Mineral authigenesis within chemosynthetic microbial mats: Coated grain formation and phosphogenesis at a Cretaceous hydrocarbon seep, New Zealand

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Abstract

Marine hydrocarbon seeps are sites of chemosynthetic microbial activity and authigenic carbonate formation. Seep limestones are typified by a range of geochemical signatures of microbial hydrocarbon oxidation, but only few seep deposits reveal mesofabrics that can be regarded as evidence of microbial activity. A Cretaceous methane-seep limestone from Waipiro Bay, New Zealand, exhibits a fabric composed of cryptocrystalline carbonate fluorapatite between carbonate coated grains and spheroidal calcite. To understand the unusual Waipiro deposit, a paragenetic sequence has been derived for coated grains, spheroidal calcite and carbonate fluorapatite using thin section petrography, scanning electron microscopy, Fourier-transform infrared spectroscopy and stable isotope geochemistry. The formation of 13C-depleted coated grains (δ13C values as low as −15.8‰ Vienna-Pee Dee Belemnite) and spheroidal calcite (δ13C values as low as −21.3‰) was favoured by hydrocarbon oxidation. Fibrous banded and botryoidal cement, a typical early diagenetic phase of hydrocarbon-seep deposits, features δ13C values as low as −22.9‰. Coated grains and spheroidal calcite grew by displacive growth in a gel-like medium, probably a microbial mat. Phosphorus is a mobile element and marine pore waters are typically undersaturated with respect to carbonate fluorapatite. Specific conditions are consequently required to retain sufficient concentrations to precipitate carbonate fluorapatite. Possible sources of phosphorus for the formation of the 13C-depleted Waipiro carbonate fluorapatite (mean δ13C value of −15.4‰) include (a) the oxidation of sedimentary organic matter by organoclastic sulphate reduction, (b) the degradation of the microbial mat itself and (c) the active release of polyphosphate by sulphide-oxidizing bacteria. This study suggests that the formation of the Cretaceous Waipiro seep limestone involved an interplay of biogeochemical processes including sulphate-driven anaerobic oxidation of methane, organoclastic sulphate reduction and possibly nitrate-dependent sulphide oxidation. It further demonstrates that
coated grains resembling oncoïds are not restricted to shallow water, photosynthesis-dependent ecosystems.

**KEYWORDS**

carbonate authigenesis, coated grains, hydrocarbon seeps, microbialites, phosphogenesis

## 1 | INTRODUCTION

Chemosynthetic microbial communities represent the most ancient form of life on Earth and are globally abundant in marine sediments today where they represent large and significant ecosystems in terms of biomass, transfer of nutrients to and from the oceans and the global carbon cycle (D’Hondt et al., 2004; Biddle et al., 2006; Jørgensen and Boetius; Orcutt et al., 2011; Kallmeyer et al., 2012). Habitats that enable the proliferation of organisms independent of sunlight and photosynthesis include sites of sea floor hydrocarbon seepage, where cold, reducing fluids provide energy for chemosynthesis-based ecosystems (Paull et al., 1984; Brooks et al., 1987; Sibuet and Olu, 1998; Jørgensen and Boetius, 2007). Hydrocarbon seeps are dynamic environments where the rates of fluid expulsion may vary on timescales from seconds to hours to years (Tryon et al., 1999, 2002; Leifer et al., 2004; Greinert et al., 2006; Klaucke et al., 2010). This variability is controlled mainly by tectonics, tidal forces and changes in sediment permeability and bottom water temperatures (Tryon et al., 2002; Solomon et al., 2008; Römer et al., 2016; Ferre et al., 2020). The effect of fluid flow dynamics is important because it affects redox conditions and the availability of chemical energy that supports chemosynthetic microbial communities (Joye et al., 2004). At seeps, methanotrophic archaea and sulphate-reducing bacteria are known to form closely associated consortia performing sulphate-driven anaerobic oxidation of methane (AOM; Boetius et al., 2000). This process triggers the precipitation of carbonate minerals and preserves traces of endemic methane-based chemosynthetic activity in the rock record (Ritger et al., 1987; Paull et al., 1992; Bohrmann et al., 1998; Peckmann et al., 2002; Bailey et al., 2009). Carbonate authigenesis can also archive fluid flow dynamics of ancient seeps. The range of mineralogical and morphological variations of seep carbonates, as well as their trace element inventory, are capable of discerning spatial and temporal seepage variability and shifting redox zones in ancient seep-impacted sediments (Feng et al., 2009; Feng and Chen, 2015).

