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REPORT

Coral calcification, mucus, and the origin of skeletal organic molecules

Sönke Hohn[1] · **Claire E. Reymond**[1]

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Abstract Biocalcification encompasses the kinetic and structural, abiotic and biologically mediated processes involved in the formation of calcium carbonate skeletons by marine organisms and represents a key process in the global carbon cycle. Throughout the geological record, this process has evolved repetitively and has altered global biogeochemical cycles. Besides the structural variability of calcium carbonate polymorphs laid down by different organisms, biogenic carbonate skeletons are characterized by the presence of organic molecules that are incorporated into the growing skeleton. Major advances have identified the macromolecules associated to the organic matrix within marine calcifiers, however, it has yet to be established the actual role these organic molecules play in the calcification process. In this study, we isolated the effect of skeletal organic molecules (SOM) on the precipitation of calcium carbonate on coral skeleton fragments by adding extracted SOM or coral mucus (CM) to oversaturated calcium carbonate solutions. We found that the precipitation rate did not change regardless if organic molecules were present or not. However, the primary polymorph did change between the treatments, suggesting that organic molecules influence the surface processes that lead to the formation of the crystal lattice but not the kinetic processes that transport ions to the crystal surface. Since SOM and CM both altered the crystal polymorph but not the crystallization rate, we argue that SOM may not represent a specialized biomineralization toolkit, but that SOM originate from CM and the requirement of the polyp to adhere to the substratum.

Keywords Coral · Calcification · Skeletal organic matrix · Biomineralization

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Sönke Hohn and Claire E. Reymond have contributed equally to this work.

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✉ Sönke Hohn
soenke.hohn@leibniz-zmt.de

[1] Leibniz Centre for Tropical Marine Research, Fahrenheitstraße 6, 28359 Bremen, Germany

Introduction

Corals (Anthozoa) evolved 570 million years before present (Oliver 1996) as simple, soft-bodied metazoans consisting of only two cell layers and a connecting collagenous mesoglea (Galloway et al. 2007). Modern, reef-building, corals (Scleractinia) appeared in the Mid Triassic, ca. 240 mybp (Romano and Palumbi 1996; Stanley 2003; Stolarski et al. 2011). Corals are colonial organisms of individual polyps that share a common gastrovascular system to distribute nutrients within the coral colony (Gateño et al. 1998). The polyps are suspension feeders and perform muco-ciliary feeding (Goldberg 2002; Brown and Bythell 2005; Wijgerde et al. 2011) to capture small plankton (Anthony 1999). Stinging cells, nematocysts, in the oral ectoderm paralyze larger mobile prey (Abe 1938) and enable corals to also feed on zooplankton (Carpenter 1910; Houlbrèque and Ferrier-Pagès 2009). The possession of nematocysts classifies corals into the phylum Cnidaria (Goffredo and Dubinsky 2016). However, the secretion of a calcium carbonate skeleton distinguishes corals from the rest of the Cnidaria.

Marine biocalcification is a key process in the global carbon cycle because it removes carbon from the ocean–atmosphere system and stores it in a geologic reservoir (Lippmann 1973) on a time scale of hundreds of thousands of years (Kump et al. 2000). On the short-term scale, however, calcification consumes alkalinity and increases the pCO_2 of seawater, causing CO_2 to degas from the ocean into the atmosphere (Ridgwell et al. 2003; Menviel and Joos 2012; Abrams et al. 2018; Lønborg et al. 2019). Rising atmospheric CO_2 concentration due to fossil fuel emissions (Ipcc 2000) is causing rapid CO_2 sequestration by the ocean (Sarmiento and Sundquist 1992; Sabine 2004) and consequently leads to ocean acidification (Caldeira and Wickett 2003). Increasing ocean acidity impairs the ability of corals to calcify (Hoegh-Guldberg et al. 2007) and global coral reef cover has been projected to decline drastically until the year 2100 (Freeman et al. 2013). However, not all corals will be affected equally by rising pCO_2 (Fabricius et al. 2011). Some coral species can still calcify in undersaturated waters (Venn et al. 2013), whereas others suggest that calcification may not even be prerequisite to coral survival as they can also survive as decalcified solitary polyps (Fine and Tchernov 2007). Given these extreme examples of possible responses to ocean acidification, it is of major importance to understand how corals biologically control their calcification process in order to evaluate the future of coral reef ecosystems as a fundamental economic and nutritional basis of millions of livelihoods worldwide (Nystrom et al. 2000).

