Hybrid Carbonates: *in situ* abiotic, microbial and skeletal co-precipitates

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ABSTRACT

Abiotic, Bioinduced and Biocontrolled carbonates are process-based sediment categories. They successively reflect increasing levels of biotic control over carbonate precipitation from aqueous solutions, are often closely linked to depositional environment, and change with time. Hybrid Carbonates are intimate *in situ* combinations of two or more of these categories. Hybrid Carbonates are widespread and diverse in the marine geological record and reflect large-scale changes in carbonate precipitation through time. They also occur in fluvial and lacustrine carbonates, marine and non-marine reef systems, and methane seep deposits. Plots of Hybrid Carbonate composition in time and space reveal complex 'backtracking' and 'looping' patterns that reflect changes in environmental conditions and biological processes of carbonate production. Recognition of *hybridity* emphasizes the importance of distinguishing abiotic and bioinduced precipitates. Until they were diversified by Skeletal Carbonates in the late Proterozoic, Precambrian Hybrid Carbonates were Abiotic-Bioinduced combinations. During the Phanerozoic Hybrid Carbonates were conspicuous during periods of overlap or transition between intervals of Microbial and Skeletal carbonate abundance. Microbial-Skeletal Dual Hybrids are common during the Cambrian-mid Ordovician, Late Devonian-Mississippian, and Late Jurassic-Early Cretaceous. Abiotic-Microbial-Skeletal Triple Hybrids were common from Late Pennsylvanian to mid-Triassic. Shallow marine Hybrid Carbonates declined in abundance after the mid-Cretaceous, although Late Cenozoic reefs contain some striking examples of Microbial-Skeletal Hybrids. Recognition of Hybrid Carbonates draws attention to fundamental processes underlying carbonate sedimentation, and their patterns and drivers of change in time and space.

1. Introduction

Abiotic and biological processes are often both involved in carbonate precipitation. As a result, the history of sedimentary carbonates reflects long-term changes in seawater chemistry as well as in biological evolution (James and Jones, 2015). This is evident even at the broadest scale. Precambrian carbonates are essentially abiotic and microbial (Grotzinger, 1990; Grotzinger and Knoll, 1999), whereas those of the Phanerozoic - especially after the mid-Ordovician - are often dominated by algal and invertebrate skeletons (Knoll and Fischer, 2011). Most carbonate sediments are intrabasinal in origin (Wilson, 1975) and therefore directly reflect their origins as precipitates from aqueous solutions under Earth-surface conditions (Lippmann, 1973; Stumm and Morgan, 1996). This intimate link with depositional environment has been aptly expressed: 'Carbonate sediments are born, not made' (James, 1977, p. 123). This attribute fostered studies of distinct spatial associations of process-based carbonates: 'carbonate factories' (Wilson, 1975, p. 4). In a series of pioneering contributions, Schlager (2000, 2003, 2005) integrated the carbonate factory concept with that of underlying precipitation processes. He suggested, for example, that the 'tropical shallow-water factory' is dominated by biocontrolled and abiotic precipitates, while the 'mud-mound factory' is dominated by bioinduced and abiotic precipitates (Schlager, 2003, p. 445). In addition, he showed how patterns of abiotic, bioinduced and biocontrolled carbonate production can change through time, e.g., in response to biotic crises (Schlager, 2003, fig. 13).

Here we develop this process-based approach by focusing on '*intimate in place associations of abiotic, bioinduced and biocontrolled carbonates*'. We term these combinations 'Hybrid Carbonates' (Riding, 2008; Riding and Virgone, 2018). The proportions of these three basic carbonate categories (abiotic, bioinduced, biocontrolled) define Hybrid Carbonate composition. Furthermore, this sequence from abiotic to bioinduced to biocontrolled carbonates is a trend of decreasing dependence on carbonate saturation state (Mann, 1983). Whereas abiotic and bioinduced precipitates require environmental conditions that enhance carbonate precipitation, biocontrolled calcification is less

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environmentally dependent (Section 2). Consequently, all Hybrid Carbonates broadly reflect elevated carbonate saturation state since their formation requires precipitation of at least one of either Abiotic or Microbial carbonate. Hybrid Carbonates are important because they are widespread in time and space and can reflect critical transformations in biosphere and Earth surface processes. We focus in particular on the Phanerozoic marine record since this contains numerous well-documented examples, but we also more briefly consider Hybrid Carbonates in the Precambrian and in present-day non-marine environments, to extend and explore Hybrid Carbonate concepts.

2. Categories of carbonate precipitate

The ability of both inorganic and organic processes to promote carbonate precipitation has long been recognized. Lyell (1854, p. 239) noted that 'many springs hold so much carbonic acid in solution, that they are enabled to dissolve a much larger quantity of calcareous matter than rain-water; and when the acid is dissipated in the atmosphere, the mineral ingredients are thrown down, in the form of porous tufa or of more compact travertine.' Grabau (1903, p. 351) distinguished 'Organically formed' from 'Chemically deposited' limestones, and recognized that the resulting sediments could be either *in situ* or allochthonous. More recent biomineral studies distinguished three broad process-based categories of carbonate precipitate: abiotic, bioinduced, and biocontrolled (e.g., Lowenstam, 1981; Mann, 2001). Abiotic precipitation reflects the physicochemical properties and environmental factors that determine carbonate saturation state for particular minerals (Stumm and Morgan, 1996; Zeebe, 2012). In marine environments these sedimentary conditions change over geological timescales in response to complex long-term interactions between the lithosphere and the ocean-atmosphere-biosphere system (Berner et al., 1983; Holland, 1984; Des Marais, 2001). Localized biological controls over precipitation are complex, and range from strong to weak (De Yoreo and Velikov, 2003; Weiner and Dove, 2003). Lowenstam (1981) used 'organic matrix-mediated' and 'biologically induced' to distinguish the differing degrees of influence exerted by organisms over biomineralization (including biocalcification). These processes are now often referred to as 'biologically controlled' and 'bioinduced' (Mann, 1983, 2001). Biocontrolled mineralization involves regulation of physicochemistry: solubility, supersaturation, nucleation and crystal growth (Mann et al., 1993; Mann, 2001; Weiner and Dove, 2003). In contrast, bioinduced mineralization (BIM) has been regarded as a localized response to the production of metabolic by-products (e.g., OH$^-$, HCO$_3^-$) whose interaction with ions or compounds in the environment results in crystal nucleation. In the latter view, 'BIM is presumably an unintended and uncontrolled consequence of metabolic activity' (Frankel and Bazylinski, 2003).

These processes are not simple, and precise distinction between terms can be challenging (Perry et al., 2007; Altermann et al., 2009). Here we follow Schlager's (2003, p. 446) general view that abiotic precipitates broadly include those in which 'biotic effects are negligible,' while recognizing that many complications and uncertainties remain. For example, some bacteria both induce and control mineral precipitation (e.g., Bazylinski et al., 2007), and 'biocontrolled' calcification (e.g., in foraminifers and corals) is not free from external constraint (De Nooijer et al., 2014; DeCarlo et al., 2018). In addition, organic substances - distinct from live organisms - can strongly influence precipitation (Lin et al., 2005; Zhu and Dittrich, 2016; Yin et al., 2020). There are common carbonate sediments, such as marine ooids, whose formation continues to be debated (e.g., Diaz et al., 2015, Diaz and Eberli, 2019; O'Reilly et al., 2017; Batchelor et al., 2018). These are not new questions: Grabau (1903, pp. 351-352) recognized both chemically and organically formed oolites. Discrimination among abiotic, bioinduced and biocontrolled precipitation remains research in progress. Nonetheless, in the broad context that we employ them here, these terms provide useful generalizations. Common examples of in situ Abiotic, Bioinduced and Biocontrolled carbonate sediments are,
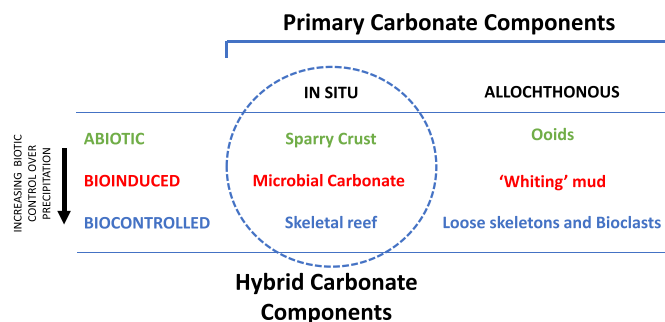
Fig. 1. Primary carbonate components can be divided into abiotic, bioinduced and biocontrolled, and into autochthonous and allochthonous. Hybrid Carbonates are in situ.

respectively, seafloor crystal crusts, stromatolites, and skeletal reefs. Allochthonous carbonate grains respectively produced by these processes could include ooids and water column 'whiting' precipitates, plus bioclasts and loose skeletons (Fig. 1).

3. Dual and triple hybrid combinations

Close in place associations of Abiotic, Bioinduced, and Biocontrolled carbonates have been termed 'Hybrid Carbonates' and 'Hybrid Crust' (Riding, 2008). We define Hybrid Carbonates as follows: *Hybrid Carbonates are intimate (e.g., hand-specimen scale) in situ combinations of two or more of abiotic, bioinduced and biocontrolled carbonates* (Riding and Virgone, 2018) (Fig. 2). These are exemplified in marine and non-marine environments by sparry crusts and in situ microbial and eukaryote deposits. *Dual Hybrids* are combinations of any two of *in situ* Abiotic, Microbial and Skeletal precipitates (Fig. 3). *Triple Hybrids* are combinations of all three of *in situ* Abiotic, Microbial and Skeletal precipitates (Fig. 4). The term 'Hybrid Crust' (Riding, 2008) was used to describe alternating light and dark layers, interpreted as a combination of abiotic and microbial fabrics in putative stromatolites, in which the dark fine-grained layer is variously composed of micritic, peloidal and filamentous microfabric. Within the classification presented here this would be classed as Abiotic-Microbial Dual Hybrid. The concept of Hybridity is an additional approach to sedimentary carbonate description and interpretation. Hybridity emphasizes hand-specimen scale and *in situ* deposits. In these respects it differs from classifications often used in thin-section description of mainly allochthonous (grainy, muddy) fabrics (e.g., Folk, 1959; Dunham, 1962).

4. Hybridity plots

The three carbonate end-members of *in situ* Hybrid Carbonates can be displayed on ternary 'Hybridity Plots' with Abiotic, Skeletal and
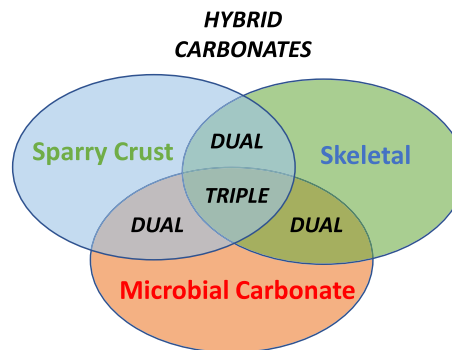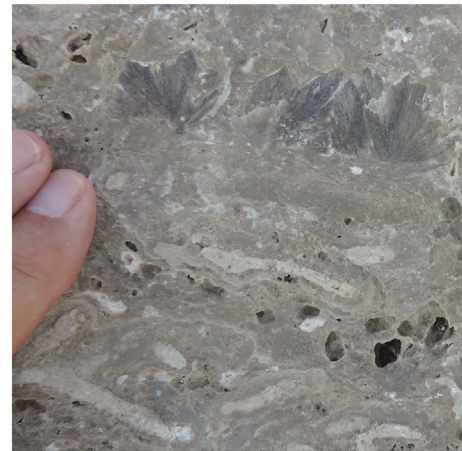

Fig. 2. Hybrid Carbonates are intimate *in situ* combinations of two or more of Abiotic, Bioinduced and Biocontrolled carbonates. Dual Hybrids are combinations of any two; Triple Hybrids are combinations of all three.
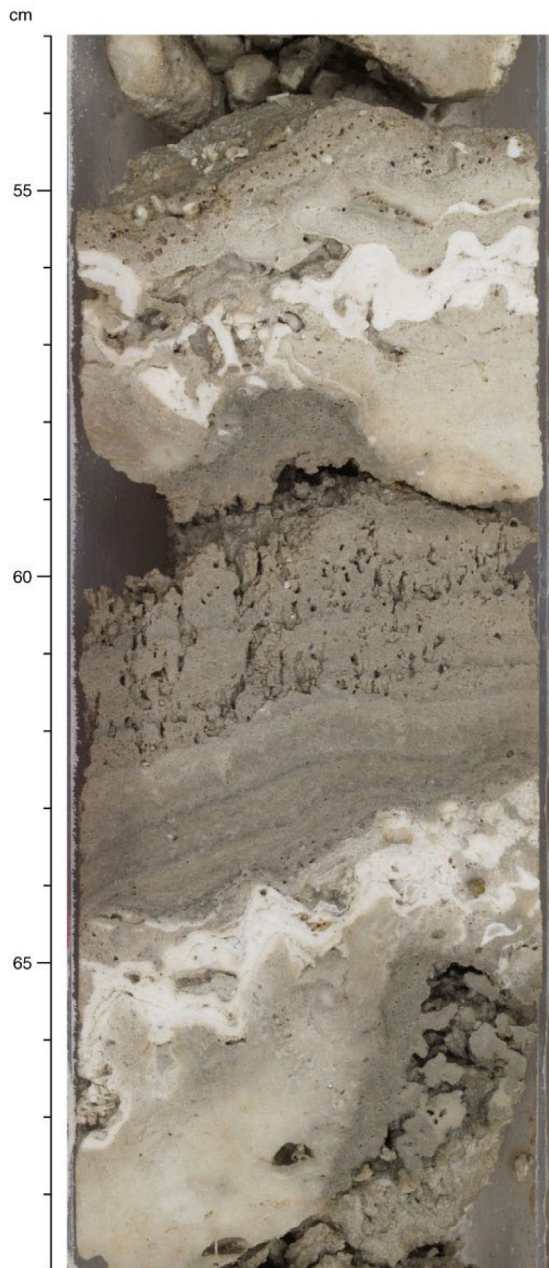
Fig. 3. Microbial-Skeletal Dual Hybrid Carbonate formed by cryptic microbial crusts (gray) on paler colored coral and coralline algal reef framework and bioclastic debris in IODP Expedition 310 core through latest Pleistocene–Early Holocene reef rock at Mara'a, SW Tahiti. Original image available at http://sedis.iodp. © IODP/ECORD.

