Microbially catalyzed dolomite formation: From near-surface to burial

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ARTICLE INFO

ABSTRACT

Over the past century a number of models have been developed to explain the vast stratigraphic distribution of authigenic dolomite. These models include hydrogeological, geochemical and geomicrobiological interpretations that shed light on kinetic constraints on low-temperature dolomite formation, and, in particular, how certain microbes can overcome such limitations. In this review, we focus on the direct and indirect mechanisms by which microbes facilitate the nucleation and shallow burial diagenetic stabilization of dolomite in marine sediments. We also consider the likely effects of local and global scale biogeochemical perturbations over the distribution and activities of subsurface microbes, and, thus, potentially over the stratigraphic distribution of dolomite. Considering the many advances that have been made in the fields of geomicrobiology and biogeochemistry during the past 20 years, investigating the important role microbes play in sedimentary systems will undoubtedly contribute to a more complete interpretation of dolomite formation in the rock record.

1. Introduction

Dolomite ($CaMg[CO_3]_2$) is a rhombohedral carbonate mineral displaying $R\overline{3}$ space group symmetry with regard to the distribution of Mg^{2+}, Ca^{2+} and CO_3^- anions in the mineral lattice, and that can be structurally visualized as alternating layers of calcite and magnesite (Lippmann, 1973; Reeder, 1983) (Fig. 1). Although it is a very minor constituent of modern unconsolidated marine sediments (Warren, 2000), substantial amounts of Ca-rich, partly ordered precursors, here collectively referred to as Ca-dolomite — can be found in Neogene continental margins and largely in the peritidal zone of Holocene carbonate platforms, where it tends to occur as a primary cement but can also replace other precursor carbonate phases (Graf and Goldsmith, 1956; Gaines, 1974; Gaines, 1977; Budd, 1997; Arvidson and Mackenzie, 1997; Gregg et al., 1992). In Holocene successions, this imperfectly-ordered, rhombohedral carbonate phase, sometimes referred to as protodolomite (after Graf and Goldsmith, 1956; Gaines, 1977; see also Gregg et al., 2015), typically occurs as sub-micron scale spherulitic crystals (Fig. 2A) that would transform to more stoichiometric euhedral rhombs with increasing burial (Fig. 2B). Nonetheless, sub-micron scale rhombs can also be seen in Holocene peritidal dolomite-forming locales, such as in Lagoa Vermelha, Brazil (e.g.,

Fig. 2C–D). There is still uncertainty as to how the Ca-rich, disordered precursor phases subsequently stabilize to partially ordered dolomite under near-surface conditions, but the occurrence of the latter in organic-rich marine Neogene sediments has been well documented (Kelts and McKenzie, 1982; Burns and Baker, 1987; Compton, 1988; Vasconcelos and McKenzie, 1997; Meister et al., 2007; Bontognali et al., 2010; Bahniuk et al., 2015; Brauchli et al., 2015).

Syngenetic (primary) dolomite represents the product of an early diagenetic stage of direct spontaneous nucleation and *in situ* stabilization from fluid (i.e., homogeneous nucleation). It rarely occurs in nature (but see Shinn and Kendall, 2011), as the abundance of available nucleation sites results in heterogeneous nucleation promoted by a high density of suitable substrata (Sibley and Gregg, 1987). Syngenetic dolomite has been recognized as the more likely precursor of many late-burial dolomites (Holland and Zimmerman, 2000). Primary dolomite contrasts with those termed secondary, as they either result from dissolution/reprecipitation of other metastable carbonate minerals (Gregg and Shelton, 1990; Sibley, 1991), or are the result of a syndepositional seeding, i.e., the transport of peritidal crystallites to subtidal realms, also followed by a dissolution/reprecipitation process (Lumsden, 1988). For secondary dolomite, the ensuing recrystallization process often leads to the development of fabric destructive textures that hamper our
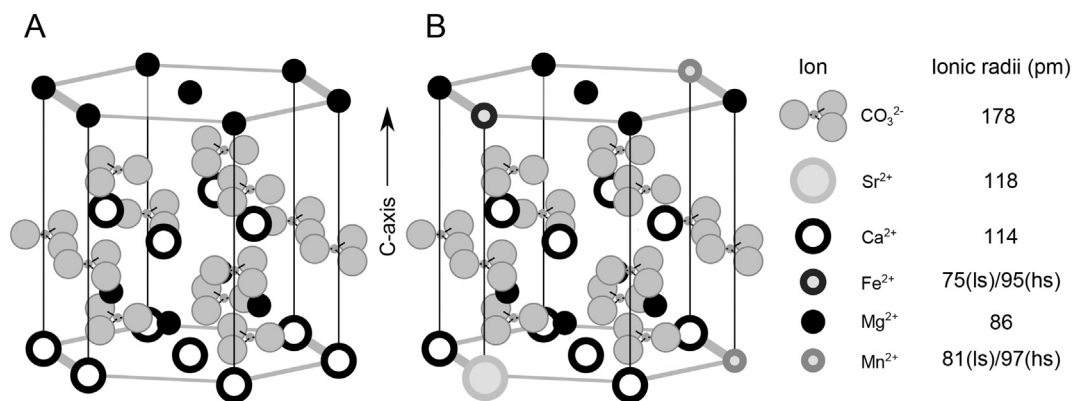
Fig. 1. Atomic structure of an idealized stoichiometric dolomite crystal (A), also showing preferred sites for elemental substitution of Sr, Mn and Fe (B). For dolomite (sensu-stricto), cation ordering results in the loss of the c-glide-plane (i.e., 3-fold rotoinversion and a glide plane parallel with the c-axis) typical of calcite, thus imparting $R\overline{3}$ space group symmetry on the rhombohedral, near stoichiometric Ca-Mg mineral (see Gregg et al., 2015).

ability to unambiguously interpret the mechanism of dolomite growth. Interestingly, the scarcity of primary Holocene dolomite contrasts with its abundance in the Precambrian sedimentary rock record, which preserves extensively lithified intervals composed essentially of fine crystalline primary dolomite (Tucker, 1982) of potential microbial origin (Grotzinger, 1989; Grotzinger and Knoll, 1995). Conversely, most dolostones are formed by interlocking mosaics of multigenic crystals that are two or three orders of magnitude larger than their primary counterparts. This difference in size, as inferred from detailed petrographic observation, would reflect multiple stages of development, most of which would have occurred syndepositionally, or within

a few million years after sedimentation (Carpenter, 1980; Morrow, 1982; Tucker, 1982; Tucker, 1983; Grotzinger and Read, 1983; Lumsden and Lloyd, 1984; Land, 1985; Machel and Mountjoy, 1986; Holail et al., 1988; Grotzinger, 1989; Knoll and Swett, 1990; Gregg and Shelton, 1990; Sibley, 1991; Montañez and Reid, 1992; Veizer et al., 1992; Tucker, 1992; Nordeng and Sibley, 1996; Arvidson and MacKenzie, 1999; Mazzullo, 2000).

Independent of their origin, the distribution of dolostone in the rock record reflects an apparent monotonic decrease in abundance relative to limestone since the Palaeozoic (Daly, 1909; Chilingar, 1956; Vinogradov and Ronov, 1956; Schmoker et al., 1985; Lumsden, 1985;
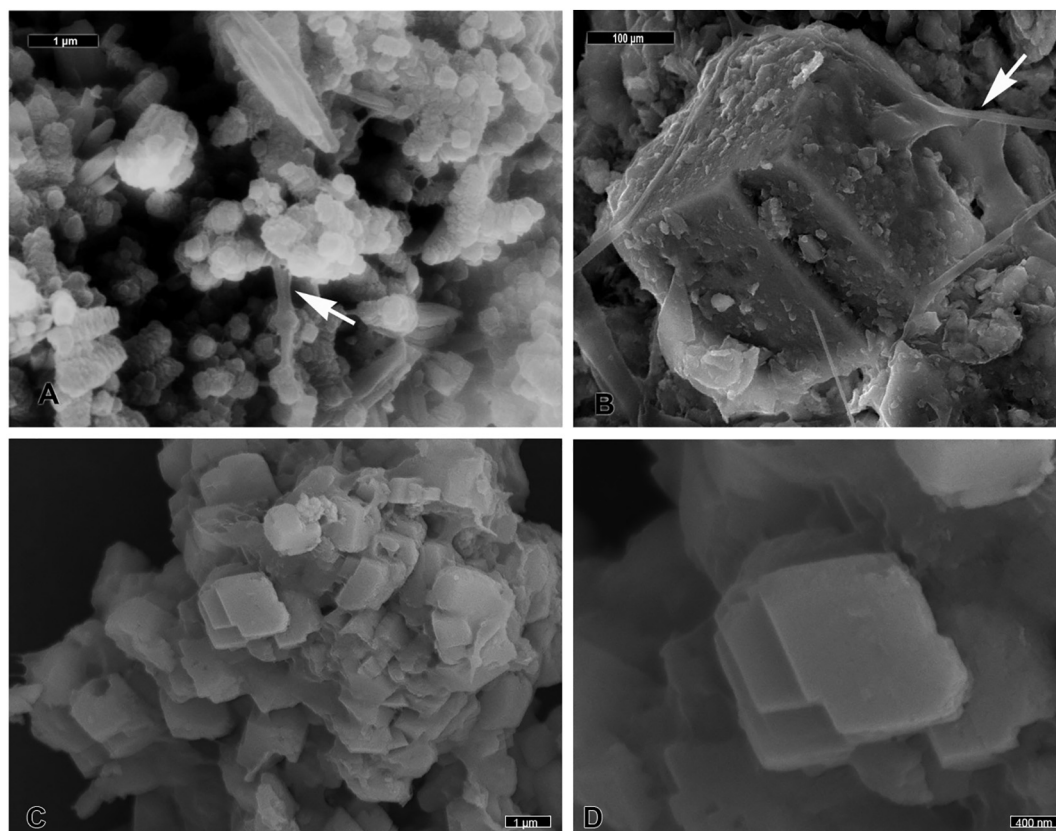

Fig. 2. SEM photomicrographs showing different morphologies of early formed shallow burial diagenetic dolomite crystals. In the early stage of crystal growth spherule-like crystallite clusters are inter-grown at a micron to sub-micron scale. As diagenesis progresses, the initial clusters can amalgamate to form a crystalline dolomite rhomb. Modern dolomite forming in association to buried microbial mats at Los Roques N.P., Venezuelan Caribbean Sea; the arrow shows EPS strings (A). EPS strings (arrow) can also be found associated to authigenic dolomite crystal comprising un-consolidated subsurface sediments, Neogene in age. The crystal has ~57% CaCO₃. Image is property of IODP-USIO. Photomicrograph by Gregg and Frank (2006); the scale-bar was corrected as per J.M. Gregg, pers. comm. (B). Note in both cases the presence of microbial EPS (arrows). At Lagoa Vermelha, Holocene Ca-dolomite from, Brazil, also forms in clusters associated to organic phases, the submicron-scale, partially ordered dolomite crystallites comprising these clusters are rhombohedral (C–D).

Holland and Zimmerman, 2000). However, some authors argue that the stratigraphic distribution of dolostone is punctuated and instead reflects global scale perturbations of the Earth system that can be linked to secular variations in seawater geochemistry (Given and Wilkinson, 1987; Wilkinson and Algeo, 1989; Wilkinson and Walker, 1989; Sun, 1994; Arvidson and Mackenzie, 1997; Burns et al., 2000; Arvidson et al., 2006). This interpretation contrasts with diagenetic models that consider that Mg-rich fluid-rock interactions during burial, along with other "poorly understood variables", contributed to the stratigraphic history of dolostones (Zenger and Dunham, 1980; Hardie, 1987; Zenger, 1989; Holland and Zimmerman, 2000).

Amongst the global scale perturbations that may have promoted syndepositional dolomite growth in the past are conditions of widespread global ocean anoxia, and particularly the expansion of shallow platforms during periods of epeiric flooding of rifted craton interiors (Shaw, 1964; Irwin, 1965; Eriksson, 1977; Given and Wilkinson, 1987; Wilkinson and Algeo, 1989; Sun, 1994; Arvidson and Mackenzie, 1997; Burns et al., 2000; Ridgwell et al., 2003; Arvidson et al., 2006). These conditions were generally followed by the development of extended, organic-rich shallow marine depositional settings that may be prone to widespread microbially-induced dolomite nucleation (Burns et al., 2000). Nevertheless, because post-depositional alterations have obscured most, if not all, of the early diagenetic textural and geochemical features of multigenerational dolostones, the actual mechanisms that led to nucleation, stabilization, and subsequent growth of dolomite in the geological past remain elusive (Zenger, 1972; Zenger and Ricketts, 1982; Hardie, 1987; Zenger, 1989; Machel, 2004).

One way forward is through the understanding of the dynamics of modern microbial communities in a variety of near-surface to shallow subsurface dolomite-forming settings and, more specifically, the progressive changes in their surface reactivity, metabolisms, and multispecies interactions with increasing burial diagenesis. With the goal of facilitating future efforts to elucidate the likely relation between the kinetics of dolomite formation and the distribution, potential energy acquisition pathways, and activity rates of subsurface communities, we examine here: (1) microbially induced early diagenetic conditions that are favorable for the precipitation of poorly ordered, non-stoichiometric (Ca-rich) dolomite; (2) the likely changes in the dynamics and structure of subsurface microbial assemblages as a response to depositionally controlled and/or diagenetically driven fluctuations in the availability of electron donors and acceptors (see Parkes et al., 1994; Cragg et al., 1996; Wellsbury et al., 1997); (3) specific depositional conditions that might promote localized microbially catalyzed precipitation reactions; and (4) the effects that past global scale geochemical perturbations may have had over ancient dolomite-forming microbial consortia and, thus, hypothetically, over the stratigraphic abundance of the mineral.

2. The dolomite "problem" today

The core of the so-called "dolomite problem" is the paradox posed by the apparent paucity of dolomite in modern marine depositional environments versus its relative abundance in the sedimentary rock record (McKenzie, 1991; Arvidson and Mackenzie, 1999). The fundamental questions of the problem are "how, where, when, and under what physico-chemical conditions does [low-temperature] dolomite crystallize" (Sass and Katz, 1982), or, as phrased by Brady et al. (1996), "what catalyzer no longer so abundant in modern oceans may have determined the non-uniform stratigraphic distribution of the mineral". In other words, what is it about the modern ocean, which despite being supersaturated with regard to dolomite, seems to preclude primary dolomite formation in most marine sediments when it was once so volumetrically abundant in the sedimentary rock record? Answers to these questions require knowledge of the conditions under which the mineral forms today and formed in the past, as well as the factors that can induce an increase in the rate of precipitation under those

conditions (Arvidson and Mackenzie, 1999).

Modern microcrystalline dolomite does, indeed, exist, but is present only in certain environments in which low water activities are accompanied by high alkalinities, such as in sabkha flats, hypersaline lagoons and playa lakes (Arvidson and Mackenzie, 1999) or organic-rich deep marine sediments (i.e., Compton, 1988; Wefer et al., 1998). An abundance of sedimentary organic matter, which allows for extensive alkalinity generation via subsurface microbial heterotrophy, giving rise to the so-called "organogenic" models (after Compton, 1980, 1988), is also an apparent requisite.

Various thermodynamic and hydrological factors have been proposed to explain the apparent lack of dolomite in modern marine sediments despite the mineral being oversaturated in surface seawater (Baker and Kastner, 1981; Hardie, 1987; Given and Wilkinson, 1987; Wilkinson and Algeo, 1989; Brady et al., 1996). Yet, as revealed by the failure of long term experiments designed to achieve cation ordering in oversaturated solutions at low temperature and under abiotic conditions, the problem may be regarded as one of mineral kinetics (Hardie, 1987; Land, 1998).