Phosphogenesis, which refers to the formation of authigenic phosphate minerals in marine sediments, has received a lot of attention, but has only rarely been reported for hydrocarbon-seep environments. One example of phosphate mineral authigenesis in methane-rich deep-sea sediments is the formation of vivianite associated with iron-dependent AOM (cf. Liu et al., 2019). The process of marine phosphogenesis results from the interplay of ocean circulation, sedimentation rate and early diagenesis (Sheldon, 1981; Froelich et al., 1988; Ingall and Jahne, 1994; Benitez-Nelson, 2000; Schenau et al., 2000; Filippelli, 2011). While most of the phosphorus in the ocean is biologically recycled in the photic zone, only a small fraction is buried in sediments (Suess, 1980). Phosphogenesis in sea floor sediments today is frequently observed in coastal upwelling zones where suboxic to anoxic redox conditions prevail (Burnett, 1977; Föllmi, 1996; Schenau et al., 2000; Arning et al., 2009; Compton and Bergh, 2016). Phosphorus is a mobile element that is cycled rapidly between ocean bottom waters and pore waters on short timescales, and its accumulation in pore waters can be the result of microbial degradation of organic matter (Ruttenberg and Berner, 1993), reductive dissolution of iron oxides (Einsele, 1936; Slomp et al., 1998; Mitar et al., 2018) and the dissolution of bone material such as fish debris and whale-fall carcasses (Schenau et al., 2000; Smith et al., 2015). Therefore, only specific geochemical conditions allow the formation and preservation of phosphate minerals including carbonate fluorapatite (CFA), whereby a main prerequisite is to achieve and retain physico-chemical supersaturation of the aqueous solution with respect to CFA (Van Cappellen and Berner, 1991). The active involvement of microbial communities in the accumulation and retention of phosphorus in marine sediments, as well as their role in the formation of phosphorites (i.e. rocks that contain at least 18 wt% P₂O₅) has long been suggested (Williams and Reimers, 1983; Dahanayake and Krumbein, 1985; Föllmi, 1996), and appears to be one key to understand the authigenesis of phosphate minerals.

This study presents an unusual hydrocarbon-seep deposit, which formed as a result of AOM-induced carbonate precipitation and phosphogenesis. With both processes being archived in the Cretaceous rock, the Waipiro seep deposit offers insight into the interplay of biogeochemical processes, which do not typically co-occur at hydrocarbon seeps. The occurrence of carbonate microfabrics such as coated grains reveals that deep-water seep environments sustained by chemosynthesis may produce similar microbial precipitates to some shallow-water environments sustained by photosynthesis. The finding of coated grains and spheroids within a seep limestone confirms that the reconstruction of water depth based on microbial rock fabrics may yield ambiguous results.
unless the metabolism of the respective microbial communities is understood.

2 GEOLOGICAL SETTING

The regional geology of the Raukumara Peninsula is related to Neogene convergence along the Hikurangi-Kermadec Subduction Zone (Lewis and Pettinga, 1993). The Hikurangi subduction zone (Figure 1A) is characterized by the low-angle, near-orthogonal submergence of the Hikurangi Plateau underneath the Raukumara Peninsula at a rate of 40–50 mm/year, giving rise to the several hundred kilometre-long Hikurangi trough along the east coast of North Island (Davey et al., 1986; Reyners et al., 1999). Crustal underplating at the northern Hikurangi Margin has been active for at least 20 Myr, triggering the large-scale accumulation of accreting subducted marine sediment and eroded material (Bassett et al., 2010). The Raukumara Peninsula is being uplifted to this day due to buoyancy created by the underplated sediments, whereby the uplift rates are some of the highest seen along the entire Hikurangi-Kermadec subduction zone (Walcott, 1987; Berryman et al., 1989). The main tectonic zones of the north-western part of North Island are the offshore outer fore arc, the onshore inner fore arc and the inner fore arc backstop, whereby the latter two units represent a relict accretionary wedge now exposed on land (Figure 1A,B; Clark et al., 2010). The Raukumara Peninsula itself consists of three distinct tectonic units, the Raukumara Range, the East Coast allochthon and Neogene sedimentary rocks that partly overlie the allochthon (Figure 1B; Reyners et al., 1999). The Raukumara Range represents the forearc backstop and comprises the Jurassic to Cretaceous Torlesse Terrane (Figure 1B; Mazengarb et al., 2000). The inner forearc is composed of autochthonous and allochthonous continental margin sedimentary successions, which are overlain by mostly Neogene sedimentary rocks (Figure 1B; Mazengarb et al., 2000). The East Coast allochthon is a sequence of Early Cretaceous to Oligocene units of sedimentary and igneous origin, which was emplaced upon the Raukumara Peninsula due to subduction of the Hikurangi margin during the early Miocene (Mazengarb et al., 2000).

The study locality at Waipiro Bay lies within the East Coast Allochthon tectonic unit (Figure 1B), adjacent to outcrops of undifferentiated mélangé that was formed in association with emplacement of the East Coast Allochthon (Kiel et al., 2013). The sampled boulder was collected as a float at the southern end of Waipiro Bay and is probably derived from the mélangé, but its exact provenance cannot be determined. It was dated as mid-Campanian (Late Cretaceous) based on well-preserved dinoflagellate cysts and contained a single specimen of a large lucinid bivalve probably belonging to the genus Ezolucina (Kiel et al., 2013). Members of this bivalve family live in symbiosis with sulphide-oxidizing bacteria, from which they derive a large part of their nutrition, and are a common faunal element at seeps at least since the late Jurassic (Kiel, 2013).