Fig. 4. Abiotic-Microbial-Skeletal Triple Hybrid Carbonate in upper (massive) Capitan Reef (Capitanian, upper Permian, ~260 Ma), Whites City, New Mexico, USA. The fabric consists of skeletons (sponges, bryozoans, phylloid algae, *Shamovella),* microbial carbonate, and sparry seafloor crusts together with *Archaeolithoporella*, which may itself be a Microbial-Abiotic Hybrid (see Grotzinger and Knoll, 1995).
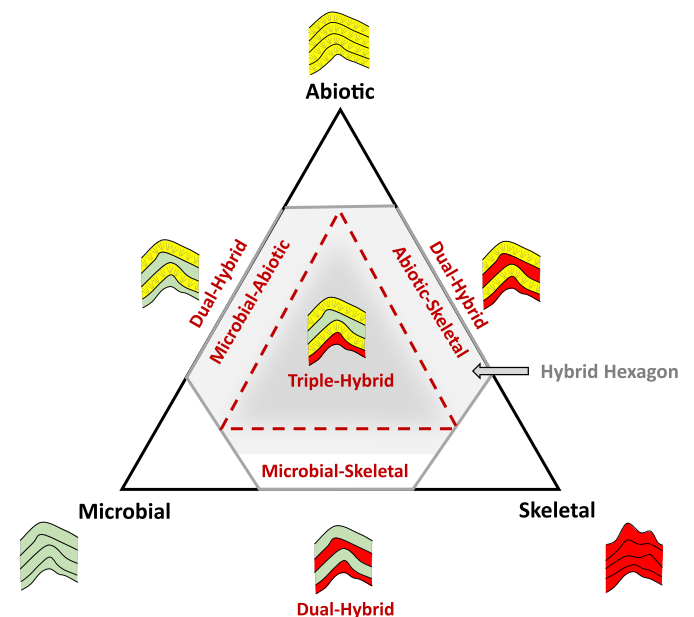
Fig. 5. Hybridity Plot with Abiotic, Skeletal and Microbial components at the apices. Dual Hybrids plot along the sides, and Triple Hybrids occupy the central area of the 'Hybrid Hexagon'. Apice areas consist of one to three components, of which one is > 80%. Dual Hybrids consist of two or three components, none > 80. Triple Hybrids consist of three components, all > 10%. Hybridity Plots assist comparison of basic carbonate compositions.

Microbial components at the apices. Dual Hybrids (Microbial-Abiotic, Abiotic-Skeletal and Microbial-Skeletal) plot along the triangle sides, and Triple Hybrids occupy the central area, the 'Hybrid Hexagon' (Fig. 5). Here we arbitrarily define these categories as follows: Apical areas can consist of one, two or three components, of which one is > 80%. Dual Hybrids consist of two or three components, none of which is > 80%. Triple Hybrids consist of three components, all > 10%. 'Hybridity Plots' therefore display fundamental compositional data for specific examples. By showing patterns that can reflect changes in processes and conditions in time and space, this visualization facilitates both presentation and interpretation of hybridity data. In this outline classification (Fig. 6) we recognize: (i) *Basic Carbonate Components* (Abiotic, Microbial, Skeletal), (ii) *Dual Hybrids* (Abiotic-Microbial,

Microbial-Skeletal, Abiotic-Skeletal); (iii) *Partial Triple Hybrids* (Abiotic-Microbial with minor Skeletal; Microbial-Skeletal with minor Abiotic; Abiotic-Skeletal with minor Microbial; and (iv) *Full Triple Hybrids* (Abiotic-Microbial-Skeletal). Over long geological timescales, *in situ* Abiotic, Microbial and Skeletal carbonates, and their potential Hybrid combinations, have distinctive secular distributions that can reflect changes in carbonate saturation state and the evolution of organisms' abilities to control calcification and form skeletons (Fig. 7).

5. Marine Precambrian

The earliest currently known skeletal carbonates are latest Proterozoic (Grant, 1990; Grotzinger et al., 2000; Kolesnikov et al.,

Outline Classification of Hybrid Carbonates

(i) Basic Carbonate Components
    Abiotic
    Microbial
    Skeletal
(ii) Dual Hybrids
    Abiotic-Microbial
    Microbial-Skeletal
    Abiotic-Skeletal
**(iii) Partial Triple Hybrids**
    Abiotic-Microbial + minor Skeletal
    Microbial-Skeletal + minor Abiotic
    Abiotic-Skeletal + minor Microbial
(iv) Triple Hybrids
    Abiotic-Microbial-Skeletal

Fig. 6. a. Outline classification of Hybrid Carbonates: (i) Carbonate component end-members, (ii) Dual Hybrids, (iii) Partial Triple Hybrids, (iv) Full Triple Hybrids.
b. Hybridity Plot of Hybrid Carbonate classification on a ternary diagram showing (i) Carbonate components end-members (Abiotic, Microbial, Skeletal), (ii) Dual Hybrids (Abiotic-Microbial, Microbial-Skeletal, Abiotic-Skeletal); (iii) Partial Triple Hybrids (Abiotic-Microbial with minor Skeletal; Microbial-Skeletal with minor Abiotic; Abiotic-Skeletal with minor Microbial; and (iv) Full Triple Hybrids (Abiotic-Microbial-Skeletal).
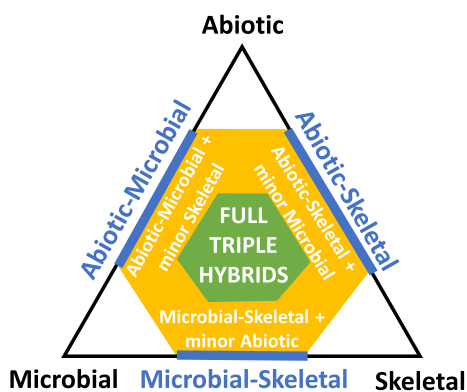
Fig. 6. (*continued*)

2018). Prior to this, sedimentary carbonates were entirely Abiotic and/ or Microbial in origin (Grotzinger and James, 2000; Ridgwell and Zeebe, 2005, p. 306; Cantine et al., 2020). Stromatolites - the signature biogenic carbonates of the Precambrian - have been documented by numerous studies in the Archean (e.g., Walter, 1972, 1983; Beukes,

1987; Hofmann, 2000; Schopf, 2006), and especially in the Proterozoic (e.g., Vologdin, 1962; Komar et al., 1965, 1973; Krylov, 1963; Donaldson, 1976a, 1976b; Hoffman, 1976; Semikhatov, 1976; Grey, 1979; Semikhatov, 1980; Liang et al., 1985; Awramik and Sprinkle, 1999; Grotzinger and Knoll, 1999; Semikhatov and Raaben, 2000; Raaben et al., 2001). Precambrian thrombolites appear to be scarce (Kah and Grotzinger, 1992; Turner et al., 2000; Nomchong and Van Kranendonk, 2020) until very late in the Proterozoic (e.g., Grotzinger, 2000). Precipitated seafloor crusts have been widely recognized but, in contrast to stromatolites, they appear to be more abundant in the Archean and Paleoproterozoic (Grey and Thorne, 1985, fig. 12; Grotzinger, 1990; Grotzinger and Kasting, 1993, p. 235; Kah and Knoll, 1996). To some extent, this assessment depends on the status of microdigitate stromatolites (see below) which may be largely Hybrid. Indeed, Hybridity could be a common feature of Precambrian carbonates. Even the earliest known well-preserved Ca-carbonate sediments (~3500 Myr) likely include intimate mixtures of both microbial and seafloor crust components (Buick et al., 1981; Buick, 1995; Lowe, 1994, 1995; Hofmann et al., 1999; Hofmann, 2000; Allwood et al., 2006). Microbial carbonates and sparry crusts are both locally common in the Neoproterozoic (Cloud et al., 1974; Wright et al., 1978; Grotzinger and James, 2000; James et al., 2001; Corsetti and Grotzinger, 2005; Bosak et al., 2013; Vieira et al., 2015; Hoffman et al., 2017; Okubo et al., 2018). Possible Hybrid combinations include 'cement-rich thickly laminated microbialaminite' in ~700 Ma Sturtian 'cap carbonate' (Pruss et al., 2010, fig. 3), ~650 Ma dolospar crusts with microbial carbonates (Hood and Wallace, 2012, fig. 6), and late Ediacaran (~550-543 Ma) thrombolite mesoclots encrusted by 'fibrous marine cement' (Grotzinger, 2000, fig. 8). In addition to these, we recognize two broad groups of Precambrian Hybrid Carbonates: Fenestral Fabric and Alternating Laminated Fabric (Fig. 8).

5.1. Fenestral fabric

Fenestral fabric consists of light-colored mesoscopic cement-filled spaces, variously flattened, lensoid or rounded in form, enclosed and defined by generally thin darker layers.

5.1.1. Convolute roll-up fabric

Well-preserved delicate convolute fabrics in the 2.6-2.52 Ga Campbellrand Subgroup resemble wispy, tufted, reticulate and enrolled microbial mats that appear to have been initially soft but were lithified by carbonate nucleation on the seafloor prior to burial (Button, 1973, 1976, fig. 3; Beukes, 1987, fig. 10; Altermann and Siegfried, 1997; Sumner, 1997, 2000; Shepard and Summer, 2010) (Fig. 9). This fabric was termed 'contorted cryptalgal laminae' at Campbellrand by Beukes (1987)fig. 9e) [although he may also have confused them with 'tufted fenestral limestone', Beukes, 1987, fig. 10a] and as 'roll-up' structures' in the slightly older ~2600Ma Wittenoom Fm and Carawine Dolomite (Simonson et al., 1993, fig. 24). The abundant voids 'preserved and filled with cements' (Sumner, 1997, p. 306) suggest to us that roll-up
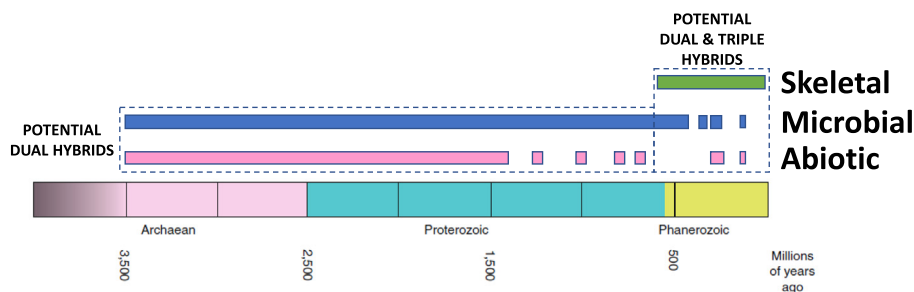
Fig. 7. Secular distribution of key components and potential Hybrid Carbonates. Over geological timescales the three basic in situ carbonate components (Abiotic, Microbial, Skeletal) and their Hybrid combinations have distinctive time distributions. Sparry Crust and Microbial Carbonates are common during much of the Precambrian from ~3500 Ma, whereas Skeletal Ca-Carbonates are restricted to the latest Ediacaran and Phanerozoic. Abiotic-Microbial Hybrids are common in much of the Precambrian. Microbial-Skeletal Hybrids are common in the Paleozoic-Mesozoic. They occur in coral reefs in the late Cenozoic, but otherwise appear to be generally

uncommon during the past ~135 Ma. Abiotic-Microbial-Skeletal Triple Hybrids are common from late Pennsylvanian to mid-Triassic. Abiotic-Skeletal Hybrids appear to be rare.

FENESTRAL FABRIC

Convolute Roll-up Fabric	'Contorted cryptalgal laminae', Roll-up' structure
Net Fabric	Net-like, tufted, plumose fabrics: 'Fenestrate microbialite', 'Cuspate Fenestral Fabric'
Tent Fabric	Thyssagetacean stromatolites

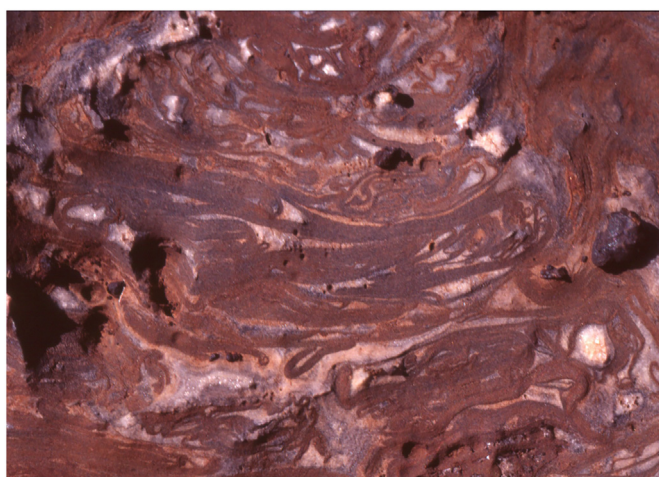**ALTERNATING LAMINATED FABRIC**

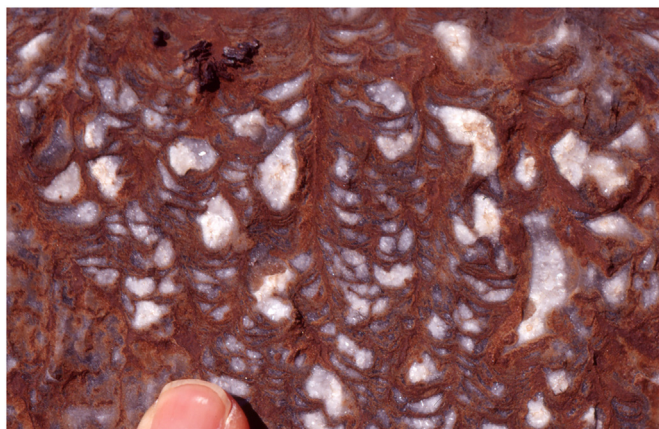**Microdigitate Stromatolite**

Boetsap fabric

Baicalia lacera fabric

Coniform stromatolite fabric

Fig. 8. Fenestral Fabric and Alternating Laminated Fabric are common Microbial-Sparry Crust Dual Hybrid meso- and microfabrics in the Precambrian.