There are three intimately related aspects of carbonate geochemistry that are believed to inhibit the early diagenetic precipitation of dolomite in most modern marine sedimentary environments. First, the high enthalpy of the double hydration shell of Mg^{2+} cations (Lippmann, 1973; Markham et al., 2002) may limit their availability to participate in dolomite nucleation reactions. Conversely, binding of partially-hydrated Mg^{2+} cations to reactive carbonccharide-catalyzed nucleation and growth of disordered dolomite: a potential precursor of sedimentaryate surfaces would systematically alter the morphology of newly formed crystals to limit the growth of dolomite (Lippmann, 1973; Mucci and Morse, 1983; Han and Aizenberg, 2003). Second, the relatively low alkalinity or low activity of dissolved CO_3^{2-}, relative to HCO_3^{-} anions, may limit the rates of dolomite crystal growth in most marine environments. Under such conditions, there is insufficient free energy for the available carbonate anions to overcome the hydration energy barriers of Mg^{2+} cations at the surfaces of growing dolomite crystals (Lippmann, 1973; Machel and Mountjoy, 1986). Third, even low concentrations of dissolved SO_4^{2-} anions are thought to inhibit the replacement of pre-existing carbonate phases by dolomite (Baker and Kastner, 1981; Kastner, 1984; but see Morrow and Ricketts, 1988). This is because Mg^{2+} cations in solution, and on the surface of growing crystals, can form a neutral complex with SO_4^{2-} anions, thereby reducing the rates of dolomite crystal growth (Slaughter and Hill, 1991; Kastner, 1999). Nonetheless, Brady et al. (1996) showed that SO_4^{2-} only exerts an inhibitory effect at mid-range concentrations. Accordingly, at elevated SO_4^{2-} concentrations, such as observed in most marine evaporitic realms, and low $[SO_4^{2-}]$ values, typical of the mixing zone, sulfate anions do not appear to exert any inhibitory effect on dolomite precipitation. This observation was further explored by experiments in which disordered dolomite precursors precipitated at elevated SO_4^{2-} concentration values, low temperature and under microbial catalysis (e.g., Sánchez-Román et al., 2009, but see Zhang et al., 2012a). It must also be considered, however, that there may be a direct link between the stratigraphic abundance of dolomite and changes in seawater chemistry potentially involving secular variations in seawater SO_4^{2-} (see Burns et al., 2000).

Notwithstanding these kinetic constraints, there are four modern dolomite-forming systems that challenge our understanding on the kinetics of precipitation of dolomite at low temperature. These include: (1) the formation of near-stoichiometric dolomite as uroliths in Dalmatian dogs (Mansfield, 1980); (2) the capacity of sea urchins to rapidly regenerate their specialized high Mg carbonate teeth — referred to as both Very High Mg Calcite (VHMC), and "protodolomite" (45 mol % $MgCO_3$) (Wang et al., 1997; Robach et al., 2006; Goetz et al., 2014); (3) the presence of micrometer-scale partially ordered dolomite intergrown within several phases similar in composition — i.e., Ca-rich magnesite and VHMC — in the lining of hypothallial cells of living

crustose coralline algae (Nash et al., 2011, 2012, see also Nash et al., 2014); and (4) some biofilm systems that have been documented to mediate the nucleation and growth of Mg-rich carbonate phases, including Ca-dolomite (e.g., Davies et al., 1975; Vasconcelos and McKenzie, 1997; Wright, 1999; Warthmann et al., 2000; van Lith et al., 2003; Sánchez-Román et al., 2008; Bontognali et al., 2008, 2010; Kenward et al., 2009). Although these examples strongly suggest that, in the carbonate rock record, the diagenetic formation of massive dolomite might have been biologically catalyzed, they do highlight two current problems. First, the available geochemical data are often amenable to a variety of genetic interpretations (cf. Vasconcelos and McKenzie, 1997; Moreira et al., 2004; Sánchez-Román et al., 2009). Second, the hydrogeological and biogeochemical constraints of diagenetic dolomite formation are still poorly understood.

In addition to the lack of details with regard to how ancient dolomite nucleated and stabilized, most dolostones are also multi-generational, i.e., they were subjected more than once to thermodynamic and kinetic conditions conducive to precipitation, at times also incorporating bands of variable composition (Katz, 1971). The changing chemical environment and concomitant growth and/or recrystallization may mask or obliterate any discernible primary phase (Tucker, 1983; Sibley, 1991; Gregg et al., 1992; Machel, 1997). This leads to various interpretations regarding what comprised the precursor phase. On the one hand, amongst the plausible dolomite phases are those called secondary or post-depositional. These are thought to form during burial in association with a precursor's dissolution/reprecipitation process. On the other hand, mineralogical, textural and geochemical evidence suggests that, prior to pervasive dolomite formation, most dolostones underwent an early diagenetic stage of direct nucleation followed by a recrystallization process in which reactants and products were transferred to the site of further precipitation without dissolution of precursor crystals (Land et al., 1975; von der Borch and Lock, 1979; Holail et al., 1988; Gregg and Shelton, 1990; Sibley, 1991). The latter mechanism offers an interesting avenue for further research to provide a unified mechanism for low-temperature replacement of limestone, which might well point to the catalyzing role of subsurface microbes. In the next section, we review the mechanisms by which natural assemblages of benthic microbes can catalyze the nucleation reaction of dolomite precursors, regardless of whether these are ordered, partially ordered, or complete disordered (i.e., VHMC), in shallow marine sediments undergoing early to shallow burial diagenesis.

3. Microbially mediated dolomite formation

In any precipitation environment, the saturation index (Ω), which represents the precipitation potential of the mineral in an aqueous solution, is a function of the solubility product constant (K_{SP}) and the pH and activities of reactants in solution. The $\Omega = \log(IAP/K_{SP})$, where IAP is the ion activity product, determines whether the mineral can precipitate. At equilibrium $\Omega = 0$. If $IAP > K_{SP}$, then the solution is saturated, while undersaturated solutions have $IAP < K_{SP}$. The solubility product constant of dolomite, $K_{SP} = \{[Ca^{2+}][Mg^{2+}][CO_3^{2-}]^2\}$, where curly brackets denote the activities of the ions in aqueous solution, has been measured according to different methods that yielded inconsistent and unreliable results (see Morse and Mackenzie, 1990). Such diversity in K_{SP} values strongly reflects the difficulties involved with obtaining stoichiometric dolomite at low temperatures (Morse and Mackenzie, 1990; Arvidson and Mackenzie, 1999). Yet, experimental work conducted by Arvidson and Mackenzie (1997, 1999) allowed these authors to report that the K_{SP} for ordered dolomite at standard conditions (i.e., $T = 25\,°C$; $P = 1$ atm) is about 10^{-17}. Experimental and modeling work led Arvidson and Mackenzie (1999) to conclude that both Ca-dolomite and ordered dolomite growth can occur at moderate temperatures ($\sim 50\,°C$) on relatively short, although still lengthy, time scales, given an appropriate but still elusive solution chemistry.

The time span required for near-stoichiometric dolomite crystals to grow from their metastable nuclei is generally referred to as the induction period (e.g., Sibley et al., 1987). For inorganic carbonates, this is thought to be a function of the saturation state and temperature (Kaczmarek and Sibley, 2014; Kaczmarek et al., 2017). It is important to note, however, that in the geological past, and particularly during the Precambrian (Tucker, 1983), the induction period, which for dolomite seems to be largely controlled by the slow dehydration kinetics of the Mg^{2+} ion and its subsequent incorporation into the mineral lattice (Lippmann, 1973), might have been essentially shorter than that observed in the Holocene (Tucker, 1983; Wilkinson and Algeo, 1989; Sibley, 1991). Yet, important accumulations of near stoichiometric dolomite have long been known in certain Neogene diagenetic environments never subjected to elevated temperatures, strongly influenced by elevated rates of microbial activity and subsurface decay of sedimentary organic matter, including both buried peritidal (e.g., Mazzullo et al., 1987), and deep marine examples (e.g., Compton, 1988).

Microorganisms seem to induce Mg-rich carbonate precursors of dolomite, such as very high Mg calcite and imperfectly ordered Ca-dolomite, through their capacity to raise the total alkalinity and buffer the pH of marine sediment pore-waters through specific metabolic pathways (Fig. 3); particularly within zones rich in decaying amino acids and amino acid-derived organic matrices (Slaughter and Hill, 1991; Arp et al., 2003; Braissant et al., 2007; Soetaert et al., 2007). A pH buffering effect could also be relevant because CO_2 hydration occurs spontaneously at relatively slow rates at the circumneutral pH range (i.e., $k = 10^{-1}\cdot s^{-1}$; Kim et al., 2012). Yet, in a microbially influenced precipitation milieu in which an elevated pH can be locally sustained by microbial decay (see Soetaert et al., 2007), the activity of a Zn-activated enzyme, referred to as carbonic anhydrase, can also be kept at its maximum (Berg et al., 2002; Kim et al., 2012), and, thus, accelerate CO_2 hydration to rates as high as $k_{cat} = 10^6\cdot s^{-1}$ (Berg et al., 2002; Xu et al., 2016). Alternatively, an increase in pH to values above ~ 9.1 also causes a dissolved inorganic carbon species transition from HCO_3^- to CO_3^2. The latter anion, by virtue of its greater translational and vibrational energies, can better displace water dipoles bonded to Mg ions (Arvidson and Mackenzie, 1999). This facilitates the precipitation of the magnesite-like layers, which is traditionally considered to be the rate limiting step in dolomite formation (Lippmann, 1973, p. 168).

More than a decade of research on microbially induced, low-temperature dolomite formation has shown that the critical stage of nucleation is strongly controlled by the bio-inorganic chemical properties of the microbial extracellular milieu. Thus, our next section focuses on the attributes that lead microbial surfaces and their extracellular polymeric substances (EPS) to promote nucleation and, perhaps, diagenetic dolomite stabilization.

3.1. The role of EPS matrices in nucleation

In most modern deposits where authigenic dolomite occurs as a volumetrically important mineral, it has been found growing in association with thick microbial biofilms termed microbial mats, which are comprised of a heterogeneous population of microorganisms and their EPS (Decho, 1990, 2000; Konhauser, 2007; Bontognali et al., 2010). These biopolymers are secreted by the various communities inhabiting biofilms, and their chemical and physical properties confer biofilms with structural integrity (Flemming and Wingender, 2001, 2010). Although diverse in composition, EPS typically consist of repeated chains of carboxylated compounds, including methylated carboxyl-rich uronic acids, and non-carbohydrate moieties, such as pyruvate and succinate, as well as minor amounts of amines, thiosulfates, and phosphates (Sutherland, 2001; Flemming and Wingender, 2001, 2010; Petrash et al., 2011).

In classic dolomite precipitation environments, such as the prograding sabkha flats in the Persian Gulf (Purser and Seibold, 1973), or
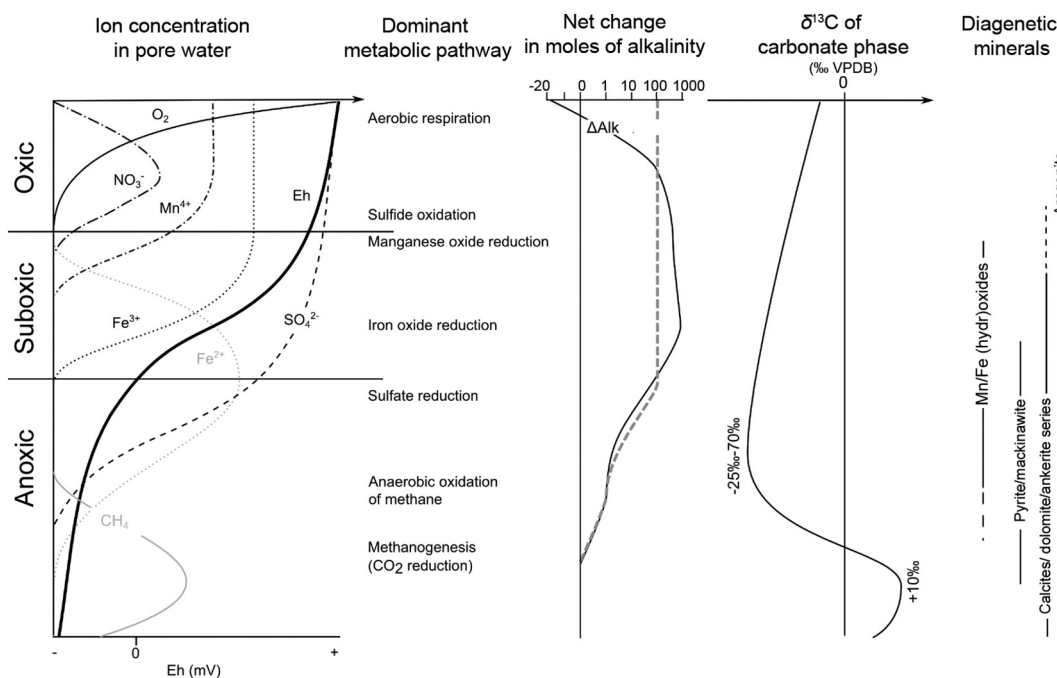
Fig. 3. Evolution of electron acceptor availability, Eh, alkalinity, isotopic composition of solution, and mineral saturation states across a depth/redox gradient.

the peritidal zone of Andros Island (Shinn et al., 1969; Shinn and Kendall, 2011), microbial mats are abundant. Microbial mats through their physiological and metabolic activity generate a physical and chemical environment with preferentiality to dolomite formation (see Section 3.3 below). A key aspect to the physical environment is EPS, which can account for 50 to 90% of the labile sedimentary organic matter (Flemming and Wingender, 2001). It has been suggested that the negatively charged functional groups comprising EPS, and their preferential binding affinity for Ca and Mg ions (Fazio et al., 1982; Decho, 1990; Körstgens et al., 2001; Braissant et al., 2007, 2009), can locally increase the saturation states of dolomite in pore-water systems influenced by an abundance of microbial exopolymeric matrices (Han and Aizenberg, 2003; Arp et al., 2003; Kwak et al., 2005; Bontognali et al., 2008; Krause et al., 2012). Yet, as discussed above, in such pore-waters systems, the activation energy barrier to the heterogeneous nucleation of dolomite can also be controlled by a number of biogeochemical variables (e.g., Decho, 1990; Trichet and Défarge, 1995; Decho, 2000; Braissant et al., 2007; Wang et al., 2009; Roberts et al., 2013). On this note, Krause et al. (2012) report a slightly higher affinity of their experimental EPS matrices for Ca than Mg cations. This observation could be directly linked to the localized variations on pH within their organic template, or alternatively to the macromolecular content of their experimental setup (see Fazio et al., 1982).

In classical nucleation theory, a cluster is defined as a group of molecules preceding the formation of a nucleus with critical radius (Kashchiev, 2000). Recent research has shown that clusters are the initial building block in dolomite formation (Paulo and Dittrich, 2013; see also Perrin et al., 2016). At low temperature, the self-rearrangement of acidic functional groups in decaying EPS may allow them to act as templates for the formation of such clusters (Wang et al., 2009), hence they are referred to as nucleation templates (Trichet and Défarge, 1995). This could be the result of differential degradation rates of sugars and amino acids, both of which comprise negatively charged ligands with different coordination geometries and characteristic affinities towards Ca and Mg cations (Trichet and Défarge, 1995; Raz et al., 2000; Han and Aizenberg, 2003; Decho et al., 2005; Gilbert et al., 2005; Visscher and Stolz, 2005; Kwak et al., 2005; Braissant et al., 2007, 2009; Wang et al., 2009). As degradation proceeds, the progressive release of these cations into the proximal fluids allows for precipitation

of amorphous carbonate minerals (ACM, Aizenberg et al., 1996), which may exhibit some degree of cation ordering (Raz et al., 2000). Upon stabilization, and provided favorable physicochemical conditions exist, the aforementioned ACM may lead to dolomite growth (Wang et al., 2009, and references therein).

The stability of early-formed dolomite is critically dependent upon the ordering of the calcium and magnesium cations in the mineral structure (Goldsmith and Heard, 1961). From experimental mineral nucleation analyses, it has become apparent that the formation of stable supernuclei (i.e., clusters larger than the critical size) is important because these are capable of spontaneous growth (see Kashchiev, 2000). Kenward et al. (2013) and Roberts et al. (2013) have provided details on how the nucleation mechanism depicted above occurs within EPS matrices. They have ascribed a direct Mg-dehydration effect to carboxyl moieties in microbial cell walls and carboxylated organic matter. Accordingly, the binding of $[Mg(H_2O)_6]^{2+}$ to carboxyl functional groups of non-metabolizing cells results in the ejection of a water molecule and the formation of a $[Mg(H_2O)_5(R-COO)]^+$ complex. This is followed by the replacement of a water molecule with CO_3^{2-} to form a surficial $MgCO_3(H_2O)_4(R-COO)$ complex associated with the cell walls, which can act, under alkaline conditions, as a template for the attachment of a Ca^{2+} and a second CO_3^{2-}, leading to a cluster. This mechanism requires a sustained elevated pH capable of maintaining the relatively high activity of CO_3^{2-} anions in solution. Thus, again, the concomitant metabolic activity of microbes capable of buffering pH in the stabilization microenvironment becomes critical. In the next section we briefly review the likely roles of microbial decay of EPS in dolomite stabilization.