FIGURE 1 (A) Map of New Zealand highlighting the study area on Raukumara Peninsula. (B) Geological map of Raukumara Peninsula (cf. Kiel et al., 2013)
3 | MATERIALS AND METHODS

One large rock sample (65 × 35 cm) was collected as a loose boulder along a coastal section of Waipiro Bay and was named Waipiro I (see Kiel et al., 2013 for details). This sample was cut into several smaller pieces and slabs for analyses. Thin sections of approximately 50 µm thickness were prepared for standard petrographical and fluorescence microscopy. Some thin sections were partially stained with a mixture of potassium ferricyanide and alizarin red solution dissolved in hydrochloric acid to enable the discrimination of various carbonate minerals (Dickson, 1966). Petrographical observations were conducted using a Leica DM4500 P polarization microscope. Photomicrographs were taken with Leica DFC 420 and DFC 450C cameras, using the Leica Application Suite 3.2.0 and 4.4.0 software. For fluorescence microscopy, a Nikon SMZ 1500 stereomicroscope connected to a Prog. Res Speed XT core 5 camera was used. Image analysis and camera control were conducted using the Prog.Res Capture pro 2.8 software. Sample powders for carbon and oxygen stable isotope analyses of the Waipiro I limestone were obtained from polished slabs using a handheld micro-drill, and analyses were conducted at the MARUM Center for Marine and Environmental Sciences, Bremen, using a Finnigan MAT 251 gas isotope ratio mass spectrometer equipped with a Kiel III automated carbonate preparation device. Standard deviation of the Solnhofen limestone standard over the period of measurement amounted to 0.03% for δ13C and 0.08% for δ18O values. Reproducibility was assessed by replicate analysis of each sample. All values are reported in per mil relative to the Vienna PeeDee Belemnite (V-PDB) standard. The stable isotope composition of CFA samples was measured at the Leibniz Institute for Baltic Sea Research (IOW) after selective dissolution of co-existing calcite (50 h at room temperature; modified after Kolodny and Kaplan, 1970) using a Thermo Scientific Gasbench II connected to a Thermo Finnigan MAT 253 gas mass spectrometer via a Thermo Scientific Conflo IV split interface. Millimetre-sized subsamples were obtained from whole rock samples and prepared for scanning electron microscopy (SEM). The SEM and elemental mapping was conducted on a FEI Inspect S equipped with secondary electron and backscatter electron detectors, and an energy dispersive X-ray detection unit (EDAX Apollo XV) at the Geoscience Department of the University of Vienna. Data processing was conducted using the EDAX TEAM™ V3.1.1 software. Fourier-transform infrared (FTIR) spectra were acquired from 370 to 4,000 cm⁻¹ on a Bruker Tensor 27 FTIR spectrometer equipped with a globar MIR light source, a KBr beam splitter and a DLaTGS detector. A polished thin section was pressed on the 2 × 3 mm diamond window of a Harrick MVP 2 diamond attenuated total reflectance (ATR) accessory in such a way that either the apatite or the calcite components were predominantly probed. For comparison, spectra of blackboard chalk and a pure fluorapatite crystal from Durango, Mexico, were acquired. Sample and background spectra were averaged from 32 scans at 4 cm⁻¹ spectral resolution. Background spectra were obtained from the empty ATR unit. Data handling was performed with OPUS 5.5 software (Bruker Optik GmbH, 2005).

4 | RESULTS

4.1 | Petrography

The Waipiro I limestone encloses coated grains of different sizes and shapes, which are embedded in two domains (Figure 2). Both domains also include spheroidal calcite and, locally, silica grains, with the pore space between the components filled by two types of cement, corresponding to the two domains. The first domain consists of spheroidal calcite surrounded by CFA (Figures 2 and 3A), while the second domain consists of spheroidal calcite surrounded by finely crystalline calcite cement (Figures 2 and 3B). The large coated grains are 3–11 mm in diameter and are oval to spherical in shape with a non-detrital, micritic nucleus (Figure 4A). Some coated grains contain silica (Figures 4 and 5A,B), which appears to replace micrite. Micritic nuclei are surrounded by several irregular layers, variable in thickness, which are composed of silica (Figure 4) or micrite (Figures 4B and 5). Some of these layers exhibit varying degrees of fluorescence (Figure 5B,D). Spheroidal calcite is on average ten times smaller than the coated grains, measuring between 0.4 and 0.6 mm in diameter (Figures 2, 3 and 6A,B). In contrast to the coated grains, spheroidal calcite is composed of homogenous micrite, revealing no internal structure in plane-polarized...
light and appearing as radiating polycrystals under cross-polarized light. Locally present silica grains are not detrital in origin and may result from the silicification of spheroidal calcite.

Carbonate fluorapatite consists of microcrystalline subhedral crystals (Figure 6B,C). It is porous with porosity declining toward the spheroidal calcite while increasing toward the centre of locally present pore spaces, suggesting phosphate mineral aggregation from spheroidal calcite towards the pore space. Pyrite is dispersed throughout the coated grains, spheroidal calcite and the pore-filling cements. It occurs as frambooidal aggregates (Figure 6D), as well as idiomorphic grains. Another type of cement present in the samples is fibrous, banded and botryoidal calcite cement. Where banded and botryoidal calcite cement occurs in a paragenetic sequence, it postdates micrite and predates equant calcite cement (Figure 7A). Silica occurs irregularly distributed between micrite and banded and botryoidal calcite (Figure 7A), interpreted as reflecting later stage silicification. An accessory mineral phase is barite, represented by large crystals up to 0.4 mm in length (Figure 7B).