Corals calcify in an enclosed or semi-enclosed extracellular medium below their tissue (Allemand et al. 2004; Tambutté et al. 2011). Active transport of calcium ions and protons increases the calcium concentrations (Al-Horani et al. 2003a, b; DeCarlo et al. 2018; Sevilgen et al. 2019) and pH (Ries 2011; McCulloch et al. 2012; Venn et al. 2013; Georgiou et al. 2015; Cai et al. 2016; Sevilgen et al. 2019) in the calcifying medium, leading to favorable conditions for the inorganic precipitation of calcium carbonate (Lippmann 1973; Zeebe and Wolf-Gladrow 2001; Hohn and Merico 2012, 2015; Lasaga 2014). However, coral skeletons are characterized by the incorporation of organic molecules (Cuif and Dauphin 2005; Wall and Nehrke 2012). The presence of these molecules in the crystal lattice (Williams 1984; Mann 2001; Watanabe et al. 2003) could imply that they are intrinsically important for the formation of bio-minerals (Cuif and Dauphin 2005; Drake et al. 2013; Mass et al. 2013), yet the exact role of organic molecules in the biomineralization process remains unclear (Falini et al. 2015).

The strong binding potential of calcium ions with organic molecules (Kretsinger 1976; Carafoli 1987) suggests that the molecules could act as a template to facilitate or induce crystallization (Allemand et al. 1998; Watanabe et al. 2003; Cuif and Dauphin 2005; Helman et al. 2008; Mass et al. 2013). However, the presence of skeletal organic molecules (SOM) or coral mucus (CM) in oversaturated solutions was shown to delay the onset of calcification (Marin et al. 1996), suggesting an inhibiting effect at least on the nucleation of calcium carbonate. It is well known that organic molecules influence the calcium carbonate polymorph that precipitates from an oversaturated solution (Westbroek and Marin 1998; Mass et al. 2013), but it has never been quantified if the composition of organic molecules as they naturally appear in corals accelerates or decelerates the rate of calcification. This information is critical for the development of mathematical models of coral calcification (Hohn and Merico 2012, 2015; Nakamura et al. 2013; Jones et al. 2015a) that are used to predict the uncertain future of coral reefs in an acidifying ocean (Kleypas et al. 2001, 2006; Hoegh-Guldberg et al. 2007; Freeman et al. 2013). In this study, we investigate if the presence of isolated skeletal organic molecules alters the precipitation rate of calcium carbonate in oversaturated solutions. Additionally, we investigate if the molecular homology of CM and SOM (Ramos-Silva et al. 2014) indicates a functional analogy that allows identifying the origin and function of SOM.

Methods

Preparation of skeletal organic molecules and coral mucus

We isolated skeletal organic molecules (SOM) of *Stylophora pistillata* skeletons by grinding skeleton fragments to a powder and dissolving the skeletal powder with hydrochloric acid (HCl). This procedure leads to a solution of calcium chloride ($CaCl_2$) in water because the skeletal carbonate (CO_3^{2-}) reacts with the acid to bicarbonate (HCO_3^-) and carbonic acid (H_2CO_3), which, at a very low pH (< 2), leaves the solution as CO_2. The organic carbon that was incorporated into the coral skeleton as SOM remains in the $CaCl_2$ solution. We used a highly concentrated hydrochloric acid (37%) in order not to dilute the SOM to very low concentrations of dissolved organic carbon (DOC) and to be able to adjust the final DOC concentrations in the experiment solutions as required.

We additionally collected mucus from ten *Fungia* spp. corals growing in the aquarium facility at the Leibniz Centre for Tropical Marine Research (ZMT), in Bremen, by taking individual corals out of the water and placing them for maximum 5 min upside down into zip-loc bags. This procedure stressed the corals and initiated the secretion of substantial amounts of mucus. Corals were left for 2 d to recover from this stress before repeating the mucus

collection. Collected mucus was stored at − 40 °C until sufficient material for the experiment was collected. The mucus was then autoclaved and homogenized. DOC concentrations of the isolated SOM solution and coral mucus were measured with a Shimadzu TOC-VCPH instrument calibrated after German standard DIN 38402/ISO 8466-1. Both organic molecule treatments (SOM and CM) were set up to reach 50 µM DOC in the incubation chambers to exclude a potential concentration dependence on the impact on calcification.