3.2. The role of EPS matrices in stabilization

In evaporitic peritidal sediments, the abundance of EPS can be largely attributed to the activity of halophilic phototrophic microbial assemblages. They thrive under the harsh conditions characterizing these environments (i.e., high salinity, UV radiation, desiccation) because of their capability to secrete copious amounts of negatively charged hydrophilic compounds with osmolyte functions (Oren, 2000; Stal, 2000). These compounds maintain a hydrated polymer network and are responsible for key viscoelastic properties of EPS exposed to

desiccation conditions. Such properties depend, to some extent, on their binding affinity for divalent cations, such as Ca and Mg (Decho, 2000), but mostly on their affinity for multivalent minor and trace metal species, such as Fe, Mn, V, Zn, Cr, Cu, Co and Mo. These transition metals aid in the formation of cross-linked interconnections of biopolymeric chains by forming cation bridges that condense and stabilize EPS gels, thus enhancing their protective nature for cells (Stal, 2000; Amrani et al., 2007).

One of the most reactive organic macromolecules towards metals in EPS secreted by halophilic microbes is glycine betaine, $(CH_3)_3$ NCH_2COO^- (Quagliano et al., 1962). This group of methylated amino acids is extensively produced by autotrophic microbes in order to balance the elevated molar salt concentration in their surrounding microenvironment (Gafinsky and Trüper, 1982; Garcia-Pichel et al., 1998; Stal, 2000; Oren, 2000). The degradation of glycine betaine occurs over extended periods of time (Mitterer et al., 2001) and yields acetate and trimethylamine after a decarboxylation reaction mediated by sulfate reducers. Therefore, upon degradation, these compounds also serve as organic substrates for methanogens (Larter and Douglas, 1980; Gafinsky and Trüper, 1982; Oremland et al., 1982; King, 1984; Whiticar, 1999; Oren, 2000; Mitterer et al., 2001).

As shallow burial diagenetic reactions proceed, some labile EPS compounds undergo random condensation to highly cross-linked macromolecules that are more resistant to degradation (Amrani et al., 2007). With increasing diagenetic conditions (redox potential, temperature), however, these cross-linked biopolymers are also degraded and, hence increase the availability of bioessential metals originally bound to Fe and Mn (oxy)hydroxides and organic matter, such as Co, Ni, and Mo, in deeper anoxygenic diagenetic zones. There these metals fuel a variety of microbially driven catalytic reactions involving organic and inorganic substrate utilization (see Frausto da Silva and Williams, 2001 for details). Such reactions include, but are not limited to, iron and manganese recycling in the presence of intermediate sulfur, methanogenesis and anoxygenic methane oxidation coupled to nitrogen, sulfate, and also oxidized stocks of iron and manganese (Fig. 3).

Due to their alkalinity generation capacity, the processes listed above have potential to promote, in the presence of a favorable Mg:Ca ratios, a sustained shallow burial dolomite precipitation reaction (e.g., Petrash et al., 2015). Therefore, in addition to serving as nucleation templates, the burial of EPS matrices could also exert a strong biochemical control over the progressive formation of diagenetic dolomite in a process strongly controlled by the activity of subsurface metabolisms distributed in the sediment pile in accordance to specific yet spatially and temporarily variable substrate bioavailabilities. To summarize, the burial of metal reactive EPS may also be important: (1) because their abundant carboxylated osmolitic compounds are noncompetitive substrates for two key metabolic pathways: sulfate reduction and methanogenesis (Mitterer et al., 2001) and (2) because of their important contribution to the overall flux and burial of bioactive metals into shallow burial diagenetic realms (Hunter et al., 1998; Khodse et al., 2008; Petrash et al., 2015).

Although in our discussion we have focused attention on shallow marine dolomite because of its characteristic relation with EPS-rich microbial mats, it must be mentioned that comparative 16S RNA analyses have shown striking similarities between the functionality of microbes inhabiting modern peritidal environments and communities indigenous to sapropels deposited few hundred meters below the sea surface in continental margins (e.g., Wilms et al., 2006, 2007; Batzke et al., 2007). On this note, while conducting analyses in freshly obtained Neogene sediments of the Belgica carbonate mound province, Porcupine Seabight in the North Atlantic, Gregg and Frank (2006) reported the presence of fine crystalline deep marine dolomite associated to EPS matrices. However, upon storage, this textural relation with EPS vanished possibly because degradation and/or natural dehydration of the organic matrices occurred during core storage (Gregg and Frank, 2006).

3.3. Key metabolic interactions

The anaerobic respiratory pathway that has received the most attention in terms of early diagenetic dolomite formation is microbial sulfate reduction (MSR) (Vasconcelos et al., 1995; Vasconcelos and McKenzie, 1997; Wright, 1999; Wright and Wacey, 2005; Warthmann et al., 2000; van Lith et al., 2003; Sánchez-Román et al., 2009; Bontognali et al., 2012; Bontognali et al., 2014). This MSR mechanism, proposed for a dolomite forming lagoon near Rio de Janeiro, Brazil, by Vasconcelos and McKenzie (1997), utilizes the dissolved sulfate while increasing the dolomite saturation index by producing an increase in pore-water alkalinity (Eq. (1)).

$$CH_3COO^- + SO_4^{2-} + H_2O \rightarrow H_2S + 2HCO_3^-$$
$$+ OH^- (\Delta G_r = -48 \text{ kJ/mol}). \quad (1)$$
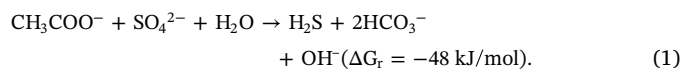
Indeed, because of their capacity at lowering pore-water concentrations of SO_4^{2-}, sulfate reducers were already considered key players promoting dolomitization reactions thirty years ago (Kastner, 1984; Burns and Baker, 1987). Furthermore, increase in the concentration of their by-product, sulfide, seems to also play a role in promoting dolomite formation (Zhang et al., 2012a). There are many ancient examples, however, in which the precipitation of dolomite seems to have been promoted by dissolved sulfate (e.g., Qing et al., 2001; Melim and Scholle, 2002), while experimental evidence has also shown that the rates of dolomite precipitation seem to increase with increasing dissolved sulfate levels in the proximity to the mineral surface (Brady et al., 1996). Moreover, the relevance of sulfate as an inhibitor of dolomite formation has been strongly debated, and more recently challenged by experiments in which disordered dolomite crystallites were precipitated together with other Ca-Mg carbonate minerals in a biofilm secreted by cultures of halotolerant aerobic heterotrophs grown in a sulfate-rich aqueous media (Sánchez-Román et al., 2009). Based on these latter results, the prevailing line of thought is that the sulfate inhibition model, as originally proposed by Baker and Kastner (1981), may only apply to inorganic dolomitization process occurring under high temperature, burial diagenetic conditions (see also Morrow and Ricketts, 1988).

Meister (2013) suggested that MSR alone might be ineffective for inducing carbonate saturation, and only with an alternative mechanism acting in parallel would MSR lead to a localized state of elevated alkalinity concomitant with dolomite supersaturation (also see Gallagher et al., 2012, 2014). On this note, while studying dolomite formation in the hypersaline mats from Lagoa Vermelha, Brazil, Moreira et al. (2004) concluded that the mineral actually forms as a result of undersaturation of competing carbonate phases by sulfide oxidation, which in oxic zones can occur with O_2 as the electron acceptor (e.g., Eq. (2)), but it could also result from anoxygenic phototrophy at relatively high temperatures in the presence of NO_3^- (Brock, 1994; Pierson, 2001) or dissolved Fe^{2+} (Melton et al., 2014). The latter mechanism would have had some relevance in shallow marine Paleoproterozoic realms where metastable Ca-carbonates cementing stromatolitic facies were pervasively silicified while early formed dolomite crystals were preserved, although with recrystallization to ankerite (e.g., Petrash et al., 2016a).

$$HS^- + 0.5O_2 \rightarrow S^0 + H_2O \ (\Delta G_r = -151.4 \text{ kJ/mol}) \quad (2)$$
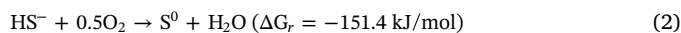
Regarding sulfate reduction, it has been suggested that an accumulation of sulfide ions may promote Mg^{2+} dehydration at the surface of a solid precursor phase, resulting in dolomite nucleation (Zhang et al., 2012a; see also Yang et al., 2012). But as mentioned above, this critical effect can also be ascribed to the presence of polysaccharides (Zhang et al., 2012b) and other carboxylated organic ligands (Roberts et al., 2013).
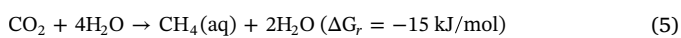
Until recently, there was a general lack of information regarding the potential role of competitive or coupled redox processes that occur concomitantly with sulfur bioutilization in dolomite formation. A new

hypothesis bridging these aspects suggests that, in a hypersaline peritidal setting in the Caribbean Sea, the activity of subsurficial microbial communities leads to dolomite formation as long as the combined effects of the production and consumption of by-products and the bioutilization of available metal and sulfur inventories sustain elevated pore-water alkalinity and pH (Petrash et al., 2015). This conclusion resulted from the observation that anaerobic biogeochemical processes involving coupled intermediate Mn and S cycling and suboxic organic matter respiration appear to catalyze the stabilization of the mineral. The significance of the mechanism is supported by the fact that sustained Mn(IV)-reduction can act as an effective pH and alkalinity buffer (Eq. (3)).

$$CH_3COO^- + 4MnO_2 + 3H_2O \rightarrow 4Mn^{2+} + 2HCO_3^-$$
$$+ 7OH^- (\Delta G_r = -569 \text{ kJ/mol}) \quad (3)$$
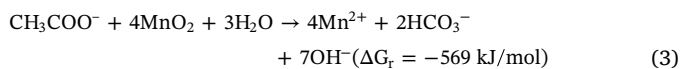
Although the reduction of Mn(IV) is coupled with the oxidation of organic matter, the formation of Mn(III) and Mn(II) and the reoxidation of the latter via intermediate forms of sulfur could be a critical driver of shallow burial dolomite stabilization (Petrash et al., 2015). However, the mechanism more commonly implicated with burial diagenetic dolomite is sulfate reduction coupled to methanogenesis. The biological production of methane might under some circumstances decrease the saturation states of dolomite (Rodriguez et al., 2000; Moore et al., 2004). Yet, methanogens employ a number of metabolic pathways for subsistence, and several of these pathways are capable of promoting carbonate saturation (Roberts et al., 2004; Madigan et al., 2008). Acetoclastic methanogens generate DIC through their metabolic pathway (Eq. (4)), while autotrophic methanogens consume CO_2, driving up solution pH with their metabolism (Eq. (5)).

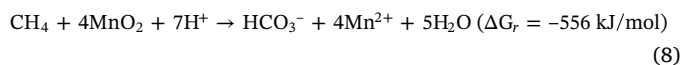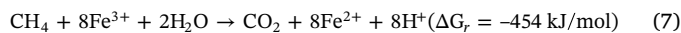$$CH_3COO^- + H_2O \rightarrow CH_4(aq) + HCO_3^- (\Delta G_r = -32 \text{ kJ/mol}) \quad (4)$$

$$CO_2 + 4H_2O \rightarrow CH_4(aq) + 2H_2O \ (\Delta G_r = -15 \text{ kJ/mol}) \quad (5)$$

A coupled mechanism that utilizes CH_4 to increase the concentration of CO_3^{2-} is called methanotrophy. This mechanism is usually coupled to sulfate reduction, and, thus, is important in the relatively narrow sulfate-to-methane diagenetic zone (SMTZ) where the rates of these two key metabolic metabolisms are known to be greatly increased (Parkes et al., 2000; D'Hondt et al., 2002, 2004). The reaction driven by the consortium between methanogens and communities dependant of any given electron acceptor is usually referred to as reverse methanogenesis or anoxygenic oxidation of methane (AOM). The net methanotrophic reaction in the presence of sulfate, or perhaps H_2 (Hoehler et al., 1994, 1998; Valentine et al., 2000; Boetius et al., 2000), involves the transfer of eight electrons (Chistoserdova et al., 2005) according to Eq. (6):

$$CH_4 + SO_4^{2-} \rightarrow HCO_3^- + HS^- + H_2O \ (\Delta G_r = -16.6 \text{ kJ/mol}) \quad (6)$$
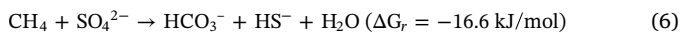
Because of the high energy requirements for microbes to cleave the particularly strong C—H bond of methane without the participation of highly reactive monooxygenases (Strous and Jetten, 2004), the AOM process is considered a thermodynamically challenging reaction (Scheller et al., 2010). In fact, it is thought that AOM only proceeds by the catalytic action of key enzymes, such as methylcobalamin and methyl-coenzyme M-reductase (Chistoserdova et al., 2005; Valentine, 2007; Scheller et al., 2010; Shima et al., 2012) and with the involvement of methanogenic archaea and specialized sulfate reducers, such as *Desulfosarcinales* and other δ-proteobacteria (Boetius et al., 2000; Thomsen, 2001). Alternatively, a range of microbes capable of denitrification (Raghoebarsing et al., 2006, but see Ettwig et al., 2008), or bacteria capable of reducing iron (FeOH₃) and manganese oxides (MnO_2) are another group of chemolithotrophic microbes posited to facilitate anaerobic oxidation of methane (AOM) in the absence of SO_4^{2-} (Slomp et al., 2013; Riedinger et al., 2014; Egger et al., 2014). There is increasing circumstantial geochemical evidence for the AOM reaction being decoupled from sulfate reduction and linked to the

chemolithotrophic reduction of the buried metal stocks (see Beal et al., 2009; Scheller et al., 2016). However, the microbes facilitating these reactions in the subsurface have yet to be identified. Their subsurficial activity must be temporally and spatially limited by the bioavailability of oxidized forms of iron (Eq. (7)) and/or manganese (Eq. (8)) in the sedimentary sequence, yet little is known about the Mn-AOM and Fe-AOM rates and what specific diagenetic conditions favor these reactions (Rooze et al., 2016).

$$CH_4 + 8Fe^{3+} + 2H_2O \rightarrow CO_2 + 8Fe^{2+} + 8H^+ (\Delta G_r = -454 \text{ kJ/mol}) \quad (7)$$

$$CH_4 + 4MnO_2 + 7H^+ \rightarrow HCO_3^- + 4Mn^{2+} + 5H_2O \ (\Delta G_r = -556 \text{ kJ/mol})$$
$$\quad (8)$$

Independently of the specific mechanisms involved, AOM is considered the oxidative process that penetrates most deeply into modern continental margins wherever suitable redox couples are readily available (Barnes and Goldberg, 1976; Reeburgh, 1976; Boetius et al., 2000; Hinrichs and Boetius, 2002; Hallam et al., 2004; Chistoserdova et al., 2005; Reeburgh, 2007; Ettwig et al., 2016). Within or around the zone of anaerobic oxidation of methane, iron sulfides are important minerals precipitated in association with hydrogen sulfide produced by organoclastic and methanotrophic metabolisms and divalent iron resulting from metal reductive processes. Other important mineral precipitates often comprise diagenetic barite (see Jørgensen and Kasten, 2006 and references therein), as well as authigenic carbonates, including Mg-calcite, aragonite and dolomite (Ussler and Paull, 2008; Crémière et al., 2016). As for dolomite, the crystals are typically multigenic, and in most, but not all cases, incorporate variable proportions of redox sensitive elements in the form of growth zones and discontinuities, truncations and peculiar cementation fabrics that are visible in cathodoluminescence (Katz, 1971; Machel, 1985).

The activity of key metalloenzymes in anoxygenic diagenetic systems is dependent on the availability of Fe, Ni, and Co (and some Mo/W and Zn) (Glass and Orphan, 2012). Thus, because Fe- and Mn-(oxy)hydroxides are the main sinks for some of these metals in modern oxic to suboxic marine environments, their dissolution-precipitation kinetics might exert a strong control over the diagenetic conditions and the depths at which the reaction occurs (Fig. 3). In fact, it is interesting to speculate that in order to sustain the activity of the dolomite-forming metabolis, in addition to the presence of basinal brines containing diffused methane, it is also critical that Fe- and Mn-(oxy)hydroxides are reduced in order to liberate previously sorbed trace metals. Incidentally, it has been observed that dolomite overgrowths formed under the influence of methanogenic processes are relatively enriched in iron (Burns and Baker, 1987, Loyd et al., 2012), which would represent a signature of other microbial functionalities operating in a deep subsurface methanotrophic diagenetic environments.