4.2 | FT-IR spectroscopy

Figure 8 shows FT-IR ATR spectra of CFA and calcite from the Waipiro I limestone compared to spectra of pure carbonate-free fluorapatite from Durango, Mexico (Becker et al., 2016), a CFA from Limburg an der Lahn, Germany (RRUFF data base R050529; ca 20% of the phosphate sites is substituted by carbonate; Downs, 2006; Lafuente et al., 2015), and a calcite reference acquired from a piece of blackboard chalk. The wavenumber region from 400 to 1,600 cm\(^{-1}\) was chosen for the figure as it displays all fundamental vibrations of the phosphate and carbonate anion groups. Regarding the exact peak positions, it must be emphasized that vibrational bands in ATR spectra are slightly red-shifted to lower wavenumbers due to the impact of the complex refractive index instead of pure absorption (Harrick, 1967). Whereas pure, carbonate-free fluorapatite shows only the overlapping stretching bands \(\nu_{1,3} (ca\ 1,100–930 \text{ cm}^{-1})\) and bending modes \(\nu_{2,4} (ca\ 630–540, 470 \text{ cm}^{-1})\) of the phosphate groups, with a flat baseline above 1,100 cm\(^{-1}\), Waipiro I CFA and...
CFA from the RRUFF data base (Downs, 2006; Lafuente et al., 2015) reveal additional characteristic bands at ca 1,425 and 1,450 cm⁻¹ (double-headed arrows in Figure 8) that have been assigned to the anti-symmetric stretching vibrations ν₃ of carbonate groups replacing phosphate groups in the apatite structure (Hofmann, 1997). In addition, the spectrum of CFA from Waipiro I reveals minor vibrational bands ν₂,₄ of carbonate anion groups of the surrounding carbonate minerals at ca 1,400, 860 and 710 cm⁻¹, respectively (White, 1974; Böttcher et al., 1997). These results confirm the presence of carbonate groups in the structure of Waipiro I CFA.

### 4.3 Stable isotopes

The carbon and oxygen stable isotope compositions of coated grains, carbonate spheroids, banded and botryoidal calcite and structural carbonate within CFA were determined (Figure 9). Mean δ¹³C and δ¹⁸O values of coated grains are −12.1‰ and −5.0‰, respectively, with δ¹³C values ranging from −15.8‰ to −6.4‰, and δ¹⁸O values ranging from −5.5‰ to −3.5‰. Carbon stable isotope values of carbonate spheroids show a larger range between the lowest value of −21.3‰ and the highest at −8.1‰. Oxygen stable isotope values of spheroidal calcite fall between −7.2‰ and −4.1‰, with a mean δ¹⁸O value of −5.7‰ and a mean δ¹³C value of −14.1‰. Banded and botryoidal cement exhibits the lowest δ¹³C values of all measured samples between −22.9‰ and −18.3‰ with a mean δ¹³C value of −20.6‰. Oxygen stable isotope values of banded and botryoidal cement average −4.4‰. Mean carbon and oxygen stable isotope values of carbonate ions within CFA are −15.4‰ and −5.4‰, respectively, similar to values obtained for spheroids.

### 5 DISCUSSION

#### 5.1 Microbially mediated formation of coated grains at an ancient hydrocarbon seep

Based on carbon stable isotope measurements and invertebrate palaeontology, the Waipiro I limestone studied herein...
has been previously interpreted as an ancient hydrocarbon seep deposit (Kiel et al., 2013). This interpretation is corroborated by the stable carbon isotope data obtained from coated grains, spheroidal calcite and banded and botryoidal cement, reflecting $^{13}$C-depletion compared to bioskeletal marine carbonates. The lowest $\delta^{13}$C value of banded and botryoidal cement of $-22.9‰$ does, however, not reflect enough depletion in $^{13}$C to confirm that seepage fluids were dominated by methane, and oil seepage cannot be excluded (Kiel and Peckmann, 2007; Smrzka et al., 2019). Unfortunately, the Waipiro I limestone proved to be thermally mature, with no lipid biomarkers of the depositional environment preserved. Based on this and the lack of element geochemical data (Smrzka et al., 2016), the composition of seepage fluids cannot be further constrained. Banded and botryoidal cement is a diagnostic and widespread carbonate phase at seeps, and an authigenic mineral phase associated with AOM (Beauchamp and Savard, 1992; Savard et al., 1996; Peckmann et al., 2002; Zwicker et al., 2018). This carbonate phase exhibits the lowest mean $\delta^{13}$C values of $-20.6‰$, a value that can be attributed to hydrocarbon oxidation (Peckmann and Thiel, 2004; Kiel et al., 2013). The mean $\delta^{13}$C values of coated grains and spheroidal calcite are slightly less negative, which may be due to mixing of carbon sources such as methane, higher hydrocarbons, or (bi)carbonate from seawater (Peckmann and Thiel, 2004; Zwicker et al., 2015; Smrzka et al., 2019). Similar to banded and botryoidal cement, authigenic barite commonly occurs at marine seeps (Aloisi et al., 2004). The accessory barite of the Waipiro I deposit is consequently in accord with the interpreted palaeoenvironmental setting.