Fig. 9. Convolute Roll-up Fabric. ~2.55 Ga, Boetsap, Campbellrand-Malmani platform, South Africa. Width of view ~8 cm.

Fig. 10. Net Fabric. ~2.55 Ga, Boetsap, Campbellrand-Malmani platform, South Africa.

structures are synsedimentarily lithified Hybrid Carbonates. Beukes (1987, p. 32) compared both roll-up and net-like fabrics (see below), with extant mats preserved by silicification in Yellowstone hot springs (Walter et al., 1976). Sumner (1997, p. 311) and Rivera and Sumner (2014) compared them with present-day mats in Antarctic lakes. There are also similarities, on a smaller scale, with present-day aragonite

encrusted biofilms in deep-sea hydrothermal vent deposits (e.g., Kelley et al., 2007, fig. 5). In addition, convolute fabrics occur in coniform stromatolites (e.g., Grey, 1984, pl. 10a) and in ~700 Ma Sturtian 'cap carbonate' sequences (Pruss et al., 2010, fig. 6; Le Ber et al., 2015, fig. 4). It has been suggested that gas bubbles supported and/or lifted the soft films. Beukes (1987), p. 32, fig. 10a) suggested that the gas was H_2S and CH_4 in the Gamohaan Fm at Campbellrand. Overall, therefore, in this model of convolute fabrics, soft organic mats create a vertical structure supported by gas bubbles and are synsedimentarily permineralized *in situ* by carbonate precipitation or, as at Yellowstone, silica.

5.1.2. Net fabric

Net fabric ranges in appearance from reticulate to tufted and plumose, and locally forms coniform structures (Beukes, 1987, fig. 10). Well-preserved variants have been described in detail from the late Archean of Campbellrand Subgroup, South Africa (Fig. 10). Beukes (1987) recognized net-like fenestrate fabric ranging from fine to tufted building small *Conophyton*. Sumner, 1997, p. 302 and Fig. 3) defined a series of end-member morphologies (planar laminae, contorted laminae, tented microbialites, cuspate microbialites, irregular columnar microbialites, plumose structures) as well as herringbone calcite beds. Early precipitation of herringbone and bladed calcite on the net-like framework (Sumner, 1997, Fig. 9) indicates that these are Hybrid fabrics. Sumner (2000) recognized similar fabrics at Bulawayo, Zimbabwe (2.6 Ga) and Steep Rock Lake, Canada (~2.8 Ga). Tufted variants can produce a dimpled pattern on the bedding surface (Beukes, 1987, Fig. 6d; Hofmann and Masson, 1994, Fig. 3c; Fralick and Riding, 2015, Fig. 20). These net fabrics have variously been termed 'net-like fenestrae' (Beukes, 1987, Fig. 6), 'fenestrate microbialite' (Sumner, 2000), 'cuspate microbialite' (Sumner, 2000) and 'cuspate fenestral fabric' (Fralick and Riding, 2015). Larger somewhat similar cuspate fabrics occur in the 2.72 Ga Tumbiana Formation in Western Australia (Flannery and Walter, 2012, Fig. 3b). At Steep Rock Lake, Canada, well-defined Hybrid Carbonates in ~2800 Ma meter-scale 'Giant Domes' consist of alternating centimetric layers of cuspate fenestral fabric (interpreted as calcified microbial mat) and crystalline crust (interpreted as originally aragonite seafloor precipitate) (Fralick and Riding, 2015, p. 164) (Fig. 11). As with convolute fabric (Section 5.1.1), there can be interesting similarities with hydrothermal vent deposits (Fig. 12).

5.1.3. Tent fabric

Broadly similar, but generally more organized and larger, 'film' fabrics that are locally common throughout Paleoarchean to Mesoproterozoic carbonates, have been classed as Thyssagetaceae (Vlasov, 1977), a family of *Conophyton*-like stromatolites with cones laterally linked by abundant laminae that cross the intercolumnar
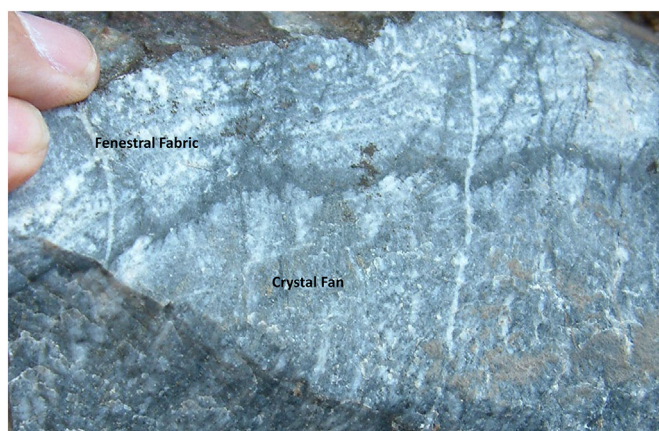
Fig. 11. Abiotic-Microbial Dual Hybrid Carbonate formed by alternation of Crystal Fan (Abiotic) and Cuspate Fenestral Fabric, interpreted as synsedimentarily lithified microbial network. ~2.8 Ga, Steep Rock Lake, Canada.

Fig. 12. Hot spring travertine vent fabric. Late Quaternary,~8 km southwest of Meadow, UT, USA. Compare with Net Fabric, Fig. 10.
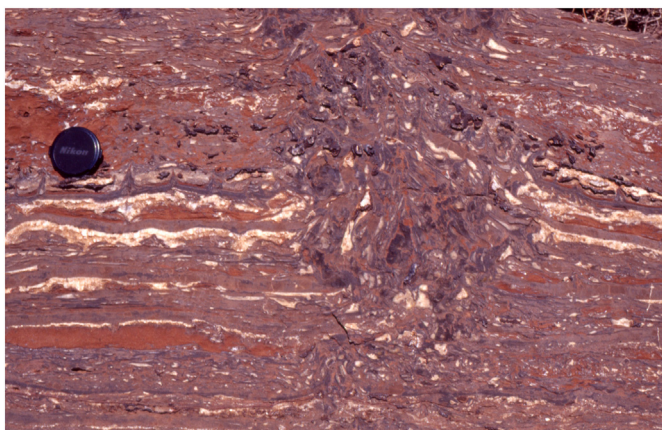

Fig. 13. Tufted and Tent Fabric. ~2.55 Ga, Boetsap, Campbellrand-Malmani platform, South Africa.
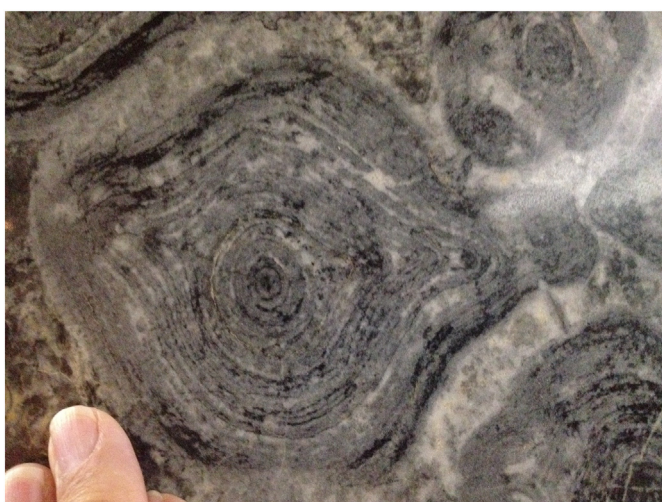

Fig. 14. Thyssagetacean stromatolite. Wall tile, Beijing. Age and locality unknown.

spaces (Hofmann et al., 1991). These can form distinctive tent-like structures (Fig. 13). They have been described from the Archean (Grey, 1981; Hofmann et al., 1991; Hofmann and Masson, 1994, Fig. 2;
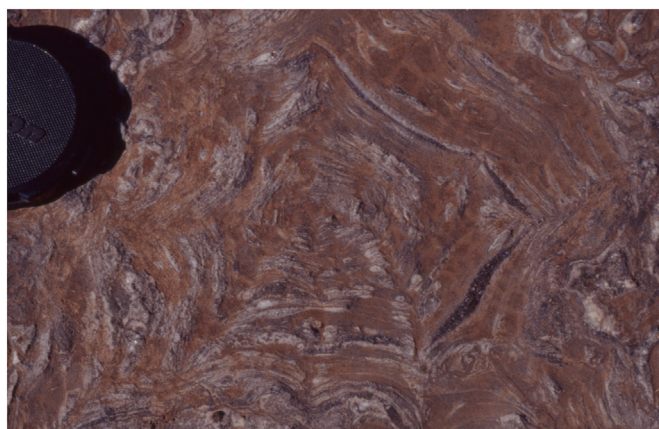

Fig. 15. Thyssagetacean stromatolite (cf., 'star shaped' 'ribbed' *Conophyton*, Beukes, 1987, fig. 9d). ~2.55 Ga, Boetsap, Campbellrand-Malmani platform, South Africa.

Sumner, 1997; Altermann and Siegfried, 1997; Altermann and Nelson, 1998; Wright and Altermann, 2000, Fig. 3; Murphy and Sumner, 2008; Flannery and Walter, 2012) and Paleoproterozoic-Mesoproterozoic (Vlasov, 1977; Hofmann, 1978, Figs. 12-14; Petrov and Semikhatov, 2001; Misra and Kumar, 2005; Bartley et al., 2015). Examples range from irregular and net-like (e.g., *Thesaurus*, Hofmann and Masson, 1994, Fig. 2c) to compact and spindle-like in cross-section (Fig. 14) (cf. Kah et al., 2009, Fig. 6B). Within this spectrum there are canopy-like structures that can be distinctively 'ribbed' or 'star-shaped' in plan-view (Beukes, 1987, Fig. 9d) (Fig. 15) with well-defined vertical supports and draping elements coated by herringbone calcite (Kerans and Donaldson, 1989; Bartley et al., 2015, Fig. 4, 5). The role of seafloor herringbone calcite cementation is also evident as multilayered isopachous rims within voids in ~1.2 Ga (Kah et al., 2012) Atar stromatolites (Kah et al., 2009, Fig. 9a-d). Thyssagetaceans have been closely compared with present-day tufted microbial mats (Walter et al., 1976) due to their 'millimetre-scale coniform peaks and reticulate patterned plan surfaces, sagging saddle ridges, radially ridged small cones and < 1 cm wide coniform laminated columns linked by 'draping' interconnecting laminae' (Flannery and Walter, 2012).

5.2. Alternating laminated fabric

Alternating laminated fabric consists thin microscopic to mesoscopic layers that are variously microcrystalline, fibrous or sparry in texture.

5.2.1. Microdigitate stromatolites

These distinctive small (typically 0.5 cm wide and a few centimeters high), narrowly branched, delicately laminated columns (Fig. 16) are common, often in widespread beds and lenticular mounds, from late Archaean and early Proterozoic (Raaben, 1980, 2005; Liang et al., 1985; Grey and Thorne, 1985, p. 193-194, fi g. 12; Zhu and Chen, 1992; Sharma and Shukla, 1998) to early Mesoproterozoic (Raaben, 1980; Kah and Knoll, 1996; Tang et al., 2013). They have variously been regarded as either essentially microbial (Semikhatov, 1978; Grey, 1984; Grey and Thorne, 1985) and given Linnean names (e.g., *Pseudogymnosolen*, *Asperia*), at least partly abiotic (Donaldson, 1963; Hoffman, 1975, Fig. 30-12; Hofmann, 1977, Fig. 11f; Grotzinger and Read, 1983, p. 712), or as a variety of 'marine cement crust' (Grotzinger and Kasting, 1993, Fig. 2) that are 'pure precipitate structures' (Grotzinger and Knoll, 1999, p. 347). The presence of radial fibrous fabrics interlayered with dark laminae in Paleoproterozoic examples (Hofmann and Jackson, 1987; Sami and James, 1994, p. 116) led Riding (2008, p. 78) to suggest that they could be Abiotic-Microbial Hybrids. Examples up to 4 cm high (e.g., Grotzinger and Knoll, 1999, Fig. 2a) somewhat

Fig. 16. Microdigitate stromatolites. ~1.5 Ga, Wumishan Fm., Sanpozhen, 85 km west-south-west of Beijing, China.

resemble rapidly precipitated hot spring feather crystals and 'shrubs' (see Chafetz and Guidry, 1999; Erthal et al., 2017, Fig. 6, 7).

5.2.2. Boetsap fabric and Baicalia lacera fabric

Decimetric stromatolite domes that dominate parts of the Campbellrand Subgroup, South Africa, consist of 'dentate cryptalgal lamination' (Beukes, 1987, Fig. 3d). This was named 'Boetsap-style Lamination' by Sumner and Grotzinger (2004, p. 1286) who described it as 'heterogeneous combinations of dark red–brown microcrystalline carbonate lamellae, lighter red–brown to grey finely crystalline lamellae and light grey coarse sparry layers'. It appears to be a delicately interlayered Hybrid fabric (Riding, 2008) (Fig. 17). Submillimetric dark-light alternations in the stromatolite *Baicalia lacera*, from the ~1020 Ma Burovaya Fm of Siberia, have been interpreted as Hybrid Crust (Riding, 2008, Fig. 9).