Roberts et al. (2004) reported the exclusive involvement of methanogenic archaea in dolomite formation under relative low supersaturation conditions (molar ratio $Mg^{2+}/Ca^{2+} \sim 3$). This is similar to molar ratio of the waters in equilibrium with dolomite purportedly precipitating in association with deep microbial activity in the subsurface of the Gulf of California (Garrison et al., 1984; Compton, 1988; Loyd et al., 2012). Such observations are significant for three reasons: First, they imply the likeliness of continuity in the microbially mediated diagenetic reactions leading to dolomite growth along and beyond the SMTZ. Second, they imply that the long-term spatial variation of the SMTZ could provide conditions favorable for widespread dolomitization as long as mechanisms for a strong pH buffering effect are present in the methanogenic zone (e.g., Meister et al., 2011). Third, they point to catalytic processes leading to widespread low-temperature dolomite formation without a need for extreme oversaturation conditions (cf. Land, 1998).

From the above discussion, it is clear that the precipitation of dolomite at low temperature is not dependant on the activity of any specific microbial functional group, but rather requires the appropriate

Table 1
Microbial metabolisms relevant to dolomite formation.

Metabolic pathway (references)	Mechanism of mediation	Organisms identified
Aerobic heterotrophy (Sánchez-Román et al., 2008)	These organisms utilize nitrogenated organic matter coupled to oxygen as a terminal electron acceptor, consuming acidity and producing alkalinity by reducing also nitrate or nitrite to ammonia.	*Halomonas meridiana* *Virgibacillus marismortui*
Chemotrophic sulfide oxidation (SO) (Moreira et al., 2004)	Organisms using sulfide, H_2O and other reduced forms of sulfur as electron donors for the reduction and fixation of CO_2 to cellular carbon at the oxygen/sulfide interface. A diel fluctuating pH gradient decreases pore-water saturation states for high-Mg calcite and aragonite to thermodynamically favor the precipitation of dolomite precursors at night.	Inferred by the isotopic composition of dissolved sulfate in dolomite forming settings. Organisms capable of anoxygenic SO include *Microcoleus* and *Thiobacillus* growing symbiotically with phototrophic *Thiocapsa* sp. (van Gemerden, 1993)
Dissimilatory sulfate reduction (Vasconcelos and McKenzie, 1997; Warthmann et al., 2000; Wright and Wacey, 2005)	This functional group oxidizes organic carbon coupled to sulfate as a terminal electron acceptor, thereby removing sulfate and generating alkalinity under anaerobic conditions.	*Desulfostipes saporovans* *Desulfosarcina* spp. Desulfovibriae
Methanogenesis (coupled to anaerobic oxidation of methane) (Moore et al., 2004, Roberts et al., 2004; Kenward et al., 2009)	Methanogenesis alone decrease the saturation state of dolomite; the coupled mechanism, however, utilize CO_2 and H_2 to increase lithoautotrophically the concentration of CO_3^{2-} through coupled sulfate reduction; driving an increase in alkalinity that may result in dolomite supersaturation.	Acetoclastic and autotrophic methanogens. These pathways were associated with *Methanosaeta* spp. and *Methanobacterium* spp., respectively.

environmental conditions shaped by interactions amongst various microorganisms during diagenesis (Table 1, see also Fig. 3). In the next section, we critically evaluate the textural and chemical attributes that have been used to characterize microbial dolomites. We also comment on emerging analytical approaches with potential to shed light into the obscure aspects of the dolomite "problem".

4. Textural features of microbial dolomites

Various biochemical factors are known to influence the morphological properties and composition of carbonate minerals (Krumbein, 1986). It has been suggested that amorphous hydrated mineral phases predominate during the early stages of biomineralization, after which these transform into more crystalline phases whose mineralogy depends on localized chemical reactions some of which may be driven by intra and extracellular processes (Riding, 2000; Wang et al., 2009). Irrespective of the specific metabolic pathways involved in their formation, early diagenetic Ca-dolomite crystals often consist of sub-micron scale aggregates grown within partially degraded EPS matrices (Fig. 2A; e.g., Warthmann et al., 2000; Bontognali et al., 2008). Due to their amorphous nature, the crystal clusters produced in culture experiments seem to lack some dolomite ordering reflections observed in high temperature ordered counterparts (as discussed by Gregg et al., 2015). However, unambiguous ordering reflections in such low-temperature, sub-micrometer-scale precipitates may not be detectable using powder XRD, and would require transmission electron microscope (TEM) or synchrotron diffraction/scattering evaluation (Gregg et al., 2015). For example, nanoscale crystals of a synthetic Ca-Mg carbonate sample studied using a TEM equipped with selective area diffractometer (TEM-SAED) have been observed to display *d*-space measurements in the crystal lattice of 2.89 Å with an Mg/Ca ratio equal to one (Fig. 4), even though the standard XRD diffraction of the same sample (not shown) does not contain detectable ordering reflection peaks (see also Roberts et al., 2013). This is in contrast with many examples of naturally forming Holocene Ca-Mg carbonates that do display unambiguous ordering reflections and therefore have dolomite symmetry. For instance, composite microbean synchrotron radiation XRD Bragg reflection patterns of dolomite forming in a modern hypersaline lagoon, Lagoa Vermelha, Brazil, reveal diffraction patterns consistent with those of dolomite standards (Fig. 5).

The presence of sub-micron scale aggregates has also been observed in Quaternary dolomites, of unspecified origin, which in their initial stages exhibit spherulitic forms that age to subhedral to euhedral rhombs ranging in size from < 1 to 20 μm (von der Borch and Jones, 1976; Arvidson and MacKenzie, 1999). Such a mineralogical reaction

sequence may be described by Ostwald's ripening (Ostwald, 1897; Nordeng and Sibley, 1994). Interestingly, in aged examples, some rhombohedra appear to be composed of numerous subcrystallites (e.g., Carballo et al., 1987) that may exhibit stepped crystal faces (Lasemi et al., 1989), indicating heterogeneous nucleation and rapid crystal growth from supersaturated solutions (Gregg, 1985; Gregg et al., 1992).

Upon maturation, if dissolution-recrystallization processes are not involved, these multiphase dolomites end up being composed of: (1) seed crystals or cores; (2) crystal cortices that concentrically enlarge the cores; and (3) pore-infilling syntaxial precipitates of limpid cement around the crystals (Choquette and Hiatt, 2008). In several Holocene dolomites a linear increase in the average crystal size with increasing depth was observed by Gregg et al. (1992), which suggests that in most cases the dolomitization process could be completed at low temperatures (< 35 °C) and shallow burial depths (< 100 m) (Gregg et al., 1992; Choquette and Hiatt, 2008).

In biotic laboratory studies, synthetic high Mg precursory dolomite carbonates, display other morphologies, including dumbbells (Warthmann et al., 2000; van Lith et al., 2003), spheroids (Sánchez-Román et al., 2008; Qiu et al., 2017), nanoscale rhombs (Roberts et al., 2004, their Fig. 1a), and nanoscale globules (Vasconcelos et al., 1995; Sánchez-Román et al., 2008, their Fig. 1b; Bontognali et al., 2008) — the latter being proposed as either mineralized nan(n)obacteria (Folk, 1993; Folk and Chafetz, 2000) or platy crystal aggregates (e.g., Kenward et al., 2009, their Fig. 1b). Aloisi et al. (2006) and Bontognali et al. (2008) found compelling evidence to suggest that the formation of these nanometer scale features takes place in the environmental fluid (EPS matrix) instead of on the microbial cell wall. This prevents cell entombment due to carbonate precipitation and leads to the development of micrometer-scale chemical gradients favorable for microbial life (Aloisi et al., 2006; Bontognali et al., 2008). More recently, Sumrall et al. (2017) provided a detailed description of the internal structure of naturally formed dumbbells comprised by VHMC. These organic-rich textural features are formed by a microbial assemblage developed in the pores of a dolomitized limestone occurred under mixing zone conditions.

There is an etching technique that has been used in attempts to observe putative microbial "cells" fossilized in ancient carbonate rocks (e.g., Perri and Tucker, 2007). It consists of placing the sample in diluted (1–10%) HCl for 30 s, then rinsing in distilled water. Details on the method were described by Folk (1993), and discussed by Folk and Lynch (2001). Following preparation, the sample is coated with a fine (~0.012 μm) layer of gold, or preferably a ~0.02 μm thick carbon-coat (Folk and Lynch, 2001), prior to observation under the scanning electron microscope (SEM). Yet, general support for a biological origin to
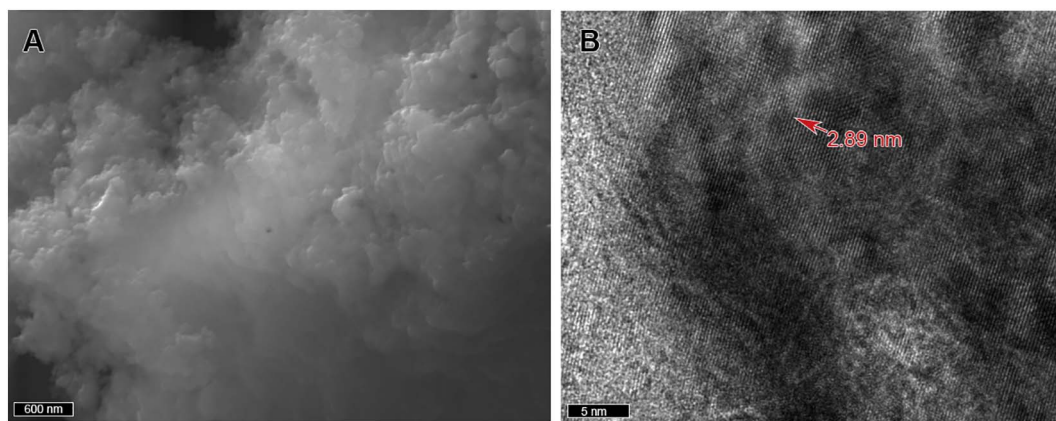
Fig. 4. Ca-Mg carbonate precipitated in culture experiment inoculated with *Desulfovibrio brasiliensis* grown in Lagoa Vermelha-like media at 40 °C after 14-year incubation period. (A). SEM photomicrograph of the experimental carbonate showing clusters of dolomite nanocrystals. (B) High Resolution TEM image of poorly ordered dolomite reveals a *d*-space of 2.89 nm within the nanocrystals.

these nanometer-scale fabrics is marginal because they may also form by abiotic processes (see Kirkland et al., 1999), or, as discussed by Folk and Lynch (1997, 2001), could even be an accessory of the sample preparation process. Unfortunately, there are many conflicting results concerning cell size, physiological responses and definitions (see review by Velimirov, 2001) that make it difficult to determine if these nano-textures actually reflect evidence for a microbial role in carbonato-genesis. On this note, one must be sceptical about the value of these fabrics in confirming a presumed critical microbial contribution to ancient dolomite formation (Jones, 2001), and accordingly, more compelling, non-microtextural evidence for microbial mediation is still required. Such evidence may be given by the *in situ* geochemical features of microbial dolomites.

5. Geochemical features of microbial dolomites

Based on the concept of Claypool and Kaplan (1974), the stable C and O isotope chemistry of dolomite has been traditionally considered as a primary tool for assessing the processes involved in its formation. In a more recent review, however, Swart (2015) highlighted that the carbon isotopic geochemistry of dolomite mostly reflects changes in the ambient diagenetic conditions, adding further complexity to inter-pretations of multigenetic crystals formed under dissimilar environ-mental conditions. In this section, we review the value of stable isotopes for identifying microbial pathways linked to dolomite precipitation. We also discuss the potential optimization of bulk rock interpretation when combining traditional stable isotope data with other chemical and isotopic proxies.

5.1. Stable O and C isotope clues

5.1.1. Stable oxygen isotopes

The oxygen isotope composition of dolomite is considered diag-nostic of the environmental conditions prevailing during crystal growth and the nature of the dolomitizing fluids (Fig. 6). When dealing with microbial carbonates precipitated at the transition from carbonates to evaporites, however, special care must be taken when interpreting shifts in the $\delta^{18}O$ towards depleted values. In evaporitic settings one may expect early diagenetic carbonates to be generally enriched in ^{18}O, reflecting precipitation in equilibrium with pore-waters derived from evaporated surface waters (Major et al., 1992), yet most of these do-lomites comprise crystals exhibiting a somewhat depleted oxygen iso-tope trend (see Mazzullo, 2000, his Fig. 5).

In the past, such trends were generally interpreted in terms of fluctuating salinity conditions; with shifts towards negative values being considered representative of mixing with meteoric waters. Yet, in cryptomicrobial dolomites, these 'anomalous' values can also be ex-plained by invoking the dissociation of oxygen from sulfate (e.g., Sass et al., 1991) and the syngenetic dissolution of gypsum (Turchyn et al., 2010). In this scenario, and because the microbial sulfate reduction of $^{32}S^{16}O_4^{2-}$ is energetically favored over $^{32}S^{18}O_4^{2-}$ (Harrison and Thode, 1958; Lloyd, 1968; Mitzutani and Rafter, 1973), microbial sul-fate consumption becomes the more likely source of ^{16}O involved in hydrolysis and carbonate hydration. Thus, care must be taken in the
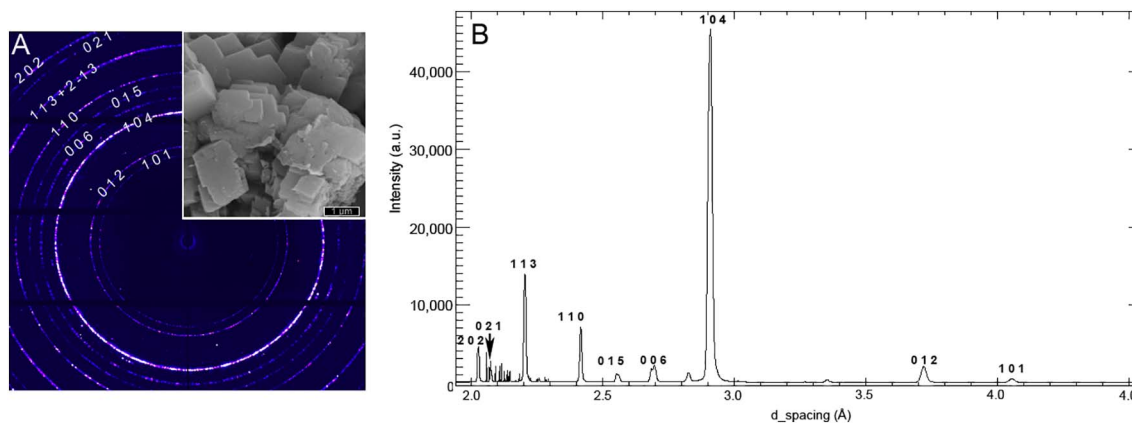

Fig. 5. High resolution XRD analyses of Lagoa Vermelha dolomite. (A) High resolution synchrotron 2D-XRD diffraction pattern. The Debye rings show d-spacing of the reflections obtained over an analytical area of 100 μm², step size 1 × 1 μm, using Fe_K$_{\alpha1}$ radiation at the MicroXAS beamline, Swiss Light Source. The inset shows a SEM photomicrograph of the sediments analyzed. (B) XRD spectra using the sum of maximum intensities of 100 microanalyses conducted over the analytical area of the sediments shown in Fig. 2C–D.
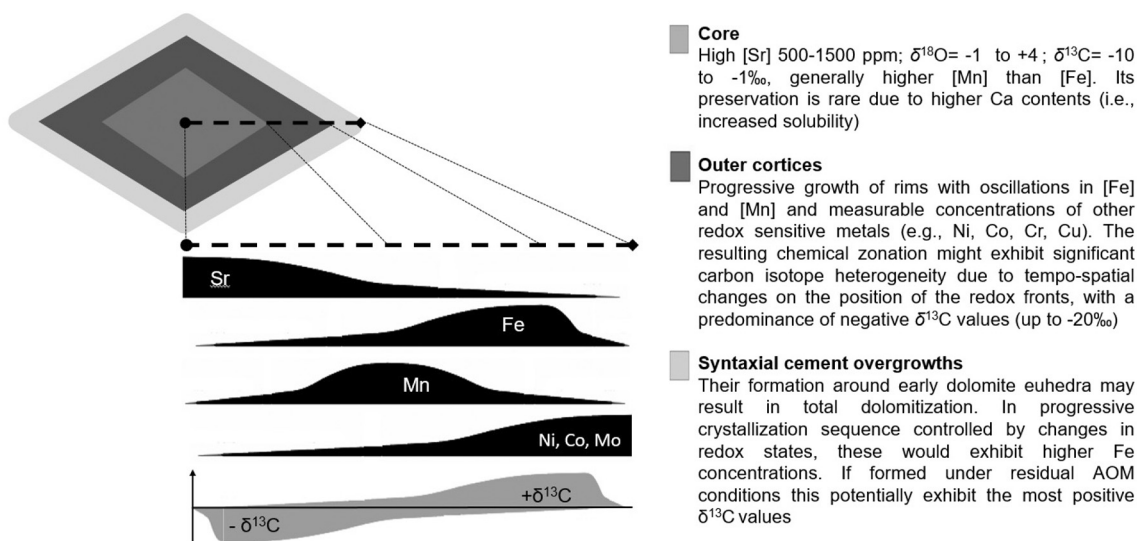
Core
High [Sr] 500-1500 ppm; $\delta^{18}O$= -1 to +4 ; $\delta^{13}C$= -10 to -1‰, generally higher [Mn] than [Fe]. Its preservation is rare due to higher Ca contents (i.e., increased solubility)

Outer cortices
Progressive growth of rims with oscillations in [Fe] and [Mn] and measurable concentrations of other redox sensitive metals (e.g., Ni, Co, Cr, Cu). The resulting chemical zonation might exhibit significant carbon isotope heterogeneity due to tempo-spatial changes on the position of the redox fronts, with a predominance of negative $\delta^{13}C$ values (up to -20‰)

Syntaxial cement overgrowths
Their formation around early dolomite euhedra may result in total dolomitization. In progressive crystallization sequence controlled by changes in redox states, these would exhibit higher Fe concentrations. If formed under residual AOM conditions this potentially exhibit the most positive $\delta^{13}C$ values

Fig. 6. Schematic of internal zonation of multi-generational dolomite crystal and evolution of Sr, Fe, Mn, and carbon isotope with the evolution of precipitating solution.

interpretation of the $\delta^{18}O$ values of peritidal carbonates since they may reflect complex fractionation processes operated by active sulfate-reducing communities (see Dela Pierre et al., 2012).