Coated grains similar to those of the Waipiro I limestone have been reported previously from one modern and one ancient methane-seep deposit. Greinert et al. (2002) observed round to oval, concentrically layered carbonate fabrics in limestones from an active methane seep from the Aleutian margin. These authors reported micritic oncoids and argued that carbonate formation of individual layers was induced by the encrustation of microbial mats. It was further suggested that the coated grains from the Aleutian margin grew within the sulphate-methane transition zone, in the vicinity of worm tubes and other substrates that would have allowed for biofilm formation by AOM communities. Similar, yet smaller ooid-like coated grains were reported from a Late Cretaceous seep deposit from Japan (Jenkins et al., 2008). It was argued...
that the formation of the Japanese coated grains took place close to the sediment–water interface as a consequence of AOM at the Cretaceous seep and two formation scenarios were suggested: (a) agitation of carbonate particles due to intense seepage and (b) coated grain formation within a microbial mat (Jenkins et al., 2008).

The studied Waipiro I limestone shows early diagenetic features represented by coated grains and spheroidal calcite postdated by CFA and calcite cement. The oval to rounded shape of coated grains and spheroidal calcite suggests concentric, displacive growth within a plastic medium that provided the necessary stabilization and sufficient time to allow for the growth of centimetre-sized coated grains. Although unhindered concentric growth within the bottom water due to agitation (possibly caused by vigorous seepage, sensu Jenkins et al., 2008) seems an alternative option, the centimetre size of the largest coated grains does not agree with this interpretation (Hjulstrøm, 1939). Growth within a gel-like medium, allowing for displacive growth of coated grains and spheroidal calcite, is thus the most probable explanation. An alternative medium for displacive growth could have been waterlogged clays. However, the lack of evidence for nucleation in clay also points to microbial mats as the most probable environment for the precipitation of the spherulitic carbonate phases, similar to other microbial carbonates forming in association with extracellular polymeric substances (EPS) of microbial mats (Braissant et al., 2003; Sanchez-Moral et al., 2003; Dupraz et al., 2009).

Spherulitic carbonate grains are common in modern microbial mats, where supersaturation triggered by metabolic processes, as well as the composition and structure of the EPS, favour the formation of spherulitic morphologies of carbonate minerals (Chafetz and Buczynski, 1992; Défarge et al., 1996; Kawaguchi and Decho, 2002; Bosak and Newman, 2005; Spadafora et al., 2010). Although many spherulitic carbonates found in modern microbial mats are less than 10 µm in size, and are thus much smaller than spheroidal calcite found in the Waipiro I limestones, larger spherulitic aggregates may have formed from initially smaller crystals. Brehm et al. (2006) have demonstrated the growth of larger spherulitic carbonate aggregates from tiny scleres, which merge and were found to build larger spherulitic structures in cyanobacterial mats. In the same study the feasibility of spherulitic carbonate formation without the need of a nucleus, which is also absent in Waipiro I spheroidal calcite (Figures 3 and 6A,B), was documented.

In contrast to spheroidal calcite, the Waipiro I coated grains are much larger, exhibit distinct lamination and micritic nuclei (Figure 5). Coated grains of variable size are

**FIGURE 7** Thin section photomicrographs of Waipiro I limestones, plane-polarized light. (A) Micrite (m), banded and botryoidal cement (bbc), patches of silica (si) intermingled with micrite and banded and botryoidal calcite, and equant calcite (ec) filling pore space. (B) Large barite (ba) crystals within micrite (m)

**FIGURE 8** Fourier-transform infrared (FTIR) attenuated total reflectance (ATR) spectra. Spectra of (1) blackboard chalk, (2) calcite of Waipiro I limestone, (3) carbonate-bearing fluorapatite (RRUFF database; Downs, 2006; Lafuente et al., 2015), (4) carbonate fluorapatite of Waipiro I limestone and (5) carbonate-free fluorapatite from Durango, Mexico (Becker et al., 2016); broken lines and shaded areas indicate the positions and areas of certain vibrations of the anion groups. The two double arrows at ca 1,425 and 1,450 cm⁻¹ indicate the anti-symmetric stretching ν₃ modes of B-type carbonate groups in apatite. Spectra have been vertically normalized and offset for better visibility. See text for details
typical features of modern microbial mats, whereby the formation of laminae has been directly associated with microbial biofilms colonizing a preexisting nucleus, using the nucleus as a growth template (Davaud and Girardclos, 2001; Duguid et al., 2010; Pacton et al., 2012; Diaz et al., 2017). The individual layers of the Waipiro I coated grains show different degrees of fluorescence (Figure 5B,D), which suggest varying contents of organic matter. This observation agrees with the interpretation of concentric lamination as a biosedimentary feature, whereby individual layers reflect mineralization within microbial biofilms. The growth process of the coated grains proceeded outward, whereby mineralizing microbial biofilms repeatedly colonized a carbonate nucleus (Gerdes et al., 1994). With the recognition of coated grain formation in deep-sea environments (Greinert et al., 2002; this study), it is important to realize that the formation of these mesofabrics is not restricted to shallow water environments. An identification of the dominant microbial metabolisms involved in coated grain formation is consequently required to correctly interpret the palaeoenvironmental setting.