Preparation of stock solutions

All experiment stock solutions were prepared with Millipore water, which was initially boiled to drive out dissolved CO_2 and then kept in a constant N_2 atmosphere to prevent recurrent CO_2 in gassing. $CaCl_2$ solutions were prepared with 15.58 g $CaCl_2$ in 5 L preboiled (CO_2-free) Millipore water, set to a final salinity of 36 g kg^{-1} by adding 164.42 g NaCl. SOM or CM was added to the $CaCl_2$ solutions to reach a DOC concentration of 50 µM, and pH was adjusted to 7.0 by adding NaOH. The amount of added $CaCl_2$ was corrected in the SOM treatment for the mass of dissolved skeleton and the resulting amount of $CaCl_2$ present in the SOM stock solution. $MgCl_2$ was added for the experiment containing Mg to a final concentration of 53 mM, yielding a molar Mg/Ca ratio of 2.5. The amount of NaCl was then adjusted to maintain a salinity of 36 g kg^{-1}.

Solutions of $NaHCO_3$ included 1.26 g $NaHCO_3$ per 5 L. Total alkalinity was adjusted by adding NaOH to the stock solution to reach a pH of 9.37, measured with a WTW-Multi 3430 Set K pH sensor at 25 °C. The final setup of the carbonate solution corresponds to a DIC of 3000 µM and TA of 5310 µM, which will be diluted by half when mixing with the calcium solution (DIC = 0 µM, TA = 0 µM) to reach realistic target conditions in the incubation chambers representative of the coral calcifying fluid, i.e., DIC = 1500 µM (Cai et al. 2016), TA = 2655 µM, pH = 9.3 (Al-Horani et al. 2003a), and Ca = 10.6 mM (Al-Horani et al. 2003a). Note, however, that these conditions are chosen to reflect conditions as measured in the CF of *Galaxea fascicularis* and may not be representative for other coral species that differ in chemical conditions and calcification rates (Raybaud et al. 2017; Sevilgen et al. 2019). Stock solutions were transferred into gas-tight 1-L Tedlar gas sampling bags (Nehrke et al. 2007) and put into the climate cabinet at constant 25 °C (± 0.5 °C).

Preparation of seeding crystals

The seeding material for all experiments was obtained from aquarium grown *S. pistillata* (ZMT, Bremen) and cleaned with hydrogen peroxide (H_2O_2 30%) for 48 h to remove any soluble components and organic tissue on the surface. After being ground in a miller for 1 min and separated into the 1–200 µm size fraction, individual fragments were handpicked under a light microscope. All fragments were washed in ethanol in an ultrasonic bath for 5 min to remove residual powder and then rinsed in Millipore water and dried in a 40 °C oven. Each fragment was weighed before and after the incubations on a Mettler Toledo scale with a 1-µg precision (room humidity 30% and temperature 22 °C).

Experimental setup

Twelve custom-built incubation chambers made of Teflon (Nehrke et al. 2007) were used to investigate the combined effect of organic molecules and Mg^{2+} on calcification. Each chamber was attached with Tygon and Marprene tubing to two Tedlar bags filled with either a calcium ($CaCl_2$) or carbonate ($NaHCO_3$) stock solution at a salinity of 36 g kg^{-1}. A constant flow rate of the solutions was maintained at 10 µL min^{-1} via an Ismatec 24 channel peristaltic pump. To prevent spontaneous crystallization inside the tubing, separate inflow tubing of the $CaCl_2$ and $NaHCO_3$ solutions was connected to the chambers. The incubation chambers contain a volume of approximately 0.25 ml, and the continuous flow from the peristaltic pump causes a mixed solution in the chambers without stirring. Seeding crystals were placed in the incubation chambers, and each experiment was run for at least 1 month (32 and 35 days, without and with Mg^{2+}, respectively) in a Rumed climate cabinet maintained at a constant 25 °C (± 0.5 °C). We conducted three cross-factor experiments with two Mg^{2+} concentrations (0 mmol kg^{-1} and 26.5 mmol kg^{-1}, or Mg/Ca ratios of 0 and 2.5, respectively) in parallel with three organic (control, mucus, or SOM) scenarios. The aragonite saturation state, Ω_{ara}, in all incubations was 16.3, with a saturation index, $SI_{ara} = \log(\Omega_{ara})$, of 2.8, which should induce aragonite precipitation. Four replicates were run for each scenario.