5.2.3. Coniform stromatolite fabrics

In addition to net-like Fenestral Fabric in thyssagetacean and similar tent-like stromatolites, laminar and lensoid structures in coniform stromatolites may represent synsedimentarily lithified gas bubble cavities. This has been suggested for bubble-like lenses in coniform stromatolites (Walter, 1972, pl. 16, Fig. 5, Walter, 1983; Donaldson, 1976a;
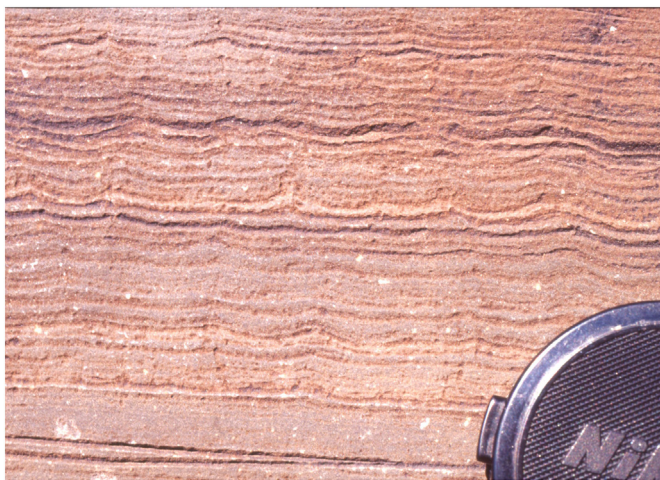
Fig. 17. Boetsap lamination in stromatolite (cf., 'dentate cryptalgal lamination', Beukes, 1987, fig. 3d). ~2.55 Ga, Boetsap, Campbellrand-Malmani platform, South Africa.

Abell et al., 1985) which have been interpreted as indicators of oxygen (Bosak et al., 2009, 2010; Hallmann and Summons, 2014). Bubble structures occur in Ordovician calcified cyanobacterial mats (Lee and Riding, 2016). Coniform stromatolites also can contain lenses formed by 'the deformation (rolling up) of a lamina', e.g., in *Conophyton garganicum australe* from the ~1000 Ma Bangemall Group of Western Australia (Walter (1972, p. 106). Riding (2008) suggested that *Conophyton garganicum* fabric could be interpreted as 'Hybrid Crust composed of thin layers of lithified microbial mat (fine-grained) separated by thicker layers of surficial crust and/or early cavity fill (sparry)', but noted that 'neomorphic spar aggradation cannot be ruled out'.

6. Marine late Ediacaran and Phanerozoic

6.1. Late Ediacaran to Mississippian

The advent of controlled biomineralization was a transformational development (Ridgwell and Zeebe, 2005; Wood, 2018) that marks the inception of Microbial-Skeletal Hybrid carbonates. Phosphatic skeletal elements occur at 810 Ma (Cohen et al., 2017), and *Cloudina* (Germs, 1972) at ~545 Ma is an early example of skeletal calcium carbonate (Penny et al., 2014). In the early Paleozoic, skeletal carbonate production occurred but remained relatively restrained and microbial carbonates were also abundant throughout the Cambrian and early Ordovician (Microbial Carbonate interval 1, MC1, Riding et al., 2019). As a result there are numerous well-documented examples of sponge-microbial Hybrid Carbonates. These include Early Cambrian archaeocyath reefs (Rowland and Shapiro, 2002; Gandin and Debrenne, 2010), Late Cambrian microbial-lithistid reefs (Hamdi et al., 1995; Lee et al., 2019) and Early Ordovician microbial-lithistid-calathiid-pulchrilaminid reefs (Lee and Riding, 2018).

Marine invertebrate diversification dramatically increased skeletal carbonate production in the mid-Ordovician (Sepkoski Jr., 1979; Bambach et al., 2002; Webby et al., 2004), coincident with temperature decline and marine oxygenation (Trotter et al., 2008; Edwards et al., 2017; Lee and Riding, 2018). A signature development was the appearance stromatoporoids, corals, and bryozoans (Pitcher, 1964). This consortium often hosted microbial carbonates and Microbial-Skeletal Dual Hybrids are prominent in mid-Ordovician (Darriwilian) reefs such as those of the Chazy Group in north-eastern North America (Pitcher, 1964; Desrochers and James, 1988; Webby, 2002; Kröger et al., 2017). Stromatoporoid-coral-bryozoan reefs remained important until the Late Devonian (Fagerstrom, 1987; Wood, 1999; Copper and Scotese, 2003; Kiessling et al., 2006, Fig. 8h; James and Wood, 2010). As skeletal abundance increased (Webby, 2002; Adachi et al., 2011), the proportion of Microbial Carbonates declined ('invertebrate interval' I1, Riding et al., 2019). Nonetheless, numerous examples of skeletal-microbial Hybrid Carbonates occur in Late Ordovician to Late Devonian reefs (Fagerstrom, 1987; Geldsetzer et al., 1988; Soja, 1994; Monty et al., 1995; Wood, 1999; Kiessling, 2002) whose skeletal frameworks created cryptic habitats well-suited to syndepositional microbial carbonate formation (Wood, 1998; Taylor and Wilson, 2003; Nose et al., 2006, Fig. 3a).

6.2. Latest Devonian-Mississippian

Frasnian-Famennian extinction, which included stromatoporoid sponges (Stearn, 2010), has been related to reduced oxygenation (Joachimski and Buggisch, 1993). This major change which particularly affected in shallow marine carbonate sedimentation (Droser et al., 2000; Webb, 2002) ushered in a prolonged interval of microbial carbonate abundance (MC2, Riding et al., 2019). Microbial-Skeletal Hybrids with corals, bryozoans and sponges were common during the Devonian-Mississippian transition (Mountjoy and Riding, 1981; Webb, 1996; Whalen et al., 2002; Wood, 2004) and in the early Mississippian (Mundy, 1994; Webb, 2001, 2002, 2005; Aretz and Chevalier, 2007;

Aretz and Webb, 2007), locally forming Triple Hybrids with synsedimentary radiaxial spar (Kerans et al., 1986, Fig. 8). Carbonate mud mounds that appeared in the Late Devonian (Dreesen et al., 1985: Boulvain, 2001), often in association with crinoids, were unusually large and abundant in the early Mississippian (Lees, 1964; Krause et al., 2004). It has been suggested that they reflect cyanobacterial precipitation of water column carbonate mud ('whitings') stimulated by decline in atmospheric CO_2 below a critical threshold (Riding, 2011, 2014). Mud mounds continued to be widespread in the early Pennsylvanian, often in association with chaetetid sponges (West and Kershaw, 1991) and phylloid algae (Webb, 2002; Wahlman, 2002) as well as problematic skeletal organisms such as *Donezella* and *Komia*.

Late Pennsylvanian increase in Microbial Carbonates (MC3, Riding et al., 2019), together with the appearance of locally conspicuous Sparry Crusts, marked the inception of a significant interval of Triple Hybrid Carbonate formation that continued until the mid-Triassic. Well-documented early examples are Virgilian (Gzhelian) Laborcita Fm mounds in New Mexico, USA, dominated by phylloid algae and Microbial Carbonates together with botryoidal Sparry Crusts described as 'sea-floor growths' (Mazzullo and Cys, 1979) and 'cementstone' (Wahlman and Janson, 2013). This association - augmented by bryozoans, calcisponges, and abundant *Shamovella* and *Archaeolithoporella* - remained common in low latitude reefs during much of the Permian (Wahlman, 2017, Fig. 2). *Archaeolithoporella* (Fig. 18) may itself be a Dual Hybrid combination of alternating calcified biofilm and thin sparry crust (Kendall and Iannace, 2001). The Late Guadalupian Capitan Reef, Texas-New Mexico, contains complex massive Dual and Triple Hybrid fabrics, dominated by *Archaeolithoporella, Shamovella* and phylloid algae, in which apparently open cavities were filled by botryoidal aragonitic seafloor crusts (Babcock, 1977; Wood et al., 1994, 1996). We use 'Sparry Crust' to describe these deposits that appear to be seafloor precipitates, but it is uncertain how far this interpretation can be extended to reports of early 'cements' (e.g., Flügel et al., 1984; Wahlman, 1985; Samankassou, 2003) and isopachous veneers of radiaxial cements and cementstones (Wahlman, 2002, p. 278, Fig. 26, 27), widely reported from Pennsylvanian and Permian calcisponge-microbial reefs. Interlayered geopetal sediment and radiaxial 'cement' in some mid-Permian reefs (e.g., Wahlman et al., 2013) appear to be synsedimentary marine phreatic deposits. They could be causally linked to coeval crystalline crusts on the open seafloor.

Late Permian decline in skeletal biotas (Schubert and Bottjer, 1992; Rampino and Shen, 2019) coincided with further increase in Microbial Carbonates (Flügel and Kiessling, 2002). These are widely reported near the Permian-Triassic boundary, e.g., in Turkey, Iran and South China, where they can form distinctive Triple Hybrid Carbonates of

Fig. 18. *Archaeolithoporella* crusts in upper (massive) Capitan Reef (Capitanian, upper Permian, ~260 Ma), Whites City, New Mexico, USA.

microbial micrite, calcimicrobes, and seafloor crystal fans (e.g., Ezaki et al., 2003; Lehrmann et al., 2003; Baud et al., 2005; Jiang et al., 2008; Kershaw et al., 2007, 2011, 2012; Yang et al., 2011). Carbonate sedimentation during much of the Lower Triassic remained predominantly microbial (Flügel, 2002, Table 1; Baud et al., 2007; Martindale et al., 2019). Nonetheless, bivalve- and sponge-microbial Hybrid Carbonates occur less than 2 Ma after the Permian-Triassic Mass Extinction (Pruss et al., 2007; Brayard et al., 2011; Vennin et al., 2015). The Middle Triassic saw a return to reefs that, in structure and composition, broadly resemble those of the Permian (Fürsich and Wendt, 1977; Biddle, 1981; Gaetani et al., 1981; Flügel, 1981; Russo et al., 1997; Payne et al., 2006; Marangon et al., 2011). Typically, these are dominated by Dual Hybrid Carbonates with algae (phylloids, '*Solenopora*'), sponges, and abundant *Archaeolithoporella* and *Shamovella*, intimately associated with micritic-peloidal Microbial Carbonates. Widespread seafloor crystal crusts, ranging from thin and inconspicuous to mesoscopic (Harris, 1993, p. 391; Seeling et al., 2005, Fig. 7), again create Triple Hybrid fabrics (e.g., Emmerich et al., 2005, Fig. 20; Marangon et al., 2011, Fig. 9; Sánchez-Beristain and Reitner, 2016). Some of these grade into botryoidal masses so distinctive that they been given a name: *Evinospongia* (Stoppani, 1858; Russo et al., 2000; Emmerich et al., 2005, Fig. 20). These enigmatic crusts locally occupy more than 60% of the rock volume (Gaetani et al., 1981, p. 44). Their precise timing and mode of formation remain uncertain (Frisia-Bruni et al., 1989; Russo et al., 2006).

6.3. Upper Triassic to Early Cretaceous

Upper Triassic reef biotas took on a more 'modern' aspect with the rise of scleractinian corals and calcareous red algae (Flügel, 2002; Stanley Jr., 2003; Russo, 2005; Tosti et al., 2014; Martindale et al., 2015). Within this dominantly skeletal interval ('invertebrate interval' I3, Riding et al., 2019), putative cryptic Microbial Carbonates are locally conspicuous in Norian Dachstein calcisponge frameworks (e.g., Flügel, 1981, 2002, p. 417) and Upper Rhaetian Steinplatte sponge-microbial boundstones (Flügel, 2002, Fig. 11b). Locally, Hybrid serpulid-microbial reefs form a distinctive additional association in restricted platform interiors (Flügel, 1981; Cirilli et al., 1999; Zamparelli et al., 1999).

The end-Triassic Extinction Event was the second largest loss in reef volume (after the Frasnian-Famennian) during the Phanerozoic, particularly affecting corals, calcisponges and bivalves (Flügel and Kiessling, 2002, p. 711). Hybrid Carbonates appear to be relatively scarce in the Lower Jurassic, consistent with fewer reports of both coral reefs (Flügel, 2002, p. 425) and microbial carbonates (Kiessling, 2002). However, this is qualified by another assessment (Kiessling et al., 2006, Fig. 1), supported - for example - by occurrences of Hybrid coral-sponge-microbial mounds in Morocco (Leinfelder et al., 2002, p. 476; Della Porta et al., 2013). Following their Late Triassic decline, coral abundance and diversity increased in the mid-Jurassic (Lathuilière and Marchal, 2009; Simpson et al., 2011, Fig. 3). Together with sponges, corals dominate Middle-Upper Jurassic reefs (Leinfelder et al., 1993). These also often contain abundant microbial carbonates (Leinfelder et al., 2002, Fig. 7), creating Hybrid Carbonates, e.g., Bajocian of Morocco (Tomás et al., 2013) and Spain (Aurell and Bádenas, 2015) and Kimmeridgian of Germany (Gwinner, 1976; Schmid et al., 2001). This marks transition to the final major episode of Microbial Carbonate abundance (MC4, Riding et al., 2019). Oxygenation is suggested to have strongly influenced the relative distributions of corals and sponges in mid-upper Jurassic reefs, with low oxygen favoring sponges and microbial carbonates (Leinfelder et al., 1993), recalling Late Cambrian conditions (Lee and Riding, 2018, p. 110). In western France, thick microbial crusts on Early Kimmeridgian coral frameworks created Microbial-Skeletal Hybrids (Taylor and Palmer, 1994; Olivier et al., 2003). In the upper Oxfordian of Crimea, radiaxially cemented microframeworks of *Crescentiella* [Problematicum] with microbial carbonates and

sclerosponges (Krajewski and Schlagintweit, 2018) evoke Permian and Triassic *Shamovella*-microbial-calcisponge Triple Hybrid Carbonate reefs. Tithonian-lower Berriasian Štramberk reefs, preserved in olistoliths, have equally complex hybrid fabrics formed by corals, microbial carbonates, problematic microencrusters and abundant synsedimentary cements (Hoffman et al., 2017). In the Aptian, especially Early Aptian (towards the end of MC4, Riding et al., 2019), dense deposits of the problematic encrusters *Lithocodium* and *Bacinella* are often associated with 'marine cements' (e.g., Immenhauser et al., 2001; Rameil et al., 2010), and Dual Hybrids in eastern Spain consist of peloidal microbial carbonate crusts on corals (Riding and Tomás, 2006).