5.2 Phosphogenesis at an ancient hydrocarbon seep

Carbonate fluorapatite is an uncommon authigenic mineral at marine hydrocarbon seeps. In marine sediments, the precipitation of CFA is usually preceded by the formation of amorphous, metastable precursor phases such as amorphous calcium phosphate and hydroxyapatite (Lazic, 1995; Gunnars et al., 2004). The transformation to the more stable CFA is usually slow, and requires diffusion of fluorine from seawater, which reduces CFA solubility and accelerates its crystal growth (Van Cappellen and Berner, 1991; Krajewski et al., 1994; Soudry and Nathan, 2001). Carbonate fluorapatite formation requires high concentrations of dissolved phosphorus in sedimentary pore waters in order to attain supersaturation. Since phosphorus concentration in the oceans is low, additional sources apart from seawater phosphorus are needed to precipitate phosphate minerals in marine sediments. Phosphorus may derive from organic matter decomposition by bacteria or the decomposition of bone material (Van Cappellen and Berner, 1988, 1991; Glenn et al., 1994; Schenau et al., 2000). Conditions for CFA supersaturation in pore waters are usually attained in sediments below upwelling zones, or within microbial mats that thrive in shallow sediments directly below the sediment–water interface, where early diagenetic CFA formation can be observed (Jahnke et al., 1983; Van Cappellen and Berner, 1988, 1991; Ruttenberg and Berner, 1993; Wilby et al., 1996; Soudry and Nathan, 2001; Berndmeyer et al., 2012).

The microbial degradation of organic matter during early diagenesis in the suboxic zone of marine sediments plays a key role in the liberation and cycling of phosphorus (Föllmi, 1996; Wilby et al., 1996; Benitez-Nelson, 2000). The Waipiro I $^{13}$C-depleted coated grains and spheroidal calcite, partially cemented by the CFA, suggest that the rock fabric represents fossilized microbial mats that thrived at an ancient hydrocarbon seep (see above). As AOM and organoclastic sulphate reduction are anaerobic processes, redox conditions in ambient pore waters must have been at least suboxic or more probably anoxic. Most modern seep carbonates form in shallow sediments close to the sediment–water interface, where active AOM communities thrive (Knittel et al., 2005; Orcutt et al., 2005; Treude et al., 2005) and occasionally form biofilms within seep sediments (Briggs et al., 2011; Gründger et al., 2019). The primary trigger for carbonate precipitation in such settings is the metabolism itself, which raises alkalinity and the saturation state of calcium carbonate minerals. This

![Cross-plot of carbon and oxygen stable isotope values in per mil versus V-PDB of carbonate phases and carbonate fluorapatite, Waipiro limestone](image-url)
mechanism favoured the formation of Waipiro I coated grains and spheroidal calcite. Calcium carbonate precipitation results in a decrease in pH and alkalinity, which may have contributed to the establishment of favourable conditions for CFA formation under sulphate-reducing conditions (Tribovillard et al., 2010). Possible sources of phosphorus in the environment of CFA precipitation are microbial degradation of sedimentary organic matter or of the organic material of the mat itself (Jørgensen, 1982; Reimers et al., 1990; Ferdelman et al., 1999; Arning et al., 2009). Another possible source of phosphorus is the metabolic activity of so-called ‘giant’ sulphide-oxidizing bacteria, which may accumulate and liberate phosphorus (Schulz and Schulz, 2005; Sievert et al., 2007; Zopfi et al., 2008; Goldhammer et al., 2010; Holmkvist et al., 2010). These chemotrophic bacteria are capable of storing polyphosphate within their cells during favourable environmental conditions, and release phosphate under anoxic conditions (Schulz and Schulz, 2005). The giant sulphide-oxidizing bacteria, including Beggiaota, Thiomargarita and Thioploca, thrive on chemosynthetic energy provided by the oxidation of reduced sulphur compounds, which are in turn produced by the sulphate-driven oxidation of organic matter and methane (Boetius and Suess, 2004; Holmkvist et al., 2011; Fike et al., 2016). Interestingly, sulphide-oxidizing bacteria are abundant at many modern methane seeps (Boetius et al., 2000; Mills et al., 2004; Niemann et al., 2006), oil seeps (Joye et al., 2004; Sahling et al., 2016), and have been suggested to have occurred at some ancient seeps (Peckmann et al., 2004). Despite their close association with the accumulation of phosphate in sea floor sediments, phosphate minerals are apparently uncommon at modern seeps. Likewise, phosphate minerals have only rarely been documented in ancient seep deposits (Peckmann et al., 2005), although microbially induced phosphogenesis may have occurred in marine environments since the Precambrian (Soudry and Champetier, 1983; Williams and Reimers, 1983; Dahanayake and Krumbein, 1985; Bailey et al., 2007, 2013).