After 1-month incubation time, the seeding crystals were removed from the chambers by flushing with ethanol to stop precipitation. Crystals were dried and weighed to determine crystal growth rate. Crystal structures of individual $CaCO_3$ polymorphs were analyzed under the Raman microscope at Alfred Wegener Institute for Polar and Marine Research (AWI) in Bremerhaven, Germany, with the help of Dr. Gernot Nehrke. Due to the uneven surface of the incubated crystals, we did not perform a mapping of the whole crystal but focused on individual crystal structures to identify the polymorphs qualitatively with the Raman spectrum (Supplementary material 1). The seeding material was then gold-sputtered for 30 s and analyzed

using the back-scattered electron detector (SEM-BSE) at 10 keV with a TESCAN Vega3 XMU SEM.

Results

Calcification rates

We performed six incubation experiments with four replicates using flow through incubation chambers that were fabricated following the design of Nehrke et al. (2007). Reservoirs with $CaCl_2$ and $NaHCO_3$ solutions were connected via tubing to the incubation chambers, and a peristaltic pump maintained a constant flow and hence constant calcium and carbonate concentrations in the chambers over a duration of at least 1 month. Precipitation of new $CaCO_3$ on the seeding crystals of fragmented coral skeleton was not enhanced by the presence of organic molecules (CM or SOM). Instead, precipitation rates were generally lower in the incubations containing SOM or CM than in the control, but the difference was not significant (Fig. 1). Precipitation rates in the incubations including Mg^{2+} were significantly reduced. Average calcification rates without Mg^{2+} were between 1.5 and 4.9 μg d^{-1}, and average calcification rates in the experiment that included Mg^{2+} were between 0.014 and 0.86 μg d^{-1}.

Crystal morphology

Despite no significant difference in the precipitation rates between the treatments and the control, we found changes in crystal morphologies (Fig. 2). All seeding crystals in the Mg-free and organic-free incubations were coated with freshly precipitated vaterite (Fig. 2a–c). Vaterite has a higher solubility than aragonite and calcite (Plummer and Busenberg 1982) and is thermodynamically not stable (Kralj et al. 1990). The fact that vaterite did not transform to calcite or aragonite in our experiments (Kralj et al. 1997) indicates very stable growth conditions throughout the incubations (Ogino et al. 1987) and is in line with the observation that the least stable phases of a mineral precipitate first, despite their high solubility favoring the thermodynamically more stable polymorph in the long run (Ostwald 1897).

The addition of mucus to the Mg-free solutions yielded three different polymorphs of calcium carbonate on the same seeding crystals (Fig. 2d–f). Aragonite dominated the newly formed material, vaterite was rare, and a few isolated blocks of calcite grew on the original coral skeleton fragments. The addition of isolated SOM to the incubations resulted in precipitation of aragonite only (Fig. 2g–i) even though calcite and not aragonite would have been expected to be the dominant polymorph at a Mg/Ca ratio equal to zero (Morse et al. 1997). The presence of SOM apparently inhibited the transformation to the more thermodynamically calcite (Gebauer et al. 2008). In all incubations containing Mg^{2+}, hardly any new crystals were formed (Fig. 3). However, all crystals that did form were aragonite, which fits with the preferential polymorph associated to the Mg/Ca ratio of 2.5 in our experiments (Morse et al. 1997).

Discussion

Organic molecules and calcification rate

It has been suggested that organic molecules could help to overcome the kinetic barriers for $CaCO_3$ precipitation imposed by the presence of Mg^{2+}, PO_4^{3-} or SO_4^{2-} (Pytkowicz 1973; Cohen 2003; Falini et al. 2015). However, in our experiments, hardly any new material formed