6.4. Mid-Cretaceous to present-day

During this long interval, marine carbonates were often dominated by biocontrolled calcifiers. In shallow water these were benthic algae and foraminifers, and other invertebrates (Johnson et al., 2001; Höfling and Scott, 2002; Kiessling et al., 2003, Fig. 12; Pomar et al., 2017). Planktic calcifiers such as coccolithophore algae (Bown et al., 2004; Monteiro et al., 2016) and globigerine foraminifers (Hannisdal et al., 2017) also produced large quantities of sediment, much of which was buried in deeper water. Throughout the Cenozoic, increased oxygenation (Lu et al., 2018) and decline in CO_2 and temperature coincided with scarcity in Microbial Carbonates relative to most of the preceding Phanerozoic (Höfling and Scott, 2002; Kiessling, 2002; Riding, 2005; Pomar and Hallock, 2008). Nonetheless, some striking examples of Hybrid Carbonates developed, particularly during the last 7 Myr. These include Late Miocene (6 Ma) Microbial-Skeletal Dual Hybrid mounds in SE Spain composed of parautochthonous *Halimeda* segments lithified by cryptic microbial crusts (Martín et al., 1997). Thick microbial crusts also veneer skeletal framework in slightly younger coral reefs in the same area (Riding et al., 1991). These closely resemble late Quaternary reef fabrics in Jamaica (Land and Goreau, 1970) and Tahiti (Camoin and Montaggioni, 1994; Seard et al., 2011; Riding et al., 2014) (Fig. 3). During the Last Deglaciation in the Great Barrier Reef, Australia, microbial crusts not only formed in framework cavities but also as seafloor coatings on corals, coralline algae and fore-reef skeletal sediment (Braga et al., 2019). These reefal Hybrid Carbonate crusts could well be the most widely developed well-lithified microbial carbonates in normal marine environments of the recent geological past. Certainly, in volume they must far exceed coarse agglutinated stromatolites such as those that at Shark Bay Australia and around Exuma Sound in the Bahamas (cf. Reid et al., 1995). Literally cryptic Microbial-Skeletal Hybrid Carbonates are exemplified by pendent 'pseudostalactites'/'biostalactites' formed by worm tubes and Microbial Carbonate in present-day marine caves in the Caribbean and Mediterranean (Macintyre, 1984; Guido et al., 2012, 2013, 2014; Sanfilippo et al., 2014).

7. Methane seeps

Carbonate precipitation occurs at methane seeps when methane-rich fluids are oxidized by methanotrophic bacteria using seawater sulfate as an electron-acceptor (Michaelis et al., 2002; Peckmann and Thiel, 2004; Knittel et al., 2005). This can result in the precipitation of both fine-grained microbial carbonates and coarsely crystalline aragonite and Mg-calcite crusts, all characterized by very negative $\delta^{13}C$ values (Paull et al., 1984; Ritger et al., 1987; Roberts and Aharon, 1994). Depending on their geological age, seep deposits often enclose a variety of invertebrates, such as brachiopods, bivalves and tube worms (Gaillard et al., 1992; Campbell and Bottjer, 1995; Campbell, 2006; Levin et al., 2015; Georgieva et al., 2019). During life these may harbor chemolithotrophic or methanotrophic bacteria to provide energy and nutrients by the oxidation of methane or reduced sulfur species (Jannasch et al., 1989; Knittel et al., 2005). Thus, seep carbonates are distinctive Dual Hybrid Carbonates which, if skeletons are present, can be Triple Hybrids. As these synsedimentarily lithified deposits accrete,

they can be repeatedly broken by high venting flux, and the resulting cavities then in turn become lined by mats and filled by cements (Teichert et al., 2005). These repeated processes can produce nodular and mound-like deposits with complex irregularly veined and brecciated fabrics of peloidal micritic microbial carbonates and crystal crusts, together with low diversity-high abundance macrofaunal communities (Kulm et al., 1986; Gaillard et al., 1992; Suess et al., 1999, Fig. 2; Michaelis et al., 2002; Peckmann et al., 2002; Reitner et al., 2005). Until their origins were recognized, seep deposits were often regarded as unusual, highly fossiliferous, relatively deep-water reef communities (e.g., Ager et al., 1976).

Seep carbonate development likely reflects sulfate supply, seep-rate and composition, water depth (pressure), and oxygenation, as well as overall seawater carbonate saturation state, temperature, and associated benthic faunas (Teichert et al., 2003; Treude et al., 2003; Campbell, 2006). They appear to increase in abundance from mid-Paleozoic to the present-day. It has been suggested that low sulfate concentrations limited seep carbonate precipitation during the Precambrian, and probably into the Palaeozoic (Bristow and Grotzinger, 2013). On the other hand, AOM can operate at very low sulfate concentrations (Beal et al., 2011). The oldest confirmed methane seep deposit currently known is Late Silurian (~425 Ma) (Jakubowicz et al., 2017). Eifelian (~390 Ma, Middle Devonian) Hollard Mound in Morocco contains clusters of worm tubes and bivalves, together with both crystalline and microbial authigenic crusts (Peckmann et al., 2005). Late Visean (~331 Ma) brachiopod-rich seep carbonates at Iberg, Germany, are laminated and thrombolitic fine-grained microbial limestones with stromatactis cavities lined with isopachous crusts of fibrous and botryoidal calcite cement (Peckmann et al., 2001; Gischler et al., 2003) (Fig. 19). Methane seep mounds surrounded by mudstones near the Jurassic-Cretaceous boundary (~145 Ma) in Svalbard consist of complex fine-grained carbonates with crystal crusts and abundant brachiopods and bivalves (Hammer et al., 2011). Cretaceous (~100 Ma) seep carbonates at Waipiro, New Zealand, consist of irregularly mottled clotted micrite with numerous irregular cavities filled with carbonate cements and silica, and contain a bivalve and gastropod fauna (Kiel et al., 2013). The Cretaceous (~75 Ma) Tepee Buttes in Colorado, USA, are low conical limestone hills, 60 m wide and 10 m high, composed of vuggy, peloidal limestone with abundant bivalves that contrasts with the enclosing poorly fossiliferous shale (Shapiro and Fricke, 2002). Mollusk-rich seep deposits in the Oligocene Lincoln Creek Fm, Washington State, USA, consist of fine-grained clotted carbonates traversed by burrows and irregular cavities (Peckmann et al., 2002).

8. Non-marine

Present-day non-marine carbonates occur in a wide range of environments, from freshwater caves, creeks and lakes, to evaporite and soda lakes, and hot springs (e.g., Pentecost, 2005; Della Porta and Barilaro, 2011; Della Porta, 2015; James and Jones, 2015; De Boever et al., 2017a, 2017b; Brasier et al., 2015, 2018; Bougeault et al., 2019), as well as near-sea crater lakes (Kempe and Kaźmierczak, 1993; Arp et al., 2003). These environments provide many opportunities for Abiotic and Microbial carbonates, in particular, to co-occur as Hybrid Carbonates. For example, distinctively banded nodules, formed by microbial carbonate interlayered with botryoidal crystalline calcite crust, in present-day saline lake Laguna Negra, Argentina (Gomez et al., 2014; Buonguorno et al., 2019) (Fig. 20). Here we briefly discuss two contrasting settings: cool water karst creeks and hot spring vents.

Karst water, rich in calcium and total inorganic carbon (such as bicarbonate and dissolved CO_2), degases as it emerges into caves or at surface springs, due to the lower atmospheric pressure. Loss of CO_2 raises pH and, together with warming, increases carbonate saturation state for $CaCO_3$ minerals (Holland et al., 1964; Barnes, 1965). Precipitation is often inconspicuous at creek springs, but may be enhanced
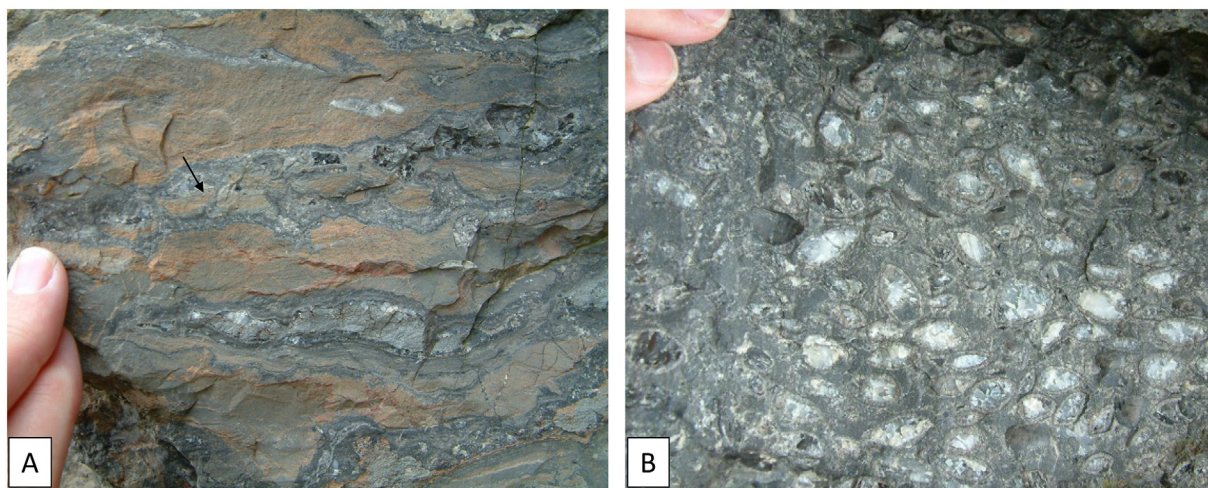
Fig. 19. Methane seep Hybrid Carbonate. A. Fine-grained Microbial Carbonate with Sparry vein fills. B. Brachiopods in Microbial Carbonate matrix. Mississippian, ~332 Ma, overlying Iberg Reef, near Bad Grund, Harz Mountains, Germany.

Fig. 20. Non-marine oncoid, Microbial-Sparry Crust Dual Hybrid. Holocene saline lake Laguna Negra, NW Argentina (see Gomez et al., 2014).

downstream by warming and evaporation, and by turbulence at rapids and falls (Jacobson and Usdowski, 1975; Pentecost, 1978, 1981). CO_2 and HCO_3^- can also be removed by photosynthesis, e.g., by cyanobacteria that produce crusts and oncoids (Merz-Preiß and Riding, 1999; Golubić et al., 2008; Berrendero et al., 2016). In these dynamic environments the interplay of abiotic and biotic effects can be complex. *In situ* studies of temperate climate creeks suggest that, relative to associated inorganic precipitation, photosynthesis-induced biofilm calcification may account for < 20% of the total Ca^{2+} loss (Shiraishi et al., 2008; Arp et al., 2010). At the same time, extracellular polymeric substances (EPS) associated with bacteria can strongly influence $CaCO_3$ precipitation (e.g., Yin et al., 2020), and e*x situ* flume experiments (Pedley et al., 2009) show that exopolymer-rich substrates affect nucleation and crystal growth, independently of whether carbonate equilibria are shifted by CO_2 degassing and/or photosynthesis. Nonetheless, under some conditions EPS can also inhibit precipitation (Decho and Gutierrez, 2017).

Fast flow promotes CO_2 degassing by enlarging the air-water interface (Zhang et al., 2001), enhancing precipitation at rapids and waterfalls (Grüninger, 1965). This creates a strong positive feedback as stream-bed aggradation increases water-flow, thereby further accelerating precipitation. In addition to bedrock, the surfaces of aquatic plants (moss, algae, etc.) become templates for encrustation. On steep slopes this can result in the growth of pendent cones and screens that enclose grotto-like spaces behind calcified tufa 'curtains' (e.g., Pedley et al., 2003). Intense precipitation at rapids often creates rimmed cascades with pools. At larger dimensions, 'tufa barrages' (Pedley, 1993; Carthew et al., 2003) form, as at classic sites such as Plitvice, Croatia, where precipitated high relief dams create series of lakes (Stoffers, 1975; Emeis et al., 1987; Brnek-Kostic, 1989; Chafetz et al., 1994). Thus, creek carbonate systems are characterized by large downstream variations in flow-rate and degassing, in which the scale and type of precipitation can switch between more abiotic at rapids and falls, and more bioinduced (e.g., cyanobacterial) precipitation in intervening sections of more moderate flow (Merz-Preiß and Riding, 1999). Where these types of precipitation coincide they often produce complex Hybrid mixtures of Abiotic and Microbial carbonates. The larvae and pupae of some aquatic insects, such as caddisflies (Trichoptera) and chironomids (Diptera), in creeks and lakes secrete silk-like material and agglutinate sediment particles to produce protective tubular and coiled cases (Chaloner and Wotton, 1996; Gaino et al., 2002; Pentecost, 2005, pp. 188-192). These tubes, individually up to centimeters in length, can build aggregated masses with a fossil record in lacustrine carbonates (e.g., Leggitt and Loewen, 2002; Leggitt et al., 2007, Fig. 5; He et al., 2015; Gong et al., 2017), often closely associated with microbial carbonates (Seard et al., 2013). Although insect tubes are generally minor carbonate components relative to abiotic and bioinduced carbonates, if these durable tubes - constructed from mineral and organic particles - are considered as skeletons then they create Microbial-Skeletal Hybrid Carbonates (Fig. 21).