Another possible modification of $\delta^{18}O$ values, which could be a relevant control of the signature of deep marine dolomite, is the formation and dissociation of clathrates (gas hydrates). In the formation of gas hydrates, there is a strong preferentiality towards incorporation of ^{18}O in the clathrate, depleting the heavy isotopes from the pore water (e.g., Teichert et al., 2005), while fluids derived from the dissociation of gas hydrates are enriched in ^{18}O. In this scenario, the low $\delta^{18}O$ in deep marine carbonates result from the metabolic utilization of CO_2 carrying a particular O isotope signature, possibly as the result of fractionation by ureolysis, hydration/hydroxylation and dehydration/dehydroxylation reactions, which may induce a large disequilibrium composition in product HCO_3^- or CO_3^{2-} as compared with the signature of marine-derived DIC (Thaler et al., 2017). Precipitates formed with a strong contribution of these ionic products in strongly oversaturated environments, such as cold seeps, may form to fast as to allow them to reach full O isotope equilibration (Lloyd et al., 2016; Thaler et al., 2017). The implication of such oxygen and carbon isotope partitioning amongst the gaseous and dissolved inorganic carbon phases is not only that both $\delta^{13}C$ and $\delta^{18}O$ should be in disequilibrium with the ambient seawater (Lloyd et al., 2016; Thaler et al., 2017), but also that the ^{18}O content of the precipitates may be strongly variable at the crystal scale. Importantly, this effect seems to also affect the clumped isotope values (Δ_{47}, see Section 5.2 below), and dolomite derived from such pathways could therefore be characterized by $\delta^{18}O$ values exceeding the fractionation factor in respect to temperature and ambient sea water composition above the sea floor.

5.1.2. Stable carbon isotopes

In marine sediments, the microbial oxidation of organic matter by heterotrophic communities produces a ^{12}C-enriched total inorganic carbon ($C_T = CO_2 + HCO_3^- + CO_3^{2-}$) (Furnes et al., 2008). Upon admixture of this ^{12}C-rich C_T into a pore-water system with abundant marine derived dissolved inorganic carbonate (DIC) pool ($\delta^{13}C \approx 0‰$), the C pool becomes isotopically negative. Authigenic carbonate precipitates often exhibit a bulk negative $\delta^{13}C_{carb}$ signature that typically lies between -8 to $-1‰$, with extreme values below $-20‰$ observed in closed diagenetic systems strongly influenced by microbial degradation processes. By contrast, methanogenic archaea use ^{12}C to generate isotopically "light" methane, leaving the remaining DIC enriched in ^{13}C (Furnes et al., 2008), and thus when methanogenic reactions are important in carbonatogenesis, they generally produce

characteristic positive $\delta^{13}C_{carb}$ values in diagenetic carbonates (Kelts and McKenzie, 1982; Roberts et al., 2004). When subsequent oxidation of methane is involved, the admixture of early-formed $^{13}C_T$ and $^{12}C_T$, derived from AOM, commonly leads to the precipitation of multigenic dolomite exhibiting significant carbon isotope heterogeneity (see Dimitrakopoulos and Muehlenbachs, 1987, and references therein). For instance, dolomites from the Monterey Formation (Miocene), considered a classic organo-diagenetic example (Compton, 1988), have bulk $\delta^{13}C$ values ranging from -25.4 to $+20.8‰$ (Murata et al., 1969).

Although the coupled metabolic activities of AOM consortia are usually recorded by distinctively depleted $\delta^{13}C$ signals in the carbonate by-products (Furnes et al., 2008), less depleted $\delta^{13}C$ could be produced under AOM conditions either from admixture of residual methanogenic $^{13}CO_2$ (e.g., Claypool and Kaplan, 1974), or alternatively from extensive AOM (Whiticar, 1999; Pancost et al., 2000; Nyman et al., 2010). Importantly, as any suitable redox couple for AOM is progressively depleted, acetoclastic methanogenesis becomes the more likely diagenetic mechanism producing CO_2 in deep AOM zones (Parkes et al., 2005; Bethke, 2011). Provided that alkaline conditions are concomitant with methanogenesis, the resulting isotopically heavier carbonates may, or may not, be interspersed with very low-$\delta^{13}C$ phases (Fig. 7; Dimitrakopoulos and Muehlenbachs, 1987). Thus, submicron-scale ^{13}C zonation could be expected in multigenic crystals growing in long lived AOM zones.

Carbon isotope heterogeneity in diagenetic dolomites may also be a consequence of multiple fractionation paths between CH_4, CO_2 and biomass (i.e., catabolic vs. anabolic pathways; Alperin and Hoehler, 2010; their Figs. 2 and 3), and relative ^{13}C-rich CO_2 has been found as a residual product of bacterial reduction of CO_2 to CH_4 (Nissenbaum et al., 1972; Claypool and Kaplan, 1974). In this regard, it has been recently suggested that the interpretation of anaerobic methanotrophy based solely on a ^{13}C depletion of the microbial biomass should be considered tentative unless corroborated by independent, concordant evidence of net methane consumption (Alperin and Hoehler, 2010). Since the difference between isotope effects associated with forward and reverse metabolic paths must be expressed in the CO_2 fixed in both the carbonate by-products of anaerobic methanotrophy and in the associated biomass, the wide range of $\delta^{13}C_{carb}$ observed in dolomite phases may not only be suggestive of precipitation in zones affected by temporarily and spatially variable rates and mechanisms of microbially induced saturation, but also reflect the effects of isotopic fractionation arising from the forward and reverse fluxes of C controlled by syntrophic benthic consortia.
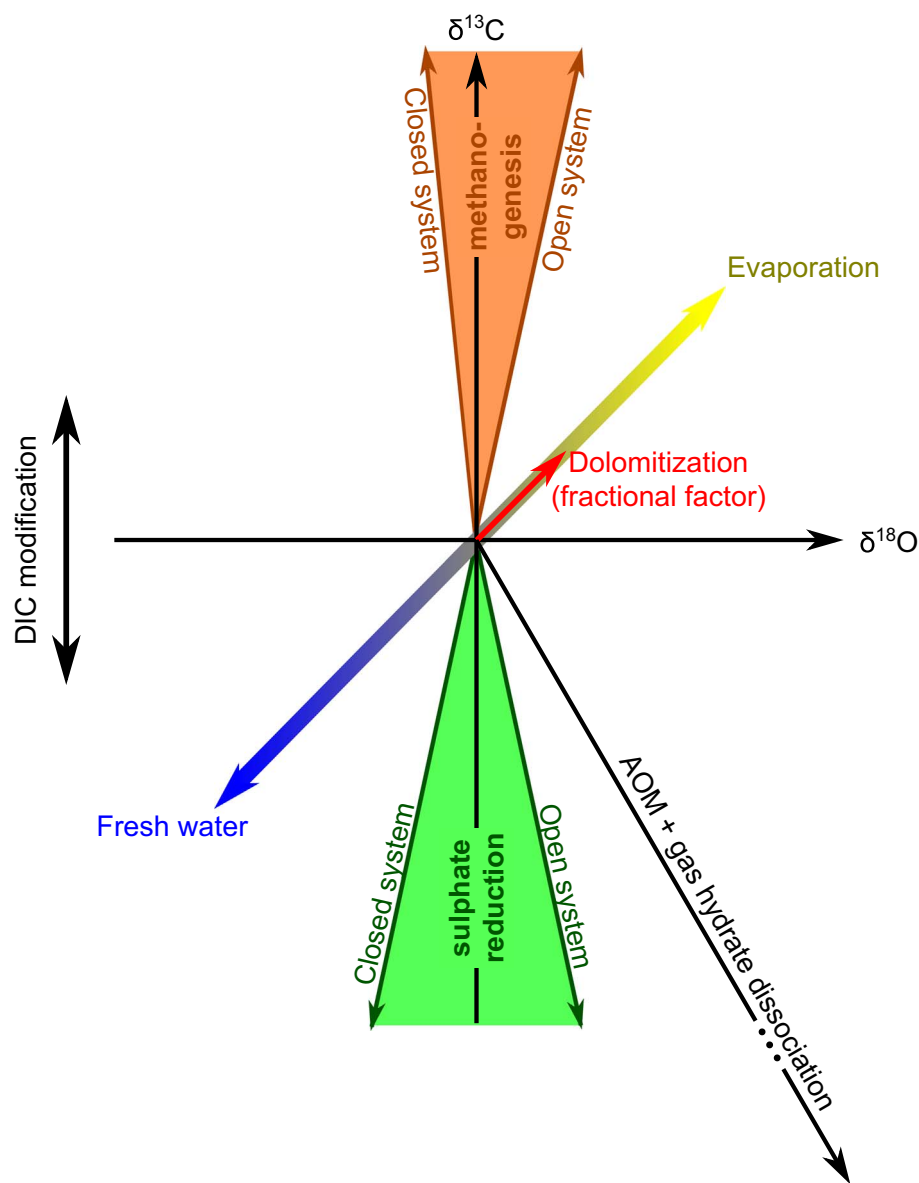
The progression of microbially influenced reactions that could promote shallow burial diagenetic growth of dolomite all have the ability to produce specific signatures in the multigenerational product. Yet, the study of such signatures is not straight forward. For instance, a crystal could have first formed under a suboxic condition, with nucleation promoted by the presence carboxyl-rich EPS probably secreted by phototrophic organisms (i.e., Roberts et al., 2013; Qiu et al., 2017), and subsequent stabilization enhanced by elevated and sustained alkalinity generation and pH produced by elemental recycling reactions involving intermediate metal and sulfur species. These reactions should produce a dolomite strongly influenced by marine-derived dissolved inorganic carbon (DIC), but admixture of DIC influenced by microbial Fe(III) reduction, Mn(IV/III), (e.g., Coleman and Raiswell, 1993; Bekker et al., 2010) and sulfate reduction (Curtis et al., 1986) generally lead to dolomite phases shifted towards lighter $\delta^{13}C$ values. Such dolomite contains minor and trace metals being released from the (oxy)hydroxides dissolved and from the decaying sedimentary organic matter, which is also metal reactive. With increasing burial, and as the vertical and lateral availability of bioreactants changes, the shallow burial precipitation environment can be influenced by a pore-water system supportive of AOM that could also impart a signature in the overgrowths of the original crystallites. Upon further burial, sulfate

depletion takes places and the signatures of the evolving crystals could be further affected by dissolution/reprecipitation reactions occurring under a methanogenic condition.

Due to variations in relative sea level, a dolomite-containing interval in a prograding continental margin could be affected by such successions of biogeochemical processes a few times over a period of, for example, 1 Myr (Meister et al., 2008). Moreover, in shallow epicontinental coastal settings affected by local/regional or relative sea level changes, an organo-diagenetic sequence as described above may occur a number of times in a period of 10^5 years, with a strong control presumably exerted by orbital eccentricity (see Haq, 2014). Because all of the microbial respiration mechanisms considered above can exert a significant influence over the chemical/isotopic signatures of the resulting multi-stepped dolomite crystals, there is a major challenge in using bulk carbonate isotope signatures as the sole proxy to recognize specific microbial processes (see Raiswell and Fisher, 2000).

As for resolving the distribution of carbon isotopes and the isotopic heterogeneity of zoned dolomite phases, there is no doubt that, with the extended utilization of novel high spatial resolution *in situ* probe techniques currently being developed (e.g., Secondary ion mass spectrometry, SIMS), it will be possible to evaluate to what extent the $\delta^{13}C$ variability of multigenic crystals reflects the effect of their passage

through various organo-diagenetic zones. Yet, for such studies to be successful, it is also critical to fully understand the sequence of crystallization of the dolomite subject to analyses, which requires the coupling of isotopic data with *in situ* minor and trace metal analyses (see below) and resolution of the interferences resulting for variable Mg and Fe contents (i.e., Riciputi et al., 1998).

5.2. Clumped isotope thermometry

Temperature is an important issue to consider in carbonate chemistry because it influences several parameters, such as metabolic rates, the partial pressure of dissolved oxygen and other gases, conductivity and salinity, etc. The paleotemperature constraints of carbonate and other minerals, using the $\delta^{18}O$ thermometry (Urey, 1947; Epstein et al., 1953), have been widely applied as a quantitative thermometric measure based on the thermodynamic constrained exchange of oxygen isotopes between two phases. However, such paleo-thermometers generally constrain temperature only when two or more co-genetic phases have mutually equilibrated and each can be measured or estimated for their $\delta^{18}O$ values. However, the oxygen isotope composition of the fluid phases of interest are generally not preserved and therefore must be estimated.

Recently, a new method, called clumped isotope thermometry or Δ_{47} thermometry, has arose as an exciting avenue to constrain the solution isotope chemistry used in carbonate thermometry. The method is based on the temperature dependent formation of $^{13}C^{18}O^{16}O_2^{-2}$ anion groups within solid carbonate minerals (Ghosh et al., 2006; Schauble et al., 2006; Eiler, 2007, 2011). Δ_{47} thermometry has been used for reconstructing temperatures in times and locations where the isotopic composition of water is unknown, as well as for reconstructing paleoenvironment or diagenetical histories (Came et al., 2007; Bristow et al., 2011; Ferry et al., 2011; Finnegan et al., 2011; Dale et al., 2014; Loyd et al., 2015; Bahniuk et al., 2015; Bonifacie et al., 2017).

The carbonate clumped isotope thermometer has been calibrated for synthetic inorganic calcite and a variety of biogenic carbonates (e.g., Ghosh et al., 2006; Dennis and Schrag, 2010; Zaarur et al., 2013; Tang et al., 2014; Defliese et al., 2015; Kluge et al., 2015; Ghosh et al., 2007; Eagle et al., 2013; Henkes et al., 2013; Came et al., 2014; Müller et al., 2017). Most recently, Bonifacie et al. (2017) reported a Δ_{47} linear calibration for dolomite samples from natural environments and laboratory experiments, which were precipitated at known temperatures from 25 to 350 °C. This range of temperatures covers most conditions under which dolomite precipitates, specifically for temperatures below 50 °C, which have been previously poorly constrained. Thus, paleotemperature constraints using carbonate clumped isotope thermometry offers an exciting approach to evaluate the formation temperature of dolomite and the diagenetic processes altering the mineral under shallow burial conditions. Application of this technique has great potential to open a new door to study "The Dolomite Problem". With this tool, it will now be possible to reevaluate dolomite models and reinterpret the environmental conditions that trigger the formation of this enigmatic mineral, yet caution must be exerted when interpreting authigenic carbonates linked to methane oxidation in oversaturated environments, such as cold seeps, which tend to exhibit anomalously low clumped isotope values ($\Delta_{47} \leq \sim 0.2\%$) that translates into apparent temperatures that are warmer than ambient temperatures by up to 50 °C (Lloyd et al., 2016).