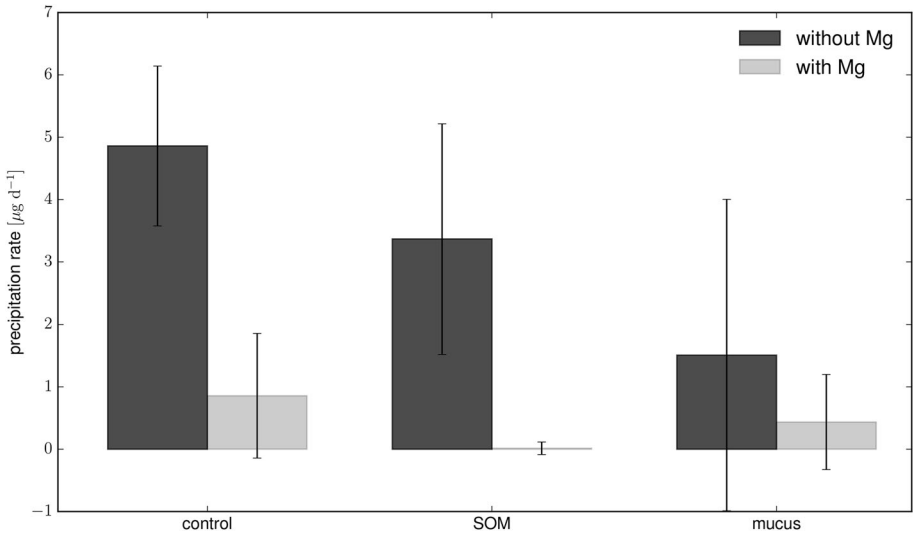

Fig. 1 Precipitation rates of calcium carbonate on seeding crystals incubated in supersaturated $CaCO_3$ solution under presence or absence of 26.5 mM Mg. The control contained no organic molecules, whereas the treatments contained 50 μmol L^{-1} dissolved organic carbon (DOC) obtained from isolated skeletal organic molecules (SOM) or freshly collected coral mucus