Travertine hot spring precipitation, as in cool water caves and creeks, appears - at the most fundamental level - to be driven by pH increase following CO_2 degassing (Allen and Day, 1935, p. 376; Nordstrom et al., 2005). Since pressurized underground thermal waters can carry abundant calcium and CO_2 in solution, degassing is very rapid and $CaCO_3$ precipitation (in contrast to most cool water creeks) is concentrated at and near the vents, creating thick layered mounds and cones (e.g., Mammoth Hot Spring, Wyoming, USA: Bargar, 1978; Fouke et al., 2000, 2003; De Boever et al., 2016). Calcite is the main $CaCO_3$ mineral but aragonite, possibly favored by high temperature, rapid CO_2-degassing and water composition (Kitano, 1962, 1963; Folk, 1994; Pentecost, 2005; Jones and Renaut, 2010; Asta et al., 2017; Jones, 2017), can also be common. In areas of rapid flow close to vents, filaments of thermophilic bacteria oriented by currents (e.g., *Thermothrix* 'streamers', Caldwell et al., 1984; Farmer and Des Marais, 1994) form

Fig. 21. Non-marine Microbial-Skeletal Dual Hybrid. Lacustrine insect larvae tubes encrusted by stromatolites. Mid-Eocene (~45 Ma), La Barge, WY, USA

prominent substrates for aragonite precipitation (Fouke et al., 2000, 2003; Fouke, 2011). Over distances of 10's to 100's of meters, the steep marginal slopes of hot spring travertine mounds typically grade into extensive tabular marsh-pool depression facies, often dominated by 'shrub' fabrics and macrophyte (reed, grass) molds (Guo and Riding, 1998). Carbonate 'shrubs' (Chafetz and Folk, 1984) are irregular vertically elongate structures, often only one or a few centimeters in height and typically arranged in sheets, with internal radial and/or layered fabrics. Mn/Fe-rich varieties in desert soils, deep sea deposits and iron formations, as well marine carbonates, have been named *Frutexites* (Maslov, 1960) (Walter and Awramik, 1979; Böhm and Brachert, 1993; Chafetz et al., 1998). Although their origins remain poorly understood, carbonate shrubs are widely recognized in two contrasting situations: Proterozoic shallow-marine carbonates (see *5.2.1. Microdigitate stromatolites*, above), and hot-spring travertines (e.g., Chafetz and Folk, 1984; Guo and Riding, 1994; Claes et al., 2017; Erthal et al., 2017). Abiotic and microbial origins for travertine 'shrub' fabrics continue to be debated (Chafetz and Folk, 1984; Pentecost, 1990; Jones and Renaut, 2010; Erthal et al., 2017). If these 'shrubs' are combinations of abiotic and microbial processes then they are Hybrid Carbonates.

Shrub fabric is just one of many examples of the problems encountered in accurately discriminating between abiotic and microbial processes, that often complicate interpretation even in present-day spring and lake carbonates (e.g., Northup and Lavoie, 2001; Arp et al., 2003; Léveillé et al., 2007; Fouke, 2011). These difficulties commonly arise where microbes are present in depositional systems where water chemistry strongly favors carbonate precipitation, e.g., due to processes such as rapid degassing, mixing, and/or evaporation. The central question is deceptively simple: did microbes actively promote, or merely act as substrates for, precipitation? Confidently elucidating this can be challenging. Depositional settings include alkaline lakes, such as Mono Lake (California) and Pyramid Lake (Nevada) (Benson, 2004) in the western USA, that experience localized and/or episodic influx of Ca^{2+}-rich spring water. Mixing of Ca^{2+}-rich spring water with Ca^{2+}-poor alkaline lake water can be expected to promote $CaCO_3$ precipitation (Runnels, 1969, p. 1190; Wigley and Plummer, 1976). At the same time, since these lakes are nutrient-rich, they host a wide variety of organisms, including benthic microbes, which can interact with and be incorporated into the resulting carbonate (tufa) deposits. Describing Pyramid Lake, Russell (1885, pp. 220-221) noted that 'Sublacustrine springs, charged with carbon dioxide and calcium carbonate, upon mingling with the waters of a lake may part with their dissolved gases and deposit calcareous tufa'. Working at Mono Lake, Dunn (1953, p. 22) agreed, and wrote 'Algal action may or may not be significant but, on the basis of the other information available, it is certainly not necessary'. However, more recently Scholl and Taft (1964 p. 309) suggested that although some Mono Lake tufa is likely abiotic, about two-thirds of it might be photosynthetically induced. Similarly, Brasier et al. (2018) concluded that Mono Lake 'tufa chimneys' *'are not solely the result of*

abiotic mixing between calcium-rich spring waters and alkaline lake waters … Rather, chimney fabric development was influenced at least at the nano- to microscales by microbes that colonised the fertile and relatively nutrient-rich vent sites.' Bougeault et al. (2019) encountered similar challenges in Bolivian Ca-Si hydrothermal springs. These examples reflect complex and intimate relationships between abiotic and biotic processes that can be difficult to disentangle. Such considerations, as with those regarding the formation of shrub fabrics, directly impact assessment of Hybridity.

9. Discussion

9.1. Anachronistic carbonates

Precambrian carbonates, except for the very youngest, are essentially non-skeletal and often contain Microbial Carbonates and Sparry Crusts (Grotzinger and James, 2000), whereas Phanerozoic carbonates, especially after the Early Ordovician, often contain skeletons. Nonetheless, Microbial and Abiotic carbonates persisted in the Phanerozoic and were periodically abundant, especially prior to the Cretaceous. This can be observed at two scales. Extended episodes of increased Microbial Carbonate (MC) abundance include MC1, Cambrian-mid-Ordovician; MC2, latest Devonian-Mississippian; MC3, mid-Permian to mid-late Triassic; and MC4, late Jurassic-early Cretaceous (Riding et al., 2019). On shorter timescales, often within these longer episodes, there are intervals characterized by abrupt decline in Skeletal carbonates and increase in Microbial and Abiotic carbonates. The best known examples of these occur in the immediate aftermaths of Mass Extinction Events, e.g., Frasnian-Famennian (e.g., Webb, 1998; Whalen et al., 2000) and Permian-Triassic (e.g., Schubert and Bottjer, 1992). The sediments and biotas associated with these relatively short-lived episodes of abrupt change, suggesting reversion to Precambrian or Early Paleozoic conditions, have been described as 'anachronistic', 'anomalous' or 'disaster' deposits or forms.

In addition to Microbial Carbonates, this terminology has also been applied to oolites, seafloor crystal crusts, and flat-pebble conglomerates near the Permian-Triassic boundary (e.g., Groves et al., 2003; Groves and Calner, 2004; Pruss et al., 2006; Baud et al., 2007; Kershaw et al., 2009; Woods and Baud, 2008; Woods, 2009, 2014; Li et al., 2015). Sepkoski Jr (1982, p. 383) suggested that after the Ordovician radiation *'deposition of flat-pebble conglomerates became confined to environments where the infauna was restricted and/or bottom sediments were eroded to considerable depths'*. Subsequently, Sepkoski Jr et al. (1991), focusing on the 'biological overprint' created by infaunal animals that *'rework sediment and distort or obliterate primary bedding features'* suggested (p. 310) that, especially after the Early Ordovician, *'environmental conditions that restrict the infauna will produce "anachronistic facies" with bedding features more characteristic of earlier time intervals'*. 'Anachronistic' facies have been described in the Late Silurian Calner (2005). Schubert and Bottjer (1992) described stromatolites in the immediate aftermath of the Permian-Triassic mass extinction as 'disaster forms', a term proposed by Fischer and Arthur (1977) for *'opportunistic taxa, typically of long stratigraphic range, which normally occur in marginal and environmentally unstable settings but become abundant and environmentally widespread during times of biotic crisis'*. Grotzinger and Knoll (1995) drew attention to late Permian sparry seafloor crusts, describing these *'large quantities of marine cement and related facies'* as 'anomalous'. Late Devonian microbial carbonates have been described as 'disaster forms' that *'proliferated following the terminal Frasnian mass extinction event'* (Whalen et al., 2000; see also Mata and Bottjer, 2012). Similarly, Ibarra et al. (2014) linked microbialites in England to the end-Triassic mass extinction event. Anachronistic Carbonates are therefore defined by both type and age. Compositionally they can include any type of Abiotic and/or Microbial Carbonate, irrespective of whether they are *in situ* (e.g., stromatolites, sparry crust) or allochthonous (e.g., flat-pebble conglomerate, oolite, carbonate mud). But they must have formed at times when widespread - preferably global - conditions limited or
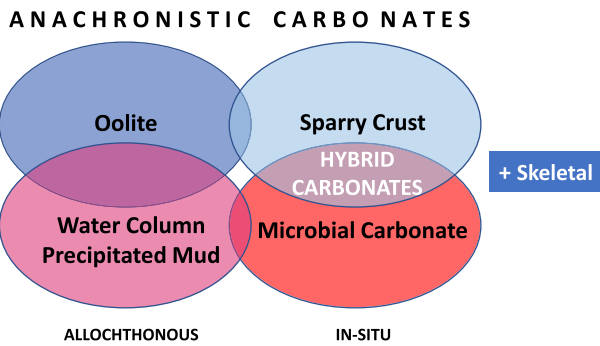
Fig. 22. Anachronistic and Hybrid Carbonates. Hybrid Carbonates are intimate combinations of two or more of *in situ* Abiotic, Microbial and Skeletal carbonates. In contrast, Anachronistic carbonates formed under conditions that limited or excluded skeletal and infaunal biotas. They can be Abiotic /or Microbial and in situ or allochthonous. Anachronistic carbonates may be, but are not necessarily, Hybrid, and are generally skeleton poor.

excluded skeletal and infaunal biotas. Anachronistic Carbonates can be, but are not necessarily, Hybrid (Fig. 22).

9.2. Secular developments and patterns: looping, backtracking

Through time, changes in the proportions and combinations of Abiotic, Microbial and Skeletal *in situ* components in Hybrid Carbonates (Fig. 7) might be expected to show broad trends, e.g., from more Abiotic to more Microbial in the Precambrian, and from more Microbial to more Skeletal in the Phanerozoic. In detail, however, such patterns – although they may be present – exhibit considerable fluctuation in time and space which we term 'backtracking' in Dual Hybrids, and 'looping' in Triple Hybrids (see Section 9.2.2.1). Backtracking and looping are particularly conspicuous in the Phanerozoic where they broadly reflect long-term fluctuations in the relative abundance of Microbial and Skeletal carbonates (Riding et al., 2019).
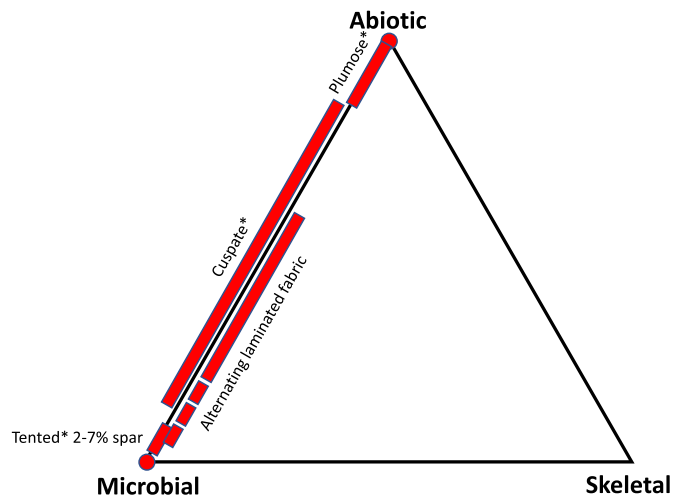
9.2.1. Precambrian

Our assessment (Section 5) suggests that, among putative Dual Abiotic-Microbial Hybrid Carbonates, Convolute Roll-up and Net fabrics are most common in the Late Archean, and more ordered Tent fabrics, that can be quite large and supported by herringbone calcite crusts, range from Neoarchean to late Mesoproterozoic. In addition, Alternating Laminated Fabric ranges Late Archean to at least Early Neoproterozoic (Fig. 23). Fenestral (Convolute, Net, Tent) fabrics range from more Abiotic to more Microbial on Hybridity Plots, whereas Alternating Laminar Fabrics tend to occur between the mid-point of the Abiotic-Microbial side and the Microbial apex (Fig. 24). Net Fabric plots closer to the Abiotic apex whereas examples of denser and more structured Tent Fabric (including thyssagetaceans) plot closer to the Microbial apex. The details of all these categories, their structure and composition and distributions require further clarification and assessment.

Microbial carbonates in general have been reported throughout the Precambrian record of sedimentary carbonates, from ~3500 Ma at Pilbara (Lowe, 1980; Walter et al., 1980; Allwood et al., 2006) to the stromatolites and thrombolites of the Ediacaran (Grotzinger, 2000; Lemon, 2000; Caird et al., 2017). Global estimates of Proterozoic stromatolite abundance differ significantly. Based on qualitative assessment, Grotzinger (1990) estimated that the 'average volume of stromatolitic sediment per unit of carbonate platform' shows overall fluctuating decline from early to late Proterozoic, with a minor peak ~950 Ma. In contrast, diversity data (number of stromatolite taxa) for the same interval, Awramik and Sprinkle (1999) show increase to a marked peak ~1250 Ma, followed by decline. Data based on 'number of stromatolite-bearing marine units normalized by all marine
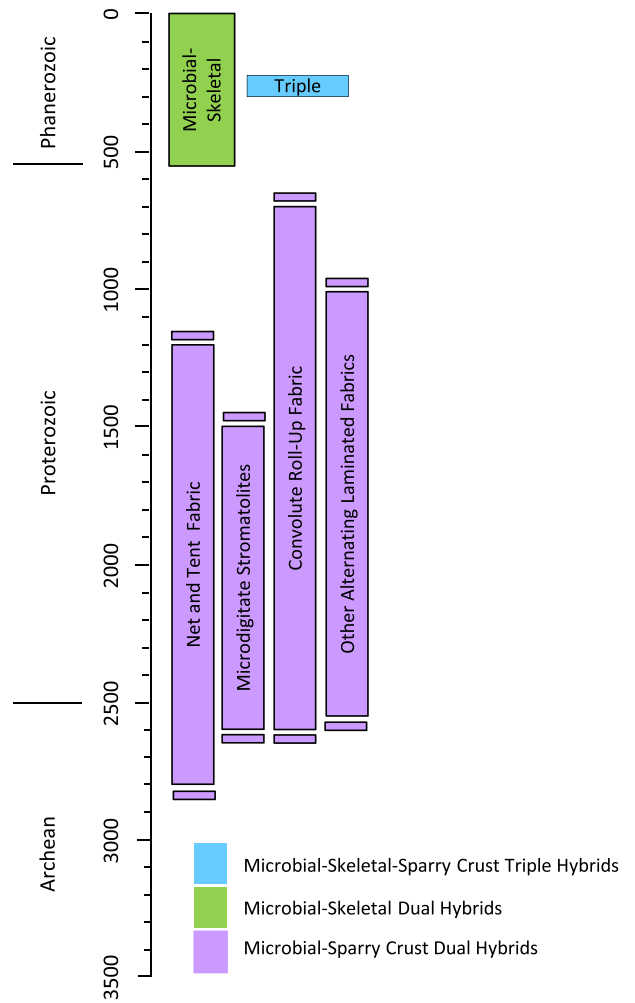
Fig. 23. Principal Phanerozoic distributions of Dual and Triple Hybrid Carbonates, and very approximate Precambrian distributions of the main varieties of Fenestral and Alternating Laminated fabrics.

