch, H., Robertson, G., & Weinstein, Y. (2008). Dynamic fluid flow and chemical fluxes associated with a seafloor gas hydrate deposit on the northern Gulf of Mexico slope. *Earth and Planetary Science Letters*, *270*, 95–105. https://doi.org/10.1016/j.epsl.2008.03.024

Stevens, E. W. N., Bailey, J. V., Flood, B. E., Jones, D. S., Gilhooly, W. P., Joye, S. B., Teske, A., & Mason, O. U. (2015). Barite encrustation of benthic sulfur-oxidizing bacteria at a marine cold seep. *Geobiology*, *13*, 588–603. https://doi.org/10.1111/gbi.12154

Stüecken, E. E., Buick, R., Guy, B. M., & Koehler, M. C. (2015). Isotopic evidence for biological nitrogen fixation by molybdenum-nitrogenase from 3.2 Gyr. *Nature*, *520*, 666–669. https://doi.org/10.1038/nature14180

Sugitani, K., Mimura, K., Takeuchi, M., Lepot, K., Ito, S., & Javaux, E. J. (2015). Early evolution of large micro-organisms with cytological complexity revealed by microanalyses of 3.4 Ga organic-walled microfossils. *Geobiology*, *13*, 507–521.

Teske, A., & Nelson, D. C. (2006). The genera *Beggiatoa* and *Thioploca*. In M. Dworkin, S. Falkow, E. Rosenberg, K.-H. Schleifer, & E. Stackebrandt (Eds.), *The prokaryotes, A handbook on the biology of bacteria: Proteobacteria: Gamma subclass* (pp. 784–810). Springer.

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. https://doi.org/10.1016/j.gca.2008.08.026

Van Dover, C. L., Aharon, P., Bernhard, J. M., Caylor, E., Dorries, M., Flickinger, W., Gilhooly, W., Goffredi, S. K., Knick, K. E., Macko, S. A., Rapoport, S., Raulfs, E. C., Ruppel, C., Salerno, J. L., Seitz, R. D., Sen Gupta, B. K., Shank, T., Turnipseed, M., & Vrijnhoek, R. (2003). Blake ridge methane seeps: Characterization of a soft-sediment, chemosynthetically based ecosystem. *Deep-Sea Research Part I*, *50*, 281–300. https://www.sciencedirect.com/science/article/pii/S0967063702001620

Van Dover, C. L., German, C. R., Speer, K. G., Parson, L. M., & Vrijenhoek, R. C. (2002). Evolution and biogeography of deep-sea vent and seep invertebrates. *Science*, *295*, 1253–1257.

Vinn, O., Kupriyanova, E. K., & Kiel, S. (2013). Serpulids (Annelida, polychaeta) at Cretaceous to modern hydrocarbon seeps: Ecological and evolutionary patterns. *Palaeogeography Palaeoclimatology, Palaeoecology*, *390*, 35–41. https://doi.org/10.1016/j.palaeo.2012.08.003

Von Rad, U., Rösch, H., Berner, U., Geyh, M., Marchig, V., & Schulz, H. (1996). Authigenic carbonates derived from oxidized methane vented from the Makran accretionary prism off Pakistan. *Marine Geology*, *136*, 55–77. https://doi.org/10.1016/S0025-3227(96)00017-5

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. https://doi.org/10.1038/ngeo1238

Walliser, O. H. (1991). Hamar el Khdad (Hamar Laghdad). In: *Field meeting of the international subcommission on Devonian stratigraphy*, guidebook, Morocco 1991 Walliser, O.H., Ed. 75-79, Göttingen.

Wendt, J., Aigner, T., & Neugebauer, J. (1984). Cephalopod limestone deposition on a shallow pelagic ridge: The Tafilalt platform (upper Devonian, eastern Anti-Atlas, Morocco). *Sedimentology*, *31*, 601–625. https://doi.org/10.1111/j.1365-3091.1984.tb01226.x

Westall, F. (1999). The nature of fossil bacteria: A guide to the search for extraterrestrial life. *Journal of Geophysical Research*, *104*, 16437–16451. https://doi.org/10.1029/1998JE900051

14724669, 2024, 1, Downloaded from https://onlinelibrary.wiley.com/doi/10.1111/gbi.12581 by Test, Wiley Online Library on [23/01/2024]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

Wojdyr, M. (2010). *Fityk*: A general-purpose peak fitting program. *Journal of Applied Crystallography*, *43*, 1126–1128. https://doi.org/10.1107/S0021889810030499

Yücel, N., Sommer, S., Dale, A. W., & Pfannkuche, O. (2017). Microbial sulfide filter along a benthic redox gradient in the eastern Gotland Basin, Baltic Sea. *Frontiers Microbiology*, *8*, 169.

Zopfi, J., Kjaer, T., Nielsen, L. P., & Jørgensen, B. B. (2001). Ecology of *Thioploca* spp: Nitrate and sulfur storage in relation to chemical microgradients and influence of *Thioploca* spp. on the sedimentary nitrogen cycle. *Applied and Environmental Microbiology*, *67*, 5530–5537.

Zwicker, J., Smrzka, D., Steindl, F., Böttcher, M. E., Libowitzky, E., Kiel, S., & Peckmann, J. (2021). Mineral authigenesis within chemosynthetic microbial mats: Coated grain formation and phosphogenesis at a Cretaceous hydrocarbon seep, New Zealand. *The Depositional Record*, *7*, 294–310. https://doi.org/10.1002/dep2.123

SUPPORTING INFORMATION

Additional supporting information can be found online in the Supporting Information section at the end of this article.

How to cite this article: Smrzka, D., Zwicker, J., Schulz-Vogt, H., Little, C. T. S., Rieder, M., Meister, P., Gier, S., & Peckmann, J. (2024). Fossilized giant sulfide-oxidizing bacteria from the Devonian Hollard Mound seep deposit, Morocco. *Geobiology*, *22*, e12581. https://doi.org/10.1111/gbi.12581

14724669, 2024, 1, Downloaded from https://onlinelibrary.wiley.com/doi/10.1111/gbi.12581 by Test, Wiley Online Library on [23/01/2024]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License