5.3. Emergent metal isotope systems

From the previous discussion, it is evident that the bulk carbon and oxygen isotope composition of dolostones, although useful in identifying the likely involvement of microbes living in the precipitation environment, does not permit conclusive interpretations to be drawn since different organo-diagenetic scenarios could have been instrumental for dolomite precipitation. The difficulty in interpreting isotopic signatures is not only due to the overlapping influences of photosynthetic CO_2 uptake; Fe(III), Mn(IV) and sulfate reduction; and methanotrophy on the isotopic composition of multigenic dolomite crystals, but also because of the analytical constraints of the emerging methods. The advent of MC-ICP-MS now enables us to measure precisely Ca and Mg, but also transition metals isotope ratios (e.g., ^{97}Mo) which can be used to derive key information about modern and ancient dolomite-precipitating environments. An exhaustive revision of emergent isotope systems and their potential applicability to the study of dolomite paragenesis is beyond the scope of this review. However, due to the capacity of dolomite to incorporate trace amounts of transition metals into its crystal lattice, correlative studies of non-traditional isotope systems in exceptionally well-preserved crystals are likely to produce useful data to distinguish isotopic signatures inherited from local to regional redox changes versus those resulting from global scale perturbations of the Earth System.

In this section, we focus on the applicability of alkali metal isotopes. Temporal variations in $\delta^{44}Ca$ ($^{44}Ca/^{40}Ca$) are thought to reflect changes in the fluxes of calcium to the oceans (Holmden, 2009; Farkaš et al., 2007a, 2007b; Blättler et al., 2012, 2015, 2016). Despite the fact that there are strong physiological and paleotemperature controls on Ca isotope uptake by biomineralizing organisms (Eisenhauer et al., 2009), the calcium isotopic composition of carbonate rocks is thought capable of providing valuable information on past ocean pH conditions and ancient carbonate saturation states, particularly when used in conjunction with other proxies, such as boron and carbon isotopes (e.g., Kasemann et al., 2005). On this note, Blättler et al., 2015 propose that an apparent negative correlation of Mg and Ca isotopes, which signify the opposing directions of pore-fluid $\delta^{26}Mg$ and $\delta^{44}Ca$ evolution during shallow burial diagenesis, can be useful as a marker for bulk geochemical alteration for carbon and oxygen isotopes. Importantly, Krause et al. (2012) provided compelling evidence for extracellular polymeric substances being able to accumulate isotopically light Ca isotopes. Their findings also suggested a two-step fractionation process might be involved in the sequestration of Ca from solution into the crystal lattice of disordered dolomite, thus questioning the applicability of the Ca isotopic system as a proxy for paleogeochemistry of seawater and the reconstruction of paleohydrological regimes of carbonate formation.

Regarding magnesium isotope ratios ($^{26}Mg/^{24}Mg$, $^{25}Mg/^{24}Mg$), there is still large uncertainty on the significance on their variations in dolostones. With the temperature dependence of the fractionation factor only recently established experimentally (Li et al., 2015), it is now possible to use this tool to evaluate high temperature dolomite and contextualize the values measured in low-temperature dolomites. However, it has been recently suggested that the $\delta^{26}Mg$ isotopic signatures of dolomite might permit the identification of different sources of Mg, enabling the distinction of weathered sourced versus magmatic sourced Mg (i.e., Shen et al., 2009). Yet, further estimates of magnesium isotope fractionation factors associated with the precipitation of dolomite under low-temperature conditions have yet to be determined in order to enable the use of Mg isotopes as a proxy for large scale geochemical cycles, such as the effects of pool partitioning of magnesium, enhanced global chemical weathering rates, or sea floor spreading rates on the long term magnesium isotopic composition of seawater. Furthermore, observed heterogeneity at sites where dolomitization occurs, due to factors such as diffusion, distillation and interaction with clays (Higgins and Schrag, 2010; Geske et al., 2015; Mavromatis et al., 2014) can influence the Mg isotope values. These local effects must be systemically evaluated in order to deconvol them from the global oceanic signal and changes.

Additional research efforts in evaluating the covariance of Mg and Ca isotopes in carbonate sequences could shed light on the timing and diagenetic environment of dolomite precipitation. The chemostratigraphic potential of this approach arises from the fact that there is no significant isotopic fractionation of Mg during high temperature

diagenetic processes (Li et al., 2015), but measurable fractionation occurs during low-temperature processes (Shen et al., 2009). In this context, the results of Galy et al. (2002) are interesting. These authors showed that despite various geological settings, the δ^{26}Mg of dolostones are consistently higher (2.0 ± 1.2‰) than those of coeval limestones. More recently, by measuring magnesium gradients in continental margin ODP sites, Higgins and Schrag (2010) found evidence to suggest that the pore-fluid δ^{26}Mg values increase with depth by about 2.0‰, thereby influencing the Mg isotope composition of growing carbonate phases. Interestingly, these ^{26}Mg enriched pore-waters were found also to be characterized by high alkalinities and relatively low [SO_4^{2-}], which, together with the bulk δ^{13}C values of dolomite crystals, are suggestive of increased subsurface microbial activity (see also Mavromatis et al., 2014). Carder et al. (2005) observed that dolomites of microbial origin would have a kinetic signature, while Saenger and Wang (2014) discussed the potential for Δ^{26}Mg$_{carb-sol}$ values of carbonates to be influenced by biologically mediated processes including the role of organic molecules. A detailed study recently conducted by Geske et al. (2015) in Holocene and Pleistocene sabkha-type dolomites demonstrated that their magnesium isotope signature is related to the complex kinetics of precursor formation, microbiologically mediated dissolution/precipitation reactions, and variable Mg sources and sinks in a temporally and spatially variable microenvironment.

5.4. Minor and trace elements

A number of trace elements (e.g., Sr, Na, Fe, and Mn) have been routinely used to try and constrain the nature of dolomitization reactions, and their relevance as diagenetic indicators has been discussed in detail in the past (e.g., Shukla, 1988; Tucker and Wright, 1990). These trace elements can be incorporated into carbonate minerals precipitating in equilibrium with aqueous solutions by discrete mechanisms including: (i) fluid inclusions; (ii) surface complexation onto growing crystals; (iii) occlusion in lattice defects; and (iv) solid-solution substitution for Ca and/or Mg (see Land, 1980; Budd, 1997; Morse and Mackenzie, 1990). The latter mechanism is thought as the most relevant factor controlling the Sr, Mn and Fe content of carbonates (Morse and Mackenzie, 1990), but the distribution coefficients of each element may be dependant of variable rates of precipitation, as well as redox potential (determining activities of Mn^{2+} and Fe^{2+}) and ionic activities of the precipitation environment (Morse and Mackenzie, 1990). In addition, diagenetic disequilibrium reactions controlled by fluid-rock interactions could determine the degree of re-partitioning within multigenic crystals (see Veizer, 1983; Machel and Mountjoy, 1990).

Regarding Sr, Na, Fe, and Mn, it has been observed that Holocene dolomite displays higher strontium concentrations than more ancient dolomites, which may, in part, be due to strontium's preferential substitution into calcium sites of poorly ordered (i.e., high Ca), early diagenetic crystals (see Shukla, 1988).

Lattice-bound concentrations of Na, on the other hand, might help in constraining the salinity of the dolomitizing fluids and support isotopic and mineralogical observations regarding the diagenetic environments of formation (Staudt et al., 1993). Therefore, Na concentrations are expected to be higher for small "supratidal" dolomite crystals than for the coarser burial diagenetic and hydrothermal dolomites (Fritz and Katz, 1972). Sodium, however, may well occur as fluid or solid halite inclusions and as $NaHCO_3$ in crystal defects. Such non-lattice bound Na contents typically make interpreting the Na content in dolomite a questionable endeavor (Budd, 1997).

For the redox-sensitive elements Fe and Mn, their reduction by Fe(III)- and Mn(IV, III)-respiring microbes allow these metals to be incorporated in their divalent state in dolomite by the partial substitution of Mg^{2+} and minor Ca^{2+} (Kastner, 1999). Multigenic dolomites include variable levels of divalent Fe and Mn as the reducing conditions that typify pore waters change during burial. However, in general, the concentrations of such elements in dolomite seem to increase with increasing depth of formation (Warren, 2000). In the presence of biologically produced sulfide anions (HS⁻), however, this condition leads to the co-precipitation of pyrite and iron-poor carbonates (Macquaker et al., 2014). On the other hand, in sediments governed by sulfide oxidation, the reduced availability of Fe leads to poorly buffered pore waters that result in metastable carbonate dissolution and Fe incorporation into newly formed carbonate overgrowths (Macquaker et al., 2014). As can be deduced from this particular observation, the activity of subsurface microbes act as a key control over the availability of reactants, and they have the ability to regulate the content of Fe and, for that matter, other bioactive elements in multigenic dolomite crystals.

Despite the importance of the trace metal inventories of dolomite for understanding biogeochemical processes in the subsurface, few studies have attempted to analyse the significance of its trace element geochemistry, and, aside from an experimental study of strontium (Sánchez-Román et al., 2011), the partitioning coefficients (K_D) of low-temperature dolomite have yet to be determined. A major analytical difficulty in measuring transition elements at very low abundances in inhomogeneous carbonate matrices results from a number of spectroscopic and non-spectroscopic interferences of first-row transition elements with highly concentrated species typically present in natural carbonates (see Evans and Giglio, 1993 for details). In addition to this challenge, the micrometer size of most synthetic and modern natural dolomite has also prevented the use of currently available Laser Ablation Inductively Coupled Plasma Mass Spectrometry systems for obtaining consistent transition metal concentration data.

However, a powerful source of information is emerging through the increasing use of *in situ* techniques stimulated by synchrotron radiation, such as micro-X-ray fluorescence, X-ray absorption and X-ray diffraction. These techniques not only allow for mapping the distribution of bioessential trace metals in dolomite at a micrometer-scale, but they might also be used for accurate quantification of concentrations and the evaluation of the effects of micro-inclusions over the heterogeneous distribution of bioactive trace elements (Johnson et al., 2013). Similarly, a recent micrometer-scale investigation of compositional variations of dolomites has been recently conducted by Olanipekun and Azmy (2017) using Electron Microprobe Analyzer (EMPA) and SIMS in combination with luminescence and other petrographic features. This study documented chemical variability (compositional zoning) across dolomite crystals at very high resolution, pointing to geochemical variations across crystal traverses being the result of a dissolution/re-precipitation process that proceeds via micrometer-scale interface reaction horizons.

6. A geomicrobiological mixing model

During the 1980s, many authors invoked a mixing diagenetic model to explain the pervasive dolomitization of widespread carbonate intervals in Neogene sequences. This model involved the admixture of meteoric and marine waters. It is based on the difference in the solubility product constants (K_{sp}) of calcite and dolomite, allowing under certain admixtures for calcite to be undersaturated while dolomite is supersaturated. This region of thermodynamic instability of calcite led to the assumption that the replacement of calcite by dolomite will proceed preferentially in such dolomitizing fluids (Hanshaw et al., 1971; Badiozamani, 1973; Folk and Land, 1975).

The observation that Neogene dolomites are generally found in coastal zones beneath freshwater lenses supported the transient popularity of the mixing model. However, by the end of the 1980s, the model not only began receiving strong criticisms (Hardie, 1987; Smart et al., 1988; Machel and Mountjoy, 1990), but it was largely abandoned, mostly because of the already established extreme oversaturation requirement, that is, the diluted conditions resulting from the admixture of marine and freshwater lenses should rather result in a decrease in the Mg/Ca ratio and an increase in the pCO_2 of the pore-waters, therefore,
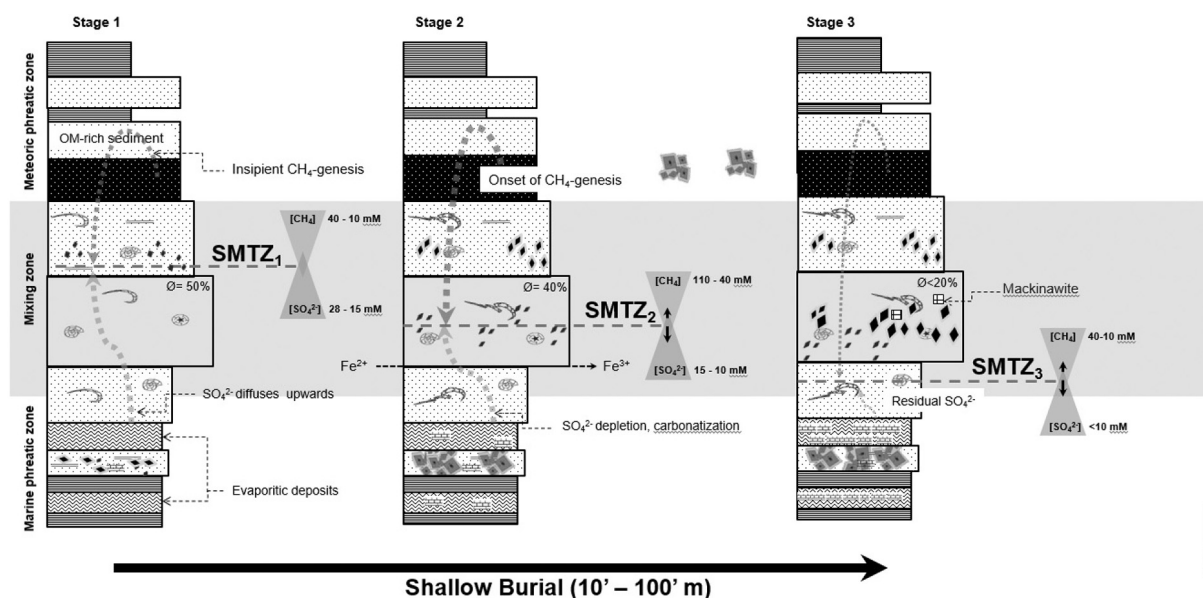
Fig. 8. Schematic of SMTZ migration on a supra evaporate carbonate strata with a CH₄ source as a conceptual illustration of the interaction of anaerobic respiration on dolomite formation and evolution.

leading to a potential decrease in the saturation state of dolomite (sensu Land, 1985).

Nonetheless, the mixing model was supported by multiple lines of evidence from well-studied Cenozoic carbonate platforms bearing dolomite-rich intervals. These occurrences include, amongst others, the matrix replacive laminar dolomicrites of the Eocene-Oligocene Florida platform, Pleistocene of Barbados and Holocene of the Yucatan Peninsula and Belize, which typically consists of fine- to medium-multigenic crystals (i.e., < 1–100 μm in size) (Ebanks, 1975; Mazzullo and Reid, 1985, 1988; Burns and Rossinsky, 1989; Mazzullo et al., 1987; Mazzullo, 2000; Smith et al., 2002).

At least one of the dolomite locales listed above is interpreted as resulting from 'normal seawater' (e.g., Ambergris Caye, Belize; Gregg et al., 1992). However, as noticed by Warren (2000), the stratigraphic levels bearing Holocene dolomite in Belize now encompass successive responses to compositionally diverse and evolving pore fluids that produce a suite of replacive and cementing phases. Considering the tectonically induced variation of relative sea level, as reflected in the marginal facies of Belize (Purdy and Gischler, 2003), and the humid tropical climate characterizing this area of the Caribbean, it is very likely that the recrystallized dolomite levels at Ambergris Caye were affected by some form of shallow burial diagenesis in what we will refer here as the "geomicrobiological mixing zone". In this zone, marked by high rates of subsurficial microbial activity, the seasonal admixture of meteoric and hybrid fluids and marine-derived pore waters produce a fluid of near normal seawater composition containing abundant electron donors and acceptors. In Belize, for instance, the 'dolomitizing fluid' exhibits strong seasonally fluctuating salinities of from ≤ 25‰ to periodically > 75‰, and its Mg/Ca ratio varies from 3:1 to 5:1 (Mazzullo et al., 1987). It was also highlighted that seasonal water mixing is clearly evident in the dolomitic crusts as indicated by their stable $^{18}O/^{16}O$ isotope ratios (Mazzullo et al., 1987; Mazzullo, 2006). Importantly, more recent studies in other post-Miocene continental margins (e.g., Aloisi et al., 2000; Greinert et al., 2001; Peckmann et al., 2001a, 2001b; Campbell et al., 2002; Moore et al., 2004; Kenward et al., 2009), have consistently shown that dolomite intervals in such continental margins occur mostly in Neogene mixing zones, in relatively shallow diagenetic environments, at temperatures < 30 °C, and with maximum depths that rarely exceed a few 100s meters.