Anaerobic oxidation of methane is a strictly anaerobic process, and potential sulphide oxidizers present at the seep site may have been able to couple sulphide oxidation to nitrate reduction, in a similar manner to the genus Thioploca that does not depend on molecular oxygen as an electron acceptor (Kühl and Jørgensen, 1992; Fossing et al., 1995; Jørgensen and Gallardo, 1999). Multiple metabolic processes are known to promote carbonate precipitation, including photosynthesis, some modes of organoclastic sulphate reduction, sulphate-driven AOM, sulphate-driven hydrocarbon oxidation, and some modes of methanogenesis (Ritger et al., 1987; Visscher et al., 1998; Teal et al., 2000; Peckmann and Thiel, 2004; Roberts et al., 2004; Dupraz et al., 2009; Sńrzkza et al., 2019). Himmler et al. (2018) provided evidence for carbonate formation induced by nitrate-dependent sulphide oxidation at methane seeps offshore Pakistan based on geochemical modelling and preserved filamentous microfossils interpreted as remains of Thioploca. A possible scenario that may explain the observed rock fabric and paragenetic sequence of the Waipiro I deposit involves both an AOM consortium and sulphide-oxidizing bacteria coupling sulphide oxidation to nitrate reduction. The microbial consortium mediating AOM induced an increase in alkalinity, which triggered the formation of coated grains and spheroidal calcite within microbial mats. The chemosynthetic microbial mat probably harboured not only AOM consortia but also sulphide oxidizers as encountered in modern chemosynthetic microbial mats on the sea floor today (Boetius and Suess, 2004; Treude et al., 2005; Niemann et al., 2006; Preisler et al., 2007; Grünke et al., 2011). An envisioned scenario is that the microbial mat was located in the suboxic to anoxic zone of shallow sediments close to the sea floor (Arning et al., 2009), where sulphide-oxidizing bacteria coupled their metabolism to nitrate reduction above the zone of AOM and provided phosphorus to solution via the active breakdown of stored polyphosphate when the environment became episodically sulphidic (Schulz and Schulz, 2005; Brock and Schulz-Vogt, 2011).

Specific conditions must have been present that enabled the retention of phosphorus in the microbial mat. The cohesive EPS meshwork of the bacterial mat may have hindered the diffusion of phosphorus into bottom waters, causing pore water supersaturation and subsequent precipitation of amorphous or other metastable phosphate minerals (Soudry and Nathan, 2001; Lécuyer et al., 2010; Löfler et al., 2019). Since phosphate minerals such as hydroxyapatite and CFA are less soluble at lower pH than calcite (Nathan and Sass, 1981; Coleman, 1985; Van Cappellen and Berner, 1991; Carlsson et al., 1997), precipitation of apatite precursors only occurred after calcite precipitation, which lowered alkalinity and pH in the ambient solution by consuming carbonate ions and releasing protons (Tribovillard et al., 2010). Therefore, phosphate accumulation and subsequent apatite precipitation occurred during degradation of the microbial mat, releasing dissolved phosphorus. This scenario explains why CFA formation postdated carbonate authogenesis, although sulphide oxidation would have occurred within the microbial mat, but above the zone of AOM. Moreover, only rapid carbonate cementation and phosphate mineral formation would have retained the structure of the microbial mat with coated grains and spheroidal calcite (Figure 2). The phosphate minerals were probably amorphous or other metastable precursors at first, and then re-crystallized to more stable CFA (Compton et al., 2002; Lécuyer et al., 2010; Löfler et al., 2019).

Apart from the preservation of the microbial rock fabric, there are further observations that indicate that formation of CFA must have occurred during or shortly after mat decomposition. First, the occurrence of pyrite dispersed between CFA (Figure 6D) suggests that sulphate reduction had not completely ceased after the onset of phosphorus liberation,
agreeing with the concept that a combination of sulphate reduction and sulphide oxidation promotes phosphogenesis (Arning et al., 2009). Second, coated grains and spheroidal calcite show a substantial range in δ13C values, suggesting a contribution from other carbon sources of carbonate besides the oxidation of methane or hydrocarbons. Assuming that coated grains and spheroidal calcite formed within a microbial mat, an admixture of carbonate species resulting from organoclastic sulphate reduction (i.e. microbial sulphate reduction fuelled by the oxidation of buried organic matter) or, to a lesser degree, bicarbonate from sedimentary pore water or seawater may have diluted the otherwise more 13C-depleted pool caused by hydrocarbon oxidation (Peckmann and Thiel, 2004). The δ13C values of carbonate within CFA are less negative than the most negative values of coated grains, spheroidal calcite, and banded and botryoidal cement, also pointing to mixed carbon sources possibly including organic matter, methane, hydrocarbons and seawater-derived bicarbonate. Still, the overall overlap of δ13C values of carbonate incorporated in CFA (mean δ13C value of −15.4‰) and the calcium carbonate fabrics indicate that the former precipitated in the same microenvironment as the carbonate minerals during early diagenesis.