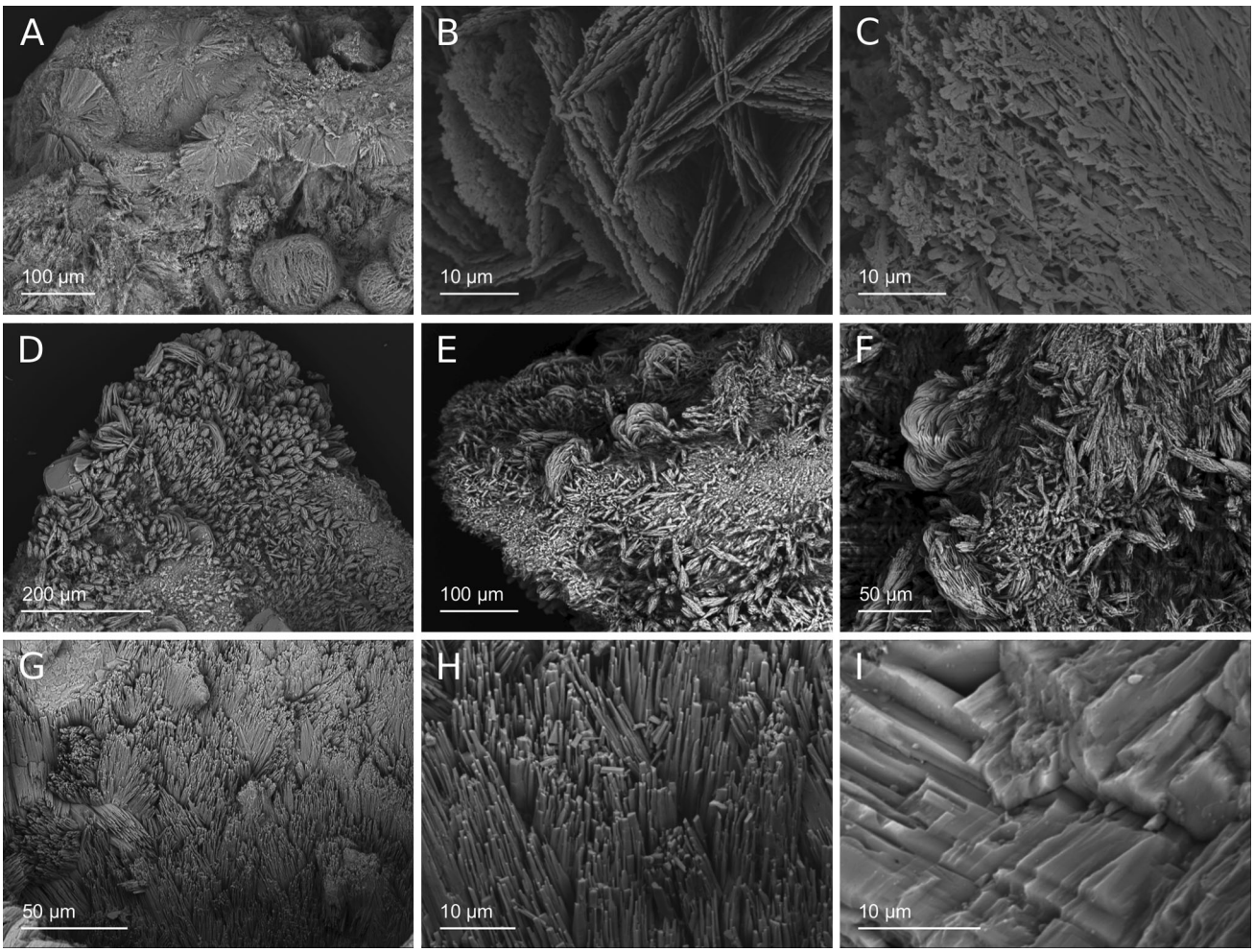

Fig. 2 Scanning electron microscope (SEM) images showing the morphology of calcium carbonate crystals precipitated in the absence of Mg^{2+}. **a–c** Different magnifications of vaterite spherulite and platelet forms in the control solution. **d–f** Images of different magnifications of vaterite platelet and bundles from the solution with mucus from *Fungia* spp. **g–i** Aragonite needles of various magnification from the solution with isolated skeletal organic matrix molecules from *Stylophora pistillata*. These images are representative of the replicates from the entire experiment

under the presence of Mg^{2+} and the addition of organic molecules did not enhance precipitation (Fig. 1). In the Mg-free solutions of calcium and carbonate ions, the addition of SOM or CM did also not increase the precipitation rate (see Fig. 1). The nonsignificant trend of reduced calcification rates with the presence of organic molecules rather supports the opposing view that organic molecules act as an inhibitor to calcification (Marin et al. 1996). This is supported by recent findings from sea urchin spines where the presence of SOM limited the supersaturation of the calcifying fluid and inhibited precipitation (Sancho-Tomás et al. 2014). The hypothesis that organic molecules induce or facilitate calcification (Allemand et al. 1998; Watanabe et al. 2003; Cuif and Dauphin 2005; Helman et al. 2008; Mass et al. 2013), therefore, cannot be supported.

Calcium binding proteins, like calmodulin, are complexing free calcium ions at the intracellular side of the plasma membrane (Carafoli 2002) and thus help to maintain calcium homeostasis at very low intracellular concentrations (Carafoli 1987; Case et al. 2007) because high intracellular calcium concentrations can be toxic (Simkiss 1977; Kaźmierczak et al. 1985; Müller et al. 2015). The fact that calcifying tissues are associated to a variety of mucoid substances (Kazmierczak et al. 2013) may therefore indicate a corresponding detoxicating role of glycoproteins also at the extracellular cell surface.

A clear example of OM resource reallocation for architectural purposes can be seen among foraminifera, which modulate calcification within intracellular vacuoles followed by exocytosis within the organic templates along the test wall (Erez 2003; Reymond et al. 2013). This biologically meditated process directs the precipitation of

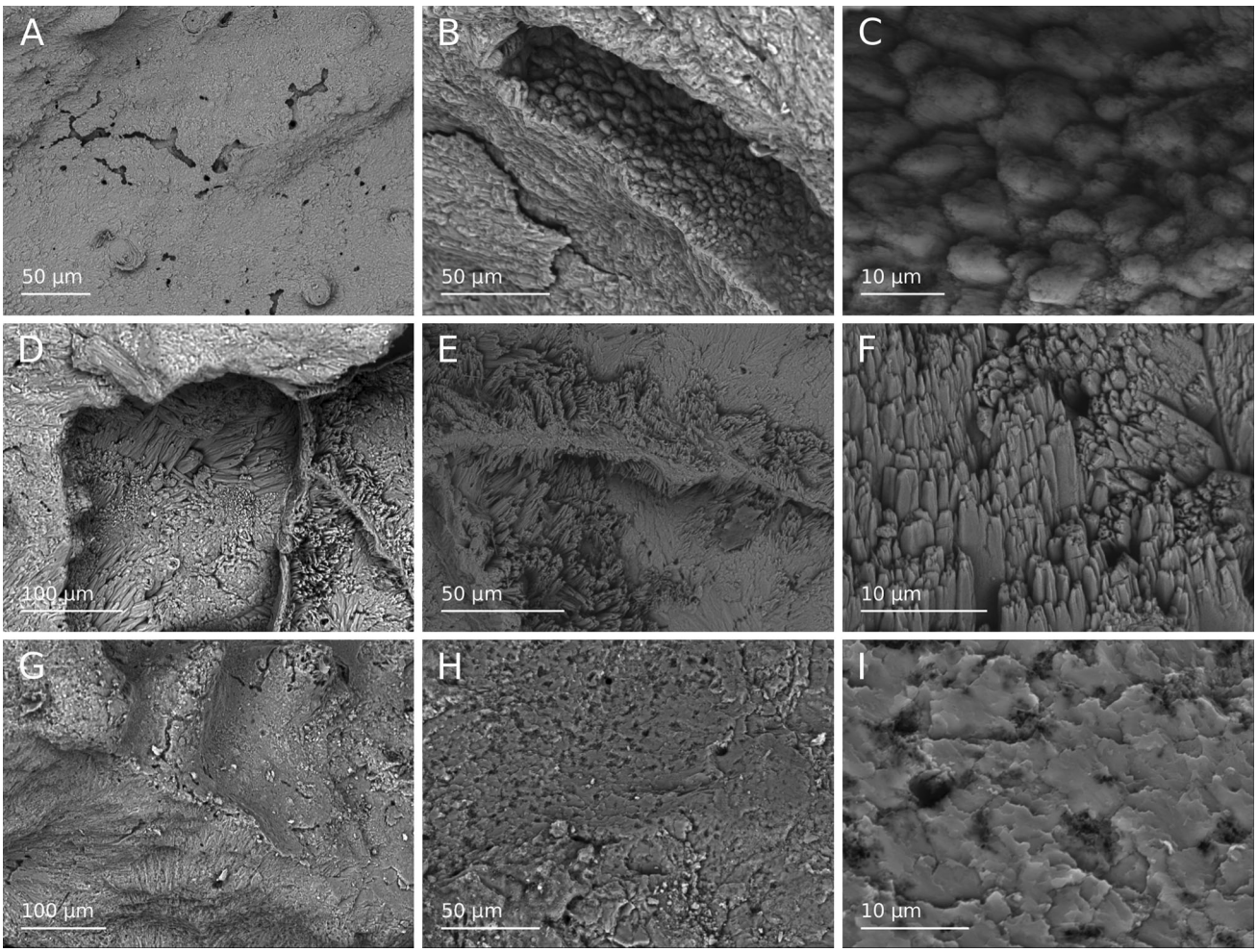

Fig. 3 Scanning electron microscope (SEM) images showing the morphology of calcium carbonate crystals precipitated in the presence of 26.5 mM Mg^{2+}. **a–c** Low relief forms with inter dispersed quasi-cylindrical forms and dissolution pits and magnification of smoothed aragonite bundles from the control solution. **d–f** Images of different magnifications of aragonite needles from the solution with mucus from *Fungia* spp. **g–i** Various magnification from the solution with isolated skeletal organic matrix molecules from *S. pistillata* which include dissolution pits and smooth flaky surfaces. These images are representative of the replicates from the entire experiment

calcite to form structures that benefit the harvesting of UV toward its photosymbiont population (Hottinger 2000). Therefore, SOM could be instrumental in the phenotypic plasticity process among corals and be triggered by environmental factors (e.g., wave energy and light). From our study, however, there is no evidence that the presence or absence of SOM influences the impact of changing ocean chemistry on the rate of calcification or dissolution.

It is possible, however, that the interaction with the crystallization rate depends on the concentration of organic molecules and that higher or lower concentrations than applied here could alter the precipitation rate. Unfortunately, the concentration of organic molecules in the coral calcifying fluid is not known. But irrespective the concentrations of organic molecules in the experiments, the observed differences in the crystal polymorphs (Figs. 2, 3) prove that the molecules did interact with the crystallization process, yet this interaction with the crystal morphology did not enhance the net precipitation rate (Fig. 1). It is also worth noting that the chemo-physical conditions within the zone of biomineralization are known to vary among coral species (e.g., Al-Horani et al. 2003a; Cai et al. 2016; Raybaud et al. 2017; Sevilgen et al. 2019) due to life stages and external environmental conditions. The chemical conditions chosen in our experiments are representative for *G. fascicularis* (Al-Horani et al. 2003a), and the hypothesized effect of organic molecules