It could be argued that dolomite in some of these intervals replace CaCO₃ phases, and therefore very high Mg:Ca are necessary for

dolomitization. Still, and as discussed above, many post-depositional dolomite intervals seem to have formed under weakly supersaturated conditions, and it has been demonstrated that in methanogenic pore-waters high dolomite supersaturation is not pre-requisite for the formation of the mineral (Roberts et al., 2004). For instance, Magaritz et al. (1980) found dolomite rhombs (up to 50 μm in size) cementing Quaternary calcareous coastal sandstones in Israel. These rhombs are forming at the present day groundwater interface between fresh and seawater. Concretions containing such dolomite rhombs have a radio-carbon age of 3200 ± 1730 years (Magaritz et al., 1980). In a later study, Shatkay and Magaritz (1987) found evidence for Holocene dolomite formed at the mixing zone, probably related to enhanced rates of sulfate reduction, which suggest that a similar mechanism may also be relevant basinwards. Similarly, Gebelein et al. (1979) documented patchy "protodolomite" formation in Holocene tidal-flat sediments on Andros Island in the Bahamas. The Ca-dolomite here occurs wherever the various sedimentary facies are intersected by the freshwater-seawater mixing zone. In these facies, Lasemi et al. (1989) found evidence pointing to microbial sulfate reduction.

As indicated above, the mixing process may not rely on the flux of basinal waters characterized by high Mg/Ca ratios towards meteoric zones to maintain favorable saturation conditions — as proposed in the Dorag model (Badiozamani, 1973), but rather on processes that enhance the subsurface availability of energy sources. Specifically, the flux of formational waters carries electron acceptors/donors required to trigger microbial diagenetic reactions prone to dolomite formation, as well as the supply of Mg^{2+} ions. One of the conditions influencing dolomite formation could be that the diagenetic mixing of sulfate-rich and methane-rich waters fuels anaerobic oxidation reactions responsible for alkalinity generation. This admixture process involves thermodynamic aspects underestimated by the critics of the mixing model, which now arises as an elegant solution for the widespread Neogene "dolomitization" process occurring at the interface between electron-acceptor-poor/DOM-rich freshwater and sulfate-rich, marine-derived formational waters (Fig. 8).

As relative sea level changes, spatial gradients prevailing in the temporarily variable Sulfate-Methane Transition Zone (SMTZ) would be responsible for the dolomitization of several hundreds of cubic kilometres of carbonates in Phanerozoic platforms. Under a retro-gradational condition, the spatial variation of the SMTZ would allow it to reach levels seeded with primary near-surface nucleated
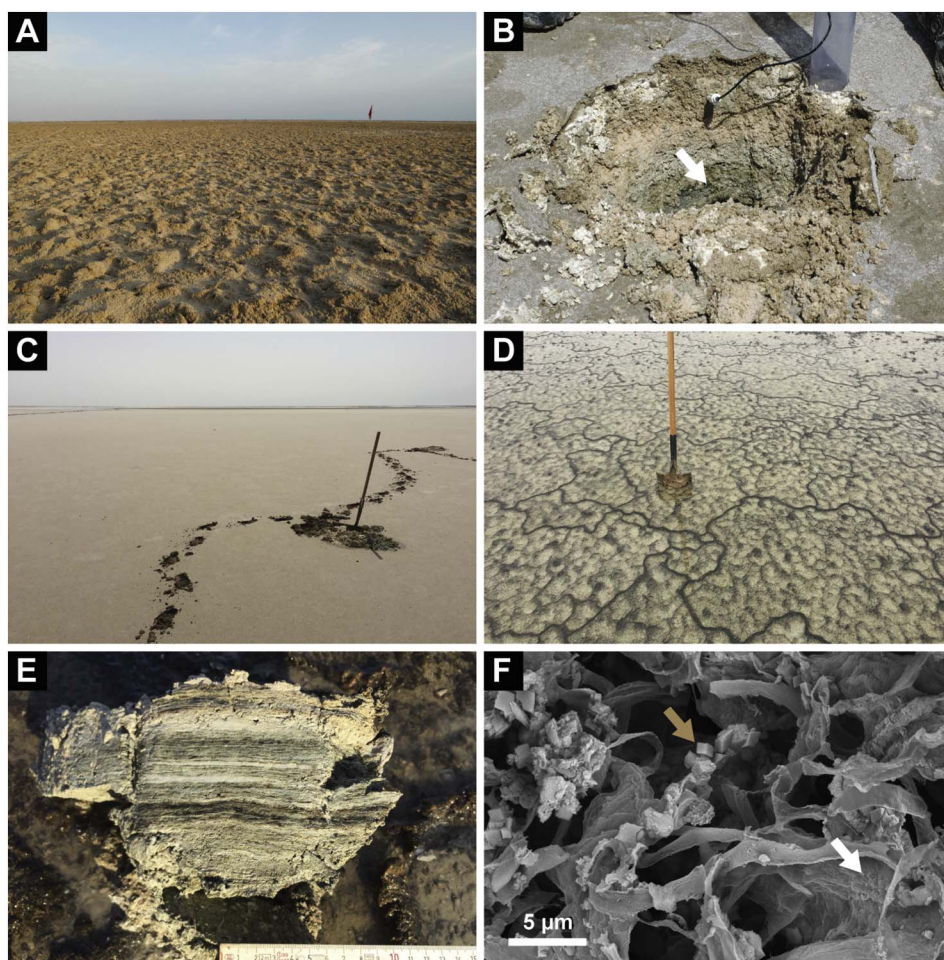
Fig. 9. A geomicrobiological sabkha model. (A) The sabkha of Abu Dhabi in the region close to Al Qanatir Island. (B) In the supratidal zone of the sabkha of Abu Dhabi, anhydrite and gypsum occur above a stratum of dolomite-rich decaying microbial mats (arrow). (C) The Dohat Faishak Sabkha in Qatar (D) The intertidal zone of the Dohat Faishak sabkha is entirely colonized by microbial mats (E) Vertical cross-section of a microbial mat living at the surface of the intertidal zone of the Dohat Faishak sabkha (F) SEM images of the decaying microbial mat pictured in "B". Rhombohedral crystals of dolomite (brown arrow) are forming in association with the partially mineralized (white arrow) extracellular polymeric substances that constitute the biomass of the microbial mat. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

microcrystals in a previous agradational/progradational phase. Such an interface could be considered a dolomitizing front where counter gradients of electron donors and acceptors are separated by limited dispersive mixing capable of increasing microbial activity (Fig. 8). Climatic variability can produce such conditions. For instance, at times in which the reduced carbon reservoirs of continental margins were destabilized (e.g., Kennedy et al., 2001), shoaling of the SMTZ would have been accompanied by the development of non-steady state diagenetic conditions that remained fixed only in the presence of sulfate-rich intervals (Meister et al., 2007).

The shoaling of the SMTZ likely allowed the admixture of diffuse DOM-rich waters and sulfate-bearing brines in ancient epeiric seas to attenuate the thermodynamic constraints that affect the activity of the deep biosphere over geological time scales (Cragg et al., 1998; Mather and Parkes, 2000; Parkes et al., 1995, 2000). Importantly, a number of studies in which the classic mixing model is invoked (e.g., Badiozamani, 1973; Land et al., 1975; Dunham and Olson, 1980) refer to the apparent migration of the dolomitization zone, which seems to have fluctuated across the dolomitized shelf as a response to high frequency relative sea level changes.

Many post-Miocene dolomite-bearing intervals, potentially formed in the geomicrobiological mixing zone, are within meter-scale shallowing-upward cycles, and their bimodal bulk $\delta^{13}C$ distributions often point to AOM as the more likely mechanism for dolomitization (see Section 5.1.2). Texturally, the dolomitized intervals show a linear increase in the average size of crystals with increasing depth (Gregg et al., 1992; see also Mazzullo et al., 1987). These textural and isotopic features are consistently accompanied by increasing Fe and Mn concentrations, and, importantly, are not accompanied by any increase in crystal stoichiometry (Mg/Ca ratio) with increasing depth. Collectively,

these textural, isotopic and geochemical trends suggest that dolomitization occurred within a few million years of sedimentation (Lumsden and Lloyd, 1984; Gregg et al., 1992), possible under the influence of microbial assemblages capable of dissolving Fe and Mn from their parent (oxy)hydroxides. In some cases, such as in the Yucatan platform, the associated $\delta^{34}S$ values (Wright and Oren, 2005), are also suggestive of sulfate reduction (see also Shatkay and Magaritz, 1987).

By controlling the partitioning of reactants, nutrients and redox pairs within their diagenetic environment, the long-term activity of subsurface microbes is capable of enhancing the stabilization and growth of early nucleated, near-surface dolomite precursors (e.g., Burns et al., 2000). Depositional conditions that have been found to support the long lasting activity of subsurface microbial AOM consortiums are: (1) diffusion of biogenic and/or thermogenic methane (Cragg et al., 1992; Pearson et al., 2005); (2) post depositional flow of sulfate-bearing fluids (Cragg et al., 1998; Mather and Parkes, 2000; Parkes et al., 2000) from large-scale evaporite deposits (e.g., Montañez and Reid, 1992; Sun, 1994) or marine derived advection; (3) *in situ* anaerobic oxidation of pyrite with iron oxide minerals as oxidants (Bottrell et al., 2000); (4) deposition of discrete intervals characterized by elevated organic matter (OM) contents (sapropels) and their progressive degradation with increasing burial temperatures (Wellsbury et al., 1997; Cragg et al., 1998; Horsfield et al., 2006; Parkes et al., 2007); (5) the destabilization of gas hydrates (Cragg et al., 1996; Wellsbury et al., 2000, 2002); (6) the occurrence of hydrothermal flows (Parkes et al., 2000); and (7) the presence of active petroleum systems below 80 °C (Head et al., 2003). Yet, to better understand to what extent these conditions resulted in the formation of distinctive dolomite-rich intervals, the relation between the kinetics of dolomite formation and how it relates to the reactions governing life at the deep biosphere, and the potential

biosignatures recorded by multigenic crystals during their passage through different organo-diagenetic zones, remains to be determined.

7. A geomicrobiological sabkha model

Starting in the 1960s, the coastal sabkhas (salt flats) of the Arabian Gulf have been extensively studied as modern-dolomite forming environments, leading to the formulation of what is — together with the mixing model discussed in the previous section — one of the most cited models for dolomite formation (Wells, 1962; Curtis et al., 1963; Illing et al., 1965; Butler, 1969). A reason fuelling special interest for this model is that sabkha-type dolomite occurs in association with gypsum and anhydrite, forming a sequence that characterizes many economically important oil and gas reservoirs (Alsharhan and Kendall, 2003). Indeed, in ancient sedimentary sequences, sabkha-type dolomite often exhibits reservoir properties, with overlaying evaporites serving as stratigraphic traps (Mazzullo, 2004).

Sabkhas mostly form on the shore of restricted lagoons and embayments that are gradually filled through sedimentation of different types of lime-muds which are mainly comprised of authigenic aragonite (Alsharhan and Kendall, 2003). In the supratidal zone, the salinity of pore-waters within muddy facies (Fig. 9A–E) increases landward due to the intense evaporation, reaching supersaturation with respect to gypsum and anhydrite. Continuous precipitation of aragonite combined with that of gypsum and/or anhydrite removes Ca from solution, resulting in pore-waters with a high Mg/Ca ratio. According to the earliest sabkha models, the formation of this warm Mg-rich brine is the key factor causing the previously precipitated aragonite to be transformed into dolomite (Illing et al., 1965). This diagenetic process, which is referred to as a penecontemporaneous replacement, would occur a few decimeters below the surface, in a depositional setting connected to the sea, where it is relatively easy to account for all the ingredients required for the formation of large amounts of dolomite.

Subsequent geochemical analyses of sabkha pore-waters led to a partial revision and refinement of the original model, mainly by recognizing that the source of solute for the dolomite and associated evaporitic minerals is not exclusively evaporated seawater but includes a significant proportion of continental brines, which are mixed with seawater through complex lateral and vertical fluid flow mechanisms (Butler, 1969; Evans et al., 1969; Hsu and Siegenthaler, 1969; Kendall and Skipwith, 1969; Kinsman, 1969; McKenzie et al., 1980; Patterson and Kinsman, 1981; Mueller et al., 1990; Wood et al., 2005). Nonetheless, the concept that precipitation of gypsum and anhydrite produces pore-waters favoring dolomitization of authigenic aragonite remained the essence of the sabkha model.

As it is the case with most models for low temperature dolomite formation, the inability to actually test the hypotheses led to criticisms regarding the validity of the proposed ideas (see Hardie, 1987). Another fundamental and still debated aspect of the sabkha-model relates to the question of whether dolomite is really a replacement product versus being a primary precipitate that forms directly from pore-waters, filling the voids or displacing the aragonite crystals (Shinn, 1973; Brauchli et al., 2015). Indeed, electron microscopy investigations have, as yet, never provided conclusive visual evidence that aragonite crystals dissolve and are progressively replaced by dolomite (McKenzie, 1981; Bontognali et al., 2010; Brauchli et al., 2015). By assuming that sabkha dolomite is a primary precipitate, CO_3^{2-} anions would likely be the limiting factor for the formation of the mineral, and different kinetic constraints were to be investigated and considered as essential for understanding the precipitation process.

In the last 10 years, following the popularization of the microbial model for dolomite formation (see Section 3), research in sabkhas entered a new phase aimed at evaluating whether a microbial factor is also important in these apparently inhospitable environments. In the sabkha of Abu Dhabi, it has been recognized that microbial mats are a widespread and important component of the sedimentary system

(Bontognali et al., 2010; Strohmenger et al., 2011). Living microbial mats entirely colonize the intertidal zone and decimeter-thick layers of partially degraded, ~1000-year-old remnant mats are also present in the supratidal zone, below a layer of gypsum and anhydrite (Fig. 9E). Investigations of these mats showed that microbial activity creates microenvironments with highly variable pH and redox conditions that differ from that characterizing the average conditions of the lagoon and sabkha's pore-waters (Bontognali et al., 2010). Moreover, microscopic investigations revealed a close spatial association between the sites of dolomite nucleation and growth and the EPS that microbes excrete (Fig. 9F, see Section 3.1). These observations led to the formulation of a revised microbial sabkha-model, proposing that EPS constituting both living and decaying microbial mats play the key role for the incorporation of Mg into the carbonate minerals (Bontognali et al., 2010). This microbial mediation process was simulated in the laboratory with a strain of sulfate reducing bacteria isolated from the sabkha of Abu Dhabi (Bontognali et al., 2012), which produce poorly ordered Ca-dolomite and disordered VHMC, and further experiments concluded that the biomineralization process can be referred to as microbially influenced, whereby EPS promote the formation of disordered dolomite also in the absence microbial respiration (Bontognali et al., 2014). More recently, the importance of microbial mats was evidenced also in the Dohat Faishak sabkha in Qatar (Brauchli et al., 2015), at the original site first described by Wells (1962). The presence of dolomite in microbial mats at the surface of the intertidal zone, the lack of replacement textures in core samples that contain both aragonite and dolomite, and the correlation between dolomite and total organic carbon along vertical sedimentary profiles, all suggest that microbes and their associated EPS have a central role for the formation of dolomite. From the sediments of this sabkha, microbes have been isolated, characterized and studied for understanding their role for the formation of Mg-rich carbonates (Al Disi et al., 2017).

Collectively, these studies demonstrate that biology is important and cannot be ignored in future research aimed at understanding sedimentary processes occurring in evaporitic environments. In particular, the recent studies cited above suggest that strong evaporation and consequent high salinity might be linked to the formation of dolomite in a subtler way than originally thought. Evaporation, besides increasing supersaturation resulting in mineral precipitation, may promote an ecological stress that induces microbes to produce abundant EPS (aimed at protecting microbial cells from desiccation, salinity, and intense UV radiation). In turn, EPS combined with supersaturated pore-waters — and possibly also high alkalinity and specific redox conditions sustained by microbial respiration in buried microbial mats (i.e., Petrash et al., 2015) — create the ensemble of conditions required for low temperature dolomite formation.