The conceived formation scenario is summarized in a cartoon (Figure 10). Coated grains and spheroidal calcite formed in a gel-like medium, a microbial mat that was situated close to or at the sediment–water interface (SWI) or within sea floor sediments. Coated grains grew within the gel-like microbial mat by displacive growth. The mat was stabilized by extracellular polymeric substances (EPS) secreted by chemotrophic microorganisms. (B) Close up image of the microbial mat in (A); activity of microbial communities leads to the release of phosphate, which is trapped in the microbial mat enabling supersaturation of apatite. (C1) Continuous phosphate release leads to carbonate fluorapatite (CFA) precipitation in the degrading part of the mat, while active microbial communities still thrive in the upper part near the SWI. (C2) Continuous sedimentation, mat shrinkage during decomposition, dewatering and cementation of void space by apatite preserve the rock fabric of Waipiro I limestones (cf. Figure 2). See text for details. No scale implied.

**FIGURE 10** Cartoon illustrating the envisaged processes producing the Waipiro I seep deposit with its microbial mesofabrics and microfabrics. (A) Microbial mat growing close to or at the sediment–water interface (SWI) or within sea floor sediments. Coated grains grew within the gel-like microbial mat by displacive growth. The mat was stabilized by extracellular polymeric substances (EPS) secreted by chemotrophic microorganisms. (B) Close up image of the microbial mat in (A); activity of microbial communities leads to the release of phosphate, which is trapped in the microbial mat enabling supersaturation of apatite. (C1) Continuous phosphate release leads to carbonate fluorapatite (CFA) precipitation in the degrading part of the mat, while active microbial communities still thrive in the upper part near the SWI. (C2) Continuous sedimentation, mat shrinkage during decomposition, dewatering and cementation of void space by apatite preserve the rock fabric of Waipiro I limestones (cf. Figure 2). See text for details. No scale implied.
released phosphate to the pore water (Figure 10B), leading to favourable conditions for apatite formation. Phosphate minerals precipitated in the course of mat decomposition, minimizing the loss of dissolved phosphate to bottom waters (Figure 10C1). Retention of phosphorus in the degrading mat created the conditions required for the precipitation of amorphous phosphate phases, which transformed into CFA during early diagenesis. The observed rock fabric of coated grains, spheroidal calcite and CFA suggests that continued mat decomposition and shrinking pushed individual spheroidal calcite grains closer to each other (Figure 6A,B) and closer to the larger coated grains (Figure 10C2), resulting in the observed rock fabric (Figure 2). The presence of thick microbial mats has further implications for seepage dynamics at this ancient seep site. Because microbial mats are indicators of vigorous gas venting at modern seeps (Tryon and Brown, 2001), the Waipiro I seep site probably emitted large quantities of gas and reduced fluids over a considerable period of time in order to support these lush microbial communities.

6 CONCLUSIONS

This study reports an unusual case of phosphogenesis at an ancient hydrocarbon seep. The rock fabric of the seep limestones features large coated grains and spheroidal calcite that are postdated by CFA. Coated grains and spheroidal calcite are interpreted as having formed in a microbial mat, allowing for the displacive growth of the spherulitic carbonates in a gel-like medium. Low δ^{13}C values of coated grains, spheroidal calcite, and associated banded and botryoidal cement agree with mixing of various carbon sources including carbonate species released by AOM, organoclastic sulphate reduction and, to a minor extent, seawater bicarbonate. Fourier-transform infrared spectroscopy documents the presence of carbonate ions within the apatite lattice, confirming that the phosphate mineral is CFA. Possible sources of phosphorus for CFA formation include (a) the oxidation of sedimentary organic matter by organoclastic sulphate reduction, (b) the heterotrophic degradation of the microbial mat itself and (c) the active release of polyphosphate by sulphide-oxidizing bacteria. Mineral authigenesis resulting in the formation of the Waipiro I seep deposit involved several biogeochemical processes. The anaerobic oxidation of methane, probably in conjunction with organoclastic sulphate reduction, triggered carbonate precipitation (coated grains, spheroidal calcite, banded and botryoidal cement). Precipitation of calcium carbonate minerals led to a decrease in pH and alkalinity in pore waters, which favoured the stability of CFA. Sulphate-reducing bacteria involved in the degradation of the microbial mat, as suggested by the presence of authigenic pyrite or, possibly, polyphosphate-storing sulphide-oxidizing bacteria provided a source of phosphorus for apatite formation. This study reveals that not only modern hydrocarbon seeps sustain the growth of chemosynthetic microbial mats, but that such mats occurred at ancient seeps as well. Although seep carbonates form by a biogeochemical process (i.e. AOM), microbial rock fabrics are not always preserved in seep limestones. The Waipiro I seep deposit reveals striking microbial fabrics, but rock fabrics like the observed large coated grains are commonly interpreted as evidence for formation in phototrophic microbial mats and shallow-water settings. Therefore, it is important to realize that features such as coated grains are not necessarily an indicator for shallow water conditions or phototropic palaeoenvironments.

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DATA AVAILABILITY STATEMENT

The authors confirm that the data supporting the findings of this study are available within the article.

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