Fig. 24. Precambrian Hybrid Carbonate compositional distributions. Dual Abiotic-Microbial Hybrids are common. There is probably widespread secular back-tracking and there may be a long-term trend from more Abiotic to more Microbial. * Indicates data from Sumner (1997), fig. 7).

sedimentary rock units' (Peters et al., 2017, Fig. 2a), for North America alone, support aspects of both these assessments. They suggest that stromatolites were abundant throughout the Paleoproterozoic and declined in the Mesoproterozoic, but recovered to a peak ~1000 Ma before declining in the Neoproterozoic. There are parallels in this pattern with the abundances of seafloor crystal crust and microdigitate stromatolites, both of which seem to be abundant in the Paleoproterozoic (Section 5. Marine Precambrian, and *5.2.1. Microdigitate stromatolites*) and decline during the Mesoproterozoic (Grotzinger and Kasting, 1993). Whereas microdigitate stromatolites appear to have remained scarce in the Neoproterozoic, crystal crusts reappear in episodes of local abundance, particularly in Cryogenian 'cap carbonates' (Grotzinger and Knoll, 1999, p. 352; Grotzinger and James, 2000, Fig. 4) (Section 5. Marine Precambrian). These secular fluctuations likely involve medium- to long-term back-tracking patterns, and remain to be elucidated.

9.2.2. Phanerozoic

The evolution of Ca-carbonate skeletons (Knoll and Fischer, 2011; Porter, 2011; Gilbert et al., 2019) was a signature development. Phanerozoic marine carbonates can be broadly divided into alternating intervals, respectively dominated by Microbial and algal-invertebrate Skeletal carbonates (Flügel and Kiessling, 2002; Kiessling et al., 2003; Riding et al., 2019). Consequently, from the Early Cambrian to Early Cretaceous, Hybrid Carbonates appear to have developed during episodes of overlap or transition between episodes dominated by Microbial or Skeletal carbonates. Overlap between Microbial and Skeletal carbonates occurred in the Early Cambrian and Late Jurassic, and transition between episodes dominated by Microbial and Skeletal carbonates occurred in the early-mid Ordovician and Late Devonian (Riding, 2005; Riding et al., 2019; Chen et al., 2019) (Fig. 25-27). Overall, Hybrid Carbonates are locally well-developed throughout the Phanerozoic until the Cretaceous, but were generally less abundant during the past 133 Ma.
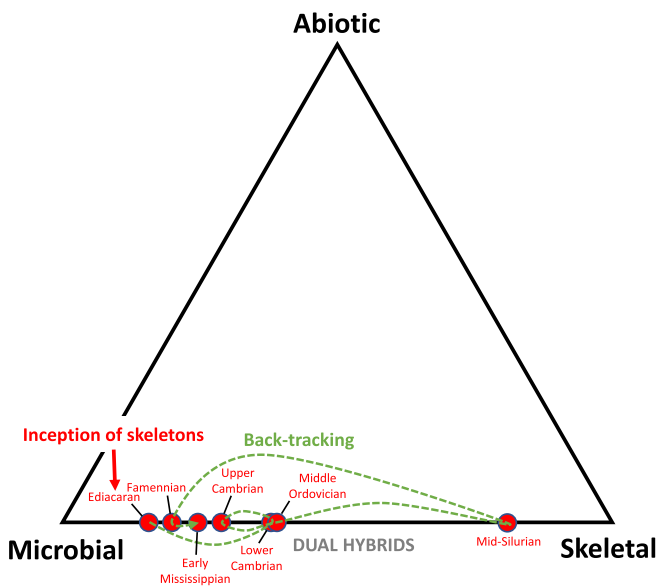

Fig. 25. Late Ediacaran-Mississippian Hybrid Carbonate compositional distributions. Late-Ediacaran inception of skeletons was the signature development that created diverse Dual Microbial-Skeletal Hybrids. These are especially common in the Cambrian-Ordovician and Late-Devonian-Mississippian. Complicated back-tracking reflects the interplay of conditions – particularly thought to involve oxygenation – that favored skeletal invertebrates at the expense of microbial carbonates, with competition for both CaCO$_3$ and space (Riding et al., 2019). Green dashes indicate timeline. See Supplemental File for data and sources.
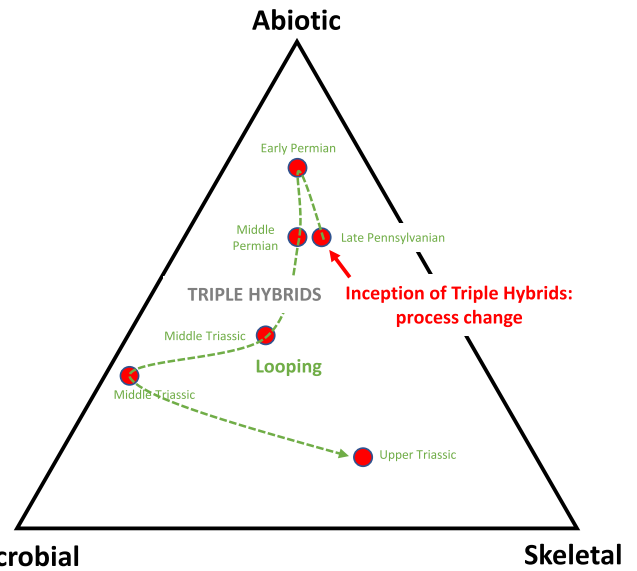

Fig. 26. Pennsylvanian-Mid Triassic Hybrid Carbonate compositional distributions. Triple Hybrids created complex looping during the Late Pennsylvanian- to mid-Triassic due to increase in the deposition of reef-associated sparry seafloor crusts. Research is needed to clarify the extent to which some of these crusts may be cryptic or secondary. Nonetheless, their widespread and locally conspicuous development indicates a significant process change. Green dashes indicate timeline. See Supplemental File for data and sources.
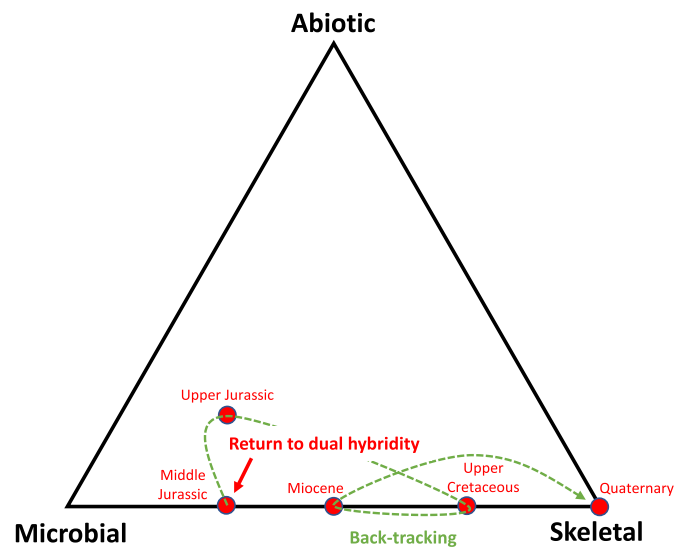

Fig. 27. Mid Triassic-Recent Hybrid Carbonate compositional distributions. The Jurassic marked a return to Microbial-Skeletal Hybrids, some - in deeper less oxygenated conditions – are reminiscent of the Late Cambrian. During the Cretaceous Microbial Carbonate formation became progressively more limited, presumably due to reduced seawater carbonate saturation state. Cryptic microbial carbonates are nonetheless locally conspicuous in coral reefs of the past 6 Myr. Green dashes indicate timeline. See Supplemental File for data and sources.

9.2.2.1. Paleozoic-Triassic. Dual Hybrid Microbial-Skeletal carbonates dominate the Cambrian-mid Ordovician and Late-Devonian-Mississippian (Section 6.1. Late Ediacaran to Mississippian). They were again common from Late Pennsylvanian-mid Triassic (Section 6.2. Pennsylvanian to Mid-Triassic) but during this interval shallow marine conditions also favored the precipitation of crystalline crusts; as a result, Triple Hybrid Carbonates formed (Fig. 4). Cambrian to Mississippian Hybridity Plots show frequent backtracking in response to changes in the proportions of Microbial and Skeletal carbonate. This

changed to a distinctive looping pattern as sparry seafloor crusts developed in the Late Pennsylvanian and persisted until the mid-Triassic (Fig. 26). However, some associated sparry deposits may be cryptic, or even secondary.

9.2.2.2. Jurassic-Cenozoic. Hybrid Carbonates are inconspicuous or scarce in the Late Triassic and Early Jurassic, but resurged in the Late Jurassic and Early Cretaceous as Microbial Carbonates encrusted corals and sponges (Section 6.3. Upper Triassic to Early Cretaceous). Some Jurassic Microbial-Sponge Hybrids in less oxygenated conditions are reminiscent of Late Cambrian examples (Lee and Riding, 2018). Hybrid Carbonates appear to have declined during the Cretaceous as planktic calcifiers augmented benthic algae and invertebrate skeletal carbonates (Section 6.4. Mid-Cretaceous to Present-day). Nonetheless, cryptic microbial carbonates are locally conspicuous in reefs of the past 7 Myr (Riding et al., 1991; Camoin and Montaggioni, 1994). All these changes, as in the Paleozoic, created complex backtracking patterns (Fig. 27).

9.2.3. Methane seeps

Methane Seeps are Dual and Triple Hybrid Carbonates whose currently known range is from Silurian to Recent (Section 7. Methane seeps). Their variation in composition, from more Skeletal to more Microbial and more Abiotic, still requires elucidation (Fig. 28).

9.2.4. Non-marine

Karst carbonate (cave-creek-fall-lake) systems show rapid downstream reversals in process that can result in linear backtracking trends as conditions change. In contrast, spatial trends in precipitation in subaerial calcium and bicarbonate hot spring vents, although also very marked, appear more unidirectional with respect to Hybrid Carbonate composition.

9.3. Hybrid carbonate recognition, arrangement and timing

Hybrid Carbonates exhibit considerable variation in the scale, arrangement, and time of formation of adjacent components. Precambrian Hybrids (Section 5), except for the very youngest, are Dual Abiotic-Microbial. Although coarse fabrics are conspicuous (e.g., Net and Tent fabric, Fig. 10), there can be difficulties in distinguishing finer combinations of abiotic and microbial precipitates (e.g., Alternating Laminated Fabric, Fig. 17), especially if fabric preservation is poor.
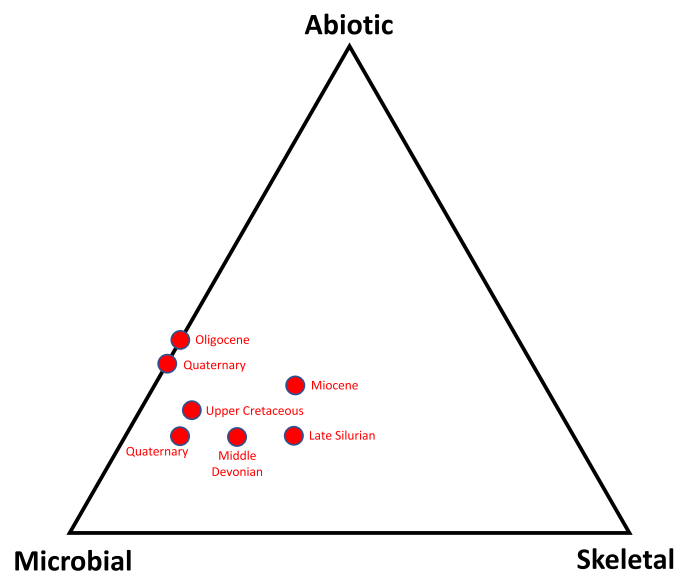

Fig. 28. Methane seep compositions. See Supplemental File for data and sources.

Many researchers have reported difficulties in confidently distinguishing between abiotic and microbial carbonates in the Precambrian, particularly where fabrics are sufficiently regular or crystalline to suggest an origin that is at least partly abiotic (Hoffman, 1975; Grotzinger and Read, 1983; Sami and James, 1994; Grotzinger and Rothman, 1996; Grotzinger and Knoll, 1999; Sumner and Grotzinger, 2004). These uncertainties have raised doubts about stromatolite recognition and definition (Semikhatov et al., 1979), and often surface when very old examples are discussed (Lowe, 1994; Riding, 2000; Allwood et al., 2018). The hardest cases to resolve may be those that could be Hybrid mixtures on a fine scale (Riding, 2008). These challenges are not restricted to the Precambrian. Pope et al. (2000) drew attention to 'stromatolites with chemically precipitated textures' at Phanerozoic carbonate-evaporite transitions in the Silurian, Permian and Miocene. Even in apparently normal marine environments, finely layered fabrics such as in *Archaeolithoporella*, a locally important component of Permian-Triassic reefs (Flügel, 2002, p. 560), although initially thought to be a red alga (Endo, 1959), has been regarded as a stromatolite (Newell et al., 1953), cement (Dunham, 1969), 'precipitated stromatolite' (Grotzinger and Knoll, 1995), and compared with abiotic speleothem (Kendall and Iannace, 2001). If Grotzinger and Knoll's (1995) interpretation is correct then *Archaeolithoporella* is a Dual Hybrid combination of alternating calcified biofilm and thin sparry crust. Most Phanerozoic marine Hybrids are Dual Microbial-Skeletal and their recognition is aided by the generally distinctive appearance of skeletal carbonate. This, together with often better age control, preservation and documentation, make it easier to track Hybrid Carbonate development in the Phanerozoic (Section 6) (Fig. 29).