8. Global scale perturbations and the stratigraphic abundance of dolomite

The dolomite conundrum remains important because it bears directly on our understanding of long-term chemical cycling between the continents, seafloor (including seawater, sedimentary, and basaltic masses), and the atmosphere (Arvidson and Mackenzie, 1997; Arvidson et al., 2011). Over a geological time scale, variations in the relative abundance of dolomite in carbonate platforms seem to be consistent with global scale perturbations, including variations in hydrothermal activity, eustatic sea level changes, and enhanced efficiency of organic matter burial (Given and Wilkinson, 1987; Morse and Mackenzie, 1990; Montañez and Reid, 1992; Sun, 1994; Burns et al., 2000).
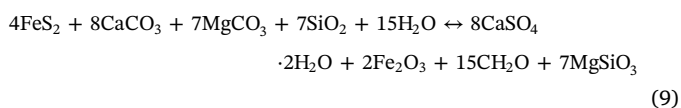
Yet, to fully understand the stratigraphic distribution of dolomite and its preferential precipitation in shallow marine environments, it is imperative to systematically compare the multiple geochemical signatures of several well-studied shallow and deep marine stratigraphic sections hosting dolostones, with special emphasis on the causes of cyclicity. Unfortunately, the available abundance data for ancient

dolomite in carbonate platforms is incomplete, and, even if such sensitive data in oil company records were ever compiled, it would be difficult to make more than a rough estimate of the dolostone to limestone ratio in certain intervals (Holland and Zimmerman, 2000). For Neogene dolomite and drowned platforms, however, the combined dataset of the Ocean Drilling Project and International Ocean Discovery Program (IODP), due to their extraordinary sedimentary preservation and dating accuracy, offers the means to re-evaluate mineralogical abundances (i.e., ODP 101, 133, 160, 166, 182, 194 and 198, as well as IODP 325 and 359, amongst others) and to further understand the influence of autocyclic vs. allocyclic controls over the stacking patterns of carbonate sequences (Goldhammer et al., 1993; Hill et al., 2012). Due to the lack of systematic analyses of these datasets with regard to Neogene dolomite abundance, in the following sections we only focus on the potential significance of the abundance of the mineral within its long-term cyclostratigraphic context.

8.1. Dolomite distribution within tectonically induced stratigraphic cycles

Dolostones, together with basalts, are considered amongst the most important sinks for Mg fluxes into seawater, with basalt being more relevant during times of widespread seafloor volcanism and dolostones exerting a negative feedback during times of tectonic quiescence and formation of epeiric seas (Berner, 1991). The inferred Mg fluxes are intimately interrelated with other geochemical fluxes and have been modeled by Garrels and Perry (1974) according to the following general equation, which is valid for a constant ocean-atmosphere CO_2 composition:

$$4FeS_2 + 8CaCO_3 + 7MgCO_3 + 7SiO_2 + 15H_2O \leftrightarrow 8CaSO_4$$
$$\cdot 2H_2O + 2Fe_2O_3 + 15CH_2O + 7MgSiO_3 \tag{9}$$

From the net reaction above, it is evident that the uptake of Mg from seawater via basalt-seawater reaction outcompetes Mg-carbonate formation as the principal mechanism of removal of Mg from the oceans over geological time (Berner, 1991). From the two Mg sinks in Eq. (9) (Mg carbonates at times of tectonic quiescence vs. Mg silicates at times of increased seafloor spreading), it is clear that during times of increased seafloor spreading, the interaction of hydrothermal waters with the oceanic crust effectively removes Mg from seawater, thus decreasing its Mg/Ca ratio (see Berner et al., 1983; Holland, 1984; Berner, 1991; Mottl and Wheat, 1994) and the supersaturation state of dolomite in seawater. Such conditions, however, can be reversed at times of diminished hydrothermal activity, when not only is less Mg removed from seawater, but sea level falls tectono-eustatically, which increases the rates of erosion and nutrient delivery to the ocean and forces platform progradation. In continental margins affected by such conditions, the burial of organic matter is enhanced, and can be accompanied by marginal evaporite sedimentation (see Sarg, 1988, 2001). Upon burial the combination of evaporitic lithologies would have favored the activity of some of the subsurficial geomicrobiological mixing process depicted above to also favor the stabilization and growth of dolomite.

Since long term, non-periodic relative sea level fluctuations are always superimposed by high-order orbitally forced cycles, changes in the proportion of dolomite to calcite within stratigraphic successions could be related to the combined influence of both long and short term cycles on the marine shallow water microbial ecosystems and their mineral by-products (Algeo et al., 2008). Below we discuss how geological cyclicity can exert a major role on the stratigraphic abundance of dolomite by drastically affecting: (1) the atmospheric pCO$_2$, and, thus the saturation state of seawater with regard to dolomite (Kerr, 1998; Kasemann et al., 2005), and (2) the amounts and rates of organic burial and the fluxes of Mg^{2+} and biolimiting nutrients to continental margin deposits (Berner, 2006).

8.2. Dolomite distribution within glacio-eustatic stratigraphic cycles

Superimposed on tectono-stratigraphic cycles ($\sim 10^6$ yrs) is a record of 10^4 to 10^5 yr climatically driven cycles. In peritidal carbonate cycles, the irregular thickness and stratigraphic distribution of dolomite-bearing horizons within shallow marine carbonate successions can be strongly determined by such forcing mechanisms that correspond to the orbital forcing Milankovitch cycles (Montañez and Reid, 1992; Weedon, 2003; Fischer et al., 2004; Miller et al., 2011). Their effects on sea-level fluctuations, erosion and nutrient delivery to the ocean, and rates of organic productivity and burial may well trigger diagenetic conditions prone to dolomite formation (Sun, 1994; Burns et al., 2000). In this regard, the observation that in the sequential framework of the Phanerozoic, the dolomitized carbonate platforms developed during ice-free periods are fundamentally different from sparsely dolomitized cap intervals that developed shortly after major glacial periods (Sun, 1994). Such a difference is believed to be related to the amplitude of sea-level fluctuations (Koerschner and Read, 1989), but might well be the result of transient conditions capable of promoting subsurface microbial activity (Grotzinger and Knoll, 1995).

For instance, an immediate consequence of postglacial transgressions, under increased tectonically induced, global warming conditions, is the release of sedimentary methane reservoirs (Chen and Benton, 2012). By being rapidly oxidized to CO_2, the post-glacial release of methane would initially lower the pH and saturation states of dolomite in seawater. Yet, once the supply of methane-derived CO_2 to the atmosphere is balanced by increased chemical weathering, a more active transference of nutrients to shallow marine carbonate reservoirs may have led to increased CO_2 fixation by primary producers. Increased chemical weathering and erosion rates also increased the concentrations of dissolved P, N, Fe, and other biolimiting elements to marine realms, which in turn resulted in the development of widespread anoxia and deposition of black shales. This condition enhanced the burial and remineralization of organic carbon during periods of hydrographic restriction and climatic aridity (i.e., Katz et al., 2005; Falkowski et al., 2005, see also Petrash et al., 2016b). As atmospheric and ocean CO_2 concentrations are re-equilibrated, the depositional conditions proceed towards a more active transference of: (1) sulfide from exhumed shale reservoirs to the oxidized sulfate reservoir in evaporites; (2) carbon from the reduced buried OM reservoir to continental margin sediments via anoxygenic methane oxidation; and (3) the transfer of Mg from silicates to carbonate reservoirs together with transition metal oxides that catalyze important biogeochemical reactions that would result in punctual globally enhanced conditions for shallow burial dolomite formation (cf. Wilkinson and Algeo, 1989; Sun, 1994).

9. The case of the stratigraphic distribution of Precambrian dolostones

To better evaluate the magnitude of the global controls over the rates of microbially induced early diagenetic dolomite growth, we now focus on the abundance and distribution of dolomite in Proterozoic carbonate sequences, which, being constructed principally by stromatolitic facies, can be considered the best developed examples of microbial carbonate platforms (Grotzinger, 1989, 1990).

As other contemporaneous rocks (e.g., banded iron formations), a significant fraction of Precambrian dolostones probably precipitated from ancient oxygen-poor and relatively metal-enriched seawater (Tucker, 1983). Interestingly, in Precambrian carbonate sequences, a common association in the Proterozoic sedimentary rock record is that of silicified stromatolitic dolostones overlain by, or in places interbedded with, small-scale evaporites and phosphorites (Cook, 1992). Since such facies assemblages and their stacking patterns are common to many Proterozoic sequences, they are thought to be indicative not of synchronicity but a resemblance on the allogenic and authigenic processes that acted thereof (Cook, 1992). The paragenetically related

deposits described above may also be the product of significant microbial activity promoted by the unique biogeochemical conditions governing diagenesis in Proterozoic peritidal to evaporitic settings (Notholt and Jarvis, 1989; Grotzinger and Knoll, 1995; Gellatly and Lyons, 2005) that were instrumental for the widespread accretion of a variety of stromatolites morphotypes (Grotzinger, 1989). Incidentally, the fraction of all Proterozoic marine carbonate units that are dolomitic is positively correlated ($\rho = 0.58$, $P < 0.0002$) with the fraction of marine stromatolite-bearing units (Peters et al., 2017).

Prior to the early stage of Earth's atmosphere oxygenation event (Bekker et al., 2004; Holland, 2006), the shallowest marine sediments were subjected to methane advection and diffusion, which allowed for the accumulation of CH_4, which photo-oxidized to CO_2 in the atmosphere (Pavlov et al., 2001). Towards the end of the Archean eon, however, and following the evolution of oxygenic photosynthesis, increasingly abundant concentrations of sulfate accompanied by an increase in the transport of oxides, started to accumulate in shallow-marine shelves leading to increasing subaqueous oxidation of methane as a source of energy by stromatolite-forming consortia (Eigenbrode and Freeman, 2006; Planavsky et al., 2014; Petrash et al., 2016a).

The direct relationship between increasing oxygen levels in the Precambrian atmosphere and increased concentrations of bioavailable metals and sulfate in ancient shallow marine setting is due to the weathering of subaerially exposed pyrite-bearing rocks on continents, or the reaction of riverine-transported oxidized metal anions with H_2S diffused from buried Neoarchean sediments to shallow Paleoproterozoic oceans (El Tabakh et al., 1999; Ojakangas et al., 2001; Kah et al., 2004; Gandin et al., 2005; Gandin and Wright, 2007; Schröder et al., 2008; Konhauser et al., 2011). Such conditions that followed major orogenic pulses (Condie, 2005; Campbell and Allen, 2008), led to more active C, S, and Fe and Mn biogeochemical cycling in coastal areas, potentially under the influence of very active near-surface AOM consortia, which were likely analogue to those now restricted to the deep biosphere. The enhanced activity of such consortia may have been instrumental for the formation of widespread near-surface stromatolitic dolomite intervals in shallow Precambrian seas.

10. Research needs

Our concept of microbially catalyzed dolomite formation in natural low-temperature ($< 60\,°C$) systems requires the interaction of microbial communities capable of controlling the activity of reactants in sediments. When the role of these communities is acknowledged, more robust interpretations are possible. Regarding recent criticism to the contention above (i.e., Gregg et al., 2015; Kaczmarek et al., 2017), it must be considered that the limited amount of material resulting from biotic synthesis experiments in the past was analyzed via standard XRD methods (i.e., detection limits 2% wt), and was likely comprised of up of three distinct carbonate phases (abundant VHMC, minor amounts of disordered to partially ordered Ca-dolomite and in cases magnesite), which together with other solid phases, such as perhaps Ca-phosphate (Gregg et al., 2015), complicate the resolution of low intensity ordering reflections.

The lack of convincing evidence of cation ordering reflections in biotic precipitates as compared with dolomite formed at high temperature could be linked to the fact that the ordering reflections of dolomite are only evident when the mineral comprises at least 9% of the bulk sample (see Kaczmarek and Sibley, 2014). Accordingly, if standard XRD patterns were envisioned as the ultimate tool for ascertaining whether or not microbial dolomite occurred in the lab, as it apparently does in organic-rich shallow marine sedimentary intervals, then it seems that such recent criticism actually points more to a 'methods problem' than a 'dolomite problem' (Nash et al., 2014). To conclude on this matter, we are confident that a research effort designed to evaluate the reproducibility of the previous experimental protocols designed to produce dolomite at low T would prove that

several microbial functionalities have the ability to produce partially ordered precursor crystallites that can transform to stoichiometric dolomite upon time. Due to their nature, however, the mineralogy of such synthetic precipitates must be reevaluated via spatially resolved techniques, i.e., synchrotron-based XRD and/or Raman spectrometry — capable of resolving the heterogeneity of the micron-scale mineral clusters that result from nucleation into organic matrices.

It must be also emphasized that the models that do not consider microbial activity in the subsurface are unable to explain the complete dolomitization of carbonate sequences in the Neogene sedimentary rock record, nor the striking abundance of primary dolomite in Precambrian stromatolitic carbonate sequences. In this regard, important questions remain unresolved, and in some cases completely unexamined. These include, but are not limited to:

(1) To what extent do dolomite supernuclei seeds, formed in supratidal settings, influence the dolomitization process of subtidal facies? An answer to this question requires evaluation of the mechanisms that induce seeded dolomite growth in bioreactors in order to produce input parameters for modeling approaches. More recent advances in our understanding of molecular-scale interfacial processes occurring during mineral growth have enabled a significant advance in our efforts to understand the phenomenon of dolomite nucleation in equilibrium with organic-rich solutions. These can now be tested coupling well-established tools, such as transmission electron microscopy, in combination with state-of-the-art nano-imaging techniques, such as Atomic Force Microscopy, Scanning Tunneling Microscope (both allowing for *in situ* real time observations to changes in the samples surface), as well as time resolved synchrotron-based X-ray scattering, which allows direct molecular-scale observation of minerals during precipitation and dissolution.

(2) What are the effects of processes intrinsically related with the S cycle, such as syntrophic methane oxidation, and dissimilatory Fe (III) and Mn(IV) reduction, on the development of specific conditions prone to diagenetic dolomite formation, and to what extent do these oxides control the kinetics of dolomite precipitation in burial diagenetic realms? This can be explored by evaluating, via omics-approaches, the functionalities of microbial communities from subsurface dolomite-precipitating realms drilled in future International Ocean Discovery Program (IODP) expeditions.

(3) What are the bioactive metals partitioning and isotopic fractionation values of microbial dolomite? *In situ* analytical experiments can provide quantitative data on the effective changes in reaction rates occurring at the microbe/fluid/mineral interface and their capacity to control the co-precipitation of trace metals with Mg and Ca ions onto dolomite lattices. This would advance the use of trace metal signatures in multigenerational dolomites as a proxy of metal mobility and speciation of their temporarily variable precipitation setting. This research effort would reflect the nature and evolution of microorganism-dolomite-fluid interactions during diagenesis, and may allow the reconstruction of ancient biogeochemical conditions using emergent isotope systems.

(4) To what extent does the Precambrian vs. Phanerozoic abundance of dolomite reflect the global preservation potential of certain deposits as a function of favorable paleogeographic conditions that allowed their emplacement while precluding their recycling (Mackenzie and Pigott, 1981; Grotzinger, 1989).

(5) In the Precambrian, there was a prolonged interval (~ 1.8 to ~ 0.8 Ga) when the carbon cycle was remarkably stable (Anbar and Knoll, 2002), and when only few major geological, or environmental events have been documented (Schopf and Klein, 1992, but see Lenton and Watson, 2011). When compared with the late Archean - Paleoproterozoic Earth system, marked by major geobiological changes, this period can be considered as a 'boring billion' (after Brasier, 1995) because it was characterized by relative climatic stability, generally low levels of atmospheric oxygen, a

decrease in major biological events, and the absence of extreme changes in the atmospheric composition and oceanic redox structure, which remained persistently anoxic in its bottom waters and at times euxinic over extended periods (Canfield, 1998; Johnston et al., 2009). In subtidal settings, there was a remarkable decrease in the abundance and distribution of microbially induced sediments (Walter and Heys, 1985), which does not seem to be accompanied by a major decrease in stromatolites prevalence on peritidal settings (Peters et al., 2017). Remarkably, a consistent positive correlation between the proportion of carbonate units that are dolomitic and those that are stromatolite-bearing have been observed, with dispersion probably resulting by late diagenetic dolomitization (Peters et al., 2017). It would be interesting to also evaluate whether the stratigraphic distribution of dolomite in the so called 'boring interval' also correlates with increasing evidence pointing to important geological and environmental perturbation events occurred during the Mesoproterozoic (Roberts, 2013) which likely led to diversification of shallow marine and terrestrial microorganisms (Kah et al., 2001; Parnell et al., 2015), and punctually enhanced the rates of organic carbon burial and subsurficial microbial activity.

In conclusion, there have been major advances made in recent years in our understanding of the influence microbial processes occurring in sedimentary sequences have on the ultimate diagenetic product observed in the rock record. Much of these new data have been derived from the study of deep sea cores and associated pore waters and microbial communities, as well as from microbial investigations of distinctive modern natural environments and culture experiments in the laboratory. This newly acquired knowledge has been facilitated by advances in molecular biology as well as highly specialized instrumentation, and demonstrates the impact that microbial metabolisms can have on the sedimentary patterns derived as a result of near-to subsurface biogeochemical diagenesis. We suggest that by adding a microbial factor to the previously proposed geochemical equations will lead to a re-examination of heretofore established models pertaining to dolomite formation under Earth surface conditions and potentially provide a more complete understanding of this long-standing enigmatic process.

Acknowledgements

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