Depositionally, Skeletal, Microbial Carbonate or Sparry Crust may form first, or all three may be relatively penecontemporaneous (Fig. 30). On the other hand, there may be extended time-gaps between components, e.g., within time-averaged reef fabrics (Edinger et al., 2007). In 16-6 Ka reefs at Tahiti, cryptic stromatolites on average are 100-500 years younger than the coral-dominated skeletal frameworks they encrust (Camoin et al., 2006). This age gap occurs in large cavities that develop relatively slowly during reef growth. For example, spaces within coral framework in Messinian reefs in SE Spain can be tens of centimeters in size (Riding et al., 1991, Fig. 10). In smaller cavities, the time difference is likely to be less, e.g., in some mid-Paleozoic skeletal frameworks (Nose et al., 2006, Fig. 3a) (Section 6: Late Ediacaran-Mississippian). An additional style of spatial arrangement is where Hybrid Carbonates are repetitively juxtaposed against an end-member carbonate component (such as Sparry Crust, Microbial Carbonate, or Skeleton). For example, in ~2.8 Ga Steep Rock Lake Hybrid domes, layers of hybrid Net Fabric (Cuspate Fenestral Fabric) repeatedly alternate with seafloor Sparry Crust (Fralick and Riding, 2015, Fig. 18, 19) to form macrolayered 'Giant Domes' (Fig. 11).

9.4. Microbial-sponge hybrids

Throughout the Phanerozoic, microbial carbonates are commonly associated with sponges (Brunton and Dixon, 1994). In the Cambrian, for example, both archaeocyaths (James and Debrenne, 1980; Rowland and Gangloff, 1988; Rowland, 2001; Rowland and Shapiro, 2002; Gandin and Debrenne, 2010) and lithistids (Hamdi et al., 1995; Lee et al., 2019) formed reefs in close association with Microbial Carbonates. Sponge biotas commonly appear relatively soon after major extinctions; e.g., end-Ordovician (Botting et al., 2017), Late Devonian (Webb, 2001); end-Permian (Vennin et al., 2015). In the mid-late Jurassic microbial carbonates are commonly associated with hexactinellids and lithistids (Keupp et al., 1993; Leinfelder et al., 1994, 1996, 2002). In addition, keratose sponges, although less conspicuous, are also locally common, e.g., Lee et al., 2010, 2014; Luo and Reitner, 2014, 2016; Park et al., 2015; Coulson and Brand, 2016; Coulson, 2018). This common mutual association appears to reflect the ability of some sponges to tolerate conditions similar to those that favor Microbial
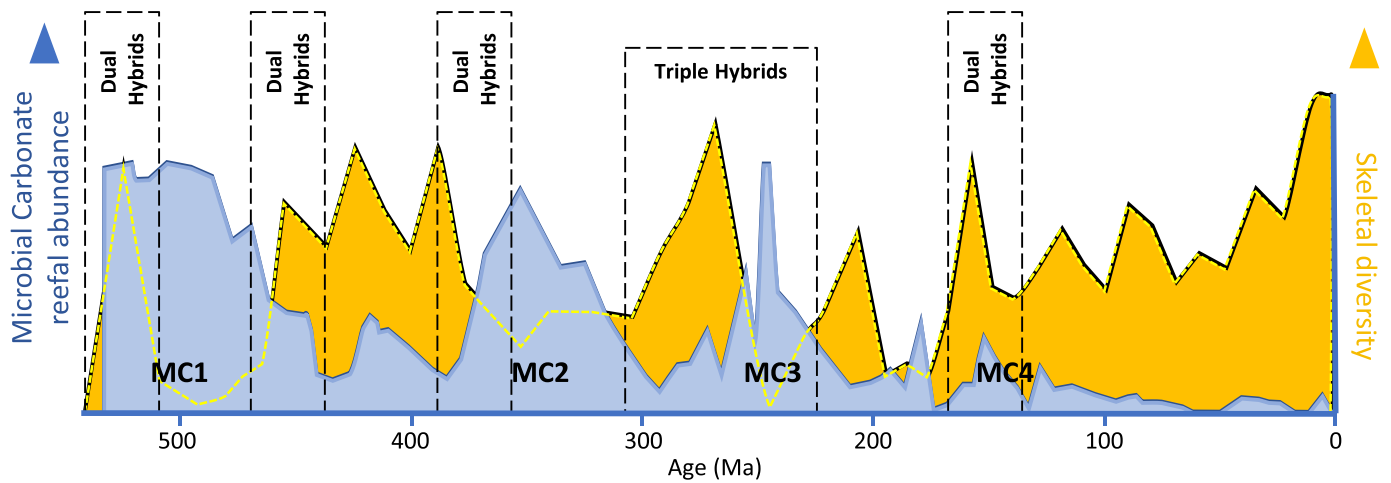
Fig. 29. Principal intervals with widespread Hybrid Carbonate plotted on Skeletal diversity (yellow) data from Riding et al., 2019, fig. 2) and Microbial Carbonate reefal abundance data (blue) from Kiessling et al., 2006, fig. 1). In general, Hybrid Carbonates occur throughout much of the Phanerozoic until the Cretaceous, but appear less common during the past 133 Ma. They are most conspicuous from Early Cambrian to Early Cretaceous, especially where Microbial Carbonate and Skeletal Carbonate abundances overlap, e.g., Early Cambrian and Late Jurassic, and during transitions between Microbial Carbonate (MC1-MC4, Riding et al., 2019) and Skeletal Carbonate episodes (e.g., Early Ordovician, Late Devonian). Triple Hybrids are relatively common from late Pennsylvanian to early Upper Triassic (Fig. 26).

Carbonates (Lee and Riding, 2018).

9.5. Scarcity of abiotic-skeletal hybrids

The marine history of Hybrid Carbonates shows that, overall, Abiotic-Microbial carbonates were common in the Precambrian and Microbial-Skeletal carbonates in the Paleozoic-Mesozoic. In comparison, Abiotic-Skeletal carbonates at all times appear to be vanishingly scarce (Fig. 25-27). This may be explained by the link that Abiotic and Microbial Carbonates both share with saturation state. Consequently, elevated carbonate saturation not only promotes Abiotic carbonate precipitation (Stumm and Morgan, 1996; Zeebe, 2012), but also the formation of Microbial Carbonates (Kempe and Kaźmierczak, 1994;

Pentecost, 2005; Riding and Liang, 2005; Arp et al., 2010; Kaźmierczak et al., 2015; Zhu and Dittrich, 2016). This connection appears to be reflected by the very broad long-term trend from Abiotic to Microbial to Skeletal carbonates in marine environments during the Precambrian-Phanerozoic (Fig. 7). This can account for the scarcity of Abiotic-Skeletal Hybrids (Fig. 24-26) since Phanerozoic Abiotic carbonates are very likely to be associated with Microbial Carbonates.

10. Conclusions

Hybrid Carbonates are *in situ* associations of two or three of Abiotic, Bioinduced and Biocontrolled carbonates. Since their formation requires precipitation of either Abiotic or Microbial Carbonate, or both,
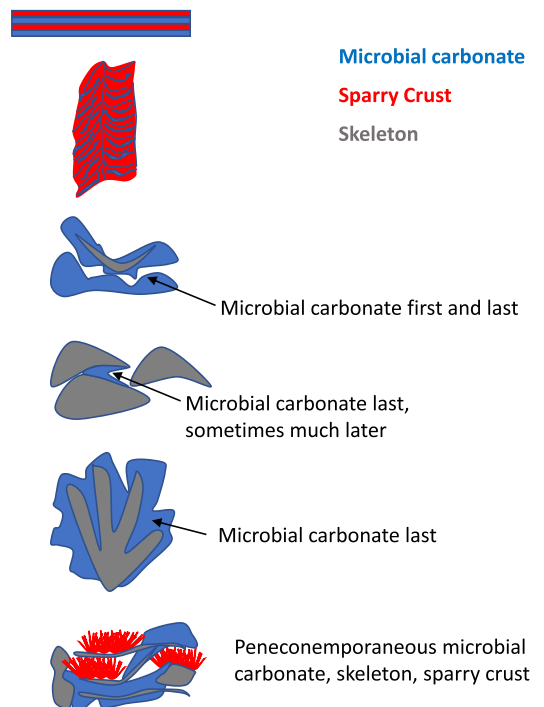

Fig. 30. Examples of Hybrid Component successive timing and arrangement. Skeletal, Microbial and Sparry Crust carbonate may each form first, or develop more-or-less simultaneously.
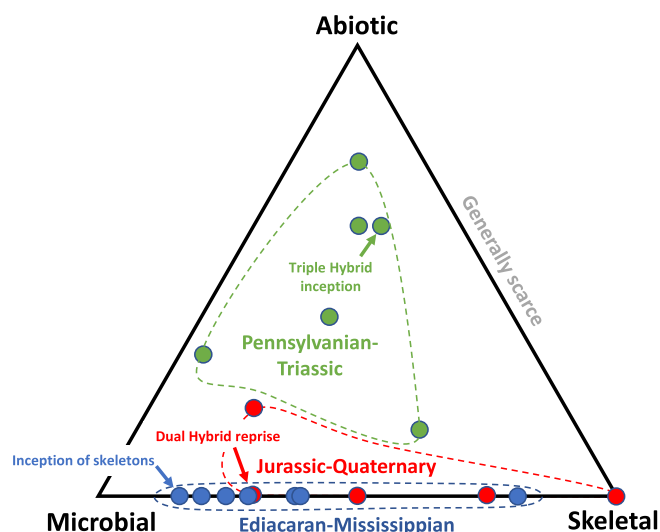
Fig. 31. Summary of successive Hybrid Carbonate time trends for the past ~600 Ma (based on Figs. 25-27).

Hybrid Carbonates can reflect water chemistry in present-day marine and non-marine environments, as well as responses to changes in carbonate precipitation over geological time-scales. Precambrian marine Hybrid Carbonates are typically combinations of Sparry Crust and Microbial Carbonate, whereas Phanerozoic Hybrids are often combinations of Microbial and Skeletal carbonate. In contrast, Abiotic-Skeletal hybrids - which could conceivably form in the Phanerozoic - appear to be scarce. This is probably because conditions that promote Abiotic carbonate precipitation also favor Microbial Carbonate formation. If Skeletons are also present then, in these circumstances, all three carbonate types are likely to co-occur, forming Triple Hybrids.

Since Hybrid Carbonates are defined here as *in situ* deposits, they often contribute to accumulations that can be broadly regarded as reefal. In relatively deep marine environments this includes methane seep carbonates: sulfur-based chemotrophic communities that create relatively deep-water Triple Hybrid deposits of Microbial and Sparry Crust carbonate, often associated with invertebrates that host bacterial endosymbionts. Non-marine Hybrid Carbonates are mainly Dual Hybrids of Sparry Crust and Microbial Carbonate, and *in situ* skeletons (including insect tubes, see Section 7) are usually only occasionally volumetrically important. Hybrid Carbonates can be conspicuous in deposits in which the components (Abiotic, Bioinduced, Skeletal) are relatively thick, but are harder to distinguish in finely layered structures such as microdigitate stromatolites.

The history of Precambrian Hybrid Carbonates, which are almost entirely dominated by Microbial Carbonate and Sparry Crust, is less well documented than Phanerozoic examples. The appearance of skeletal carbonates near the end of the Proterozoic made Hybrid Carbonates more diverse, and often also more conspicuous. Hybrid Carbonates help to define Phanerozoic intervals of biosphere evolution and environmental change. Microbial-Skeletal Dual Hybrids are common in the Cambrian and Early Ordovician, and are conspicuous during transitions between Microbial- and Skeleton-dominated intervals in the mid-Ordovician and from late Devonian-early Mississippian. Triple Hybrids (Sparry Crust, Microbial Carbonate, Skeleton) are conspicuous from Late Pennsylvanian-middle Triassic, followed by a return to widespread Dual Hybrids in the Late Jurassic-Early Cretaceous. Subsequent marine Microbial Carbonate decline reduced the overall abundance of Cenozoic Hybrid Carbonates, although good examples are present in some late Neogene reefs.

Triangular plots of Hybrid Carbonate composition help to display patterns of change, including 'backtracking' and 'looping', that reflect the proportions of Abiotic-Microbial-Skeletal components in time and space (Figs. 25-27, 31). Non-marine Hybrid Carbonates in creek-lake systems often show repeated back-tracking in response to changes in water flow rate, whereas changes along hot spring carbonate flow-paths may be less varied. Microbial-Skeletal Hybrid composition backtracked frequently during the Paleozoic, as Microbial- and Skeleton-dominated intervals alternated with one-anther. Triple Hybrids, formed by increased Sparry Crust deposition, created distinctive looping patterns late Pennsylvanian to mid-Triassic reefs. Dual Hybrids were again common in the Late Jurassic and Early Cretaceous. Overall, these patterns reflect process-based changes, such as Late Ediacaran appearance of Ca-carbonate skeletons, Late Pennsylvanian reappearance of seafloor crystalline crusts, and the environmental and biological factors regulating Phanerozoic episodes of Microbial Carbonate and Skeletal Carbonate abundance. Recognition of Hybrid Carbonates therefore draws attention to intimate mixtures of *in situ* Abiotic, Microbial and Skeletal carbonates, whose history reflects important developments in carbonate deposition in time and space.

Declaration of Competing Interest

Acknowledgements

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.earscirev.2020.103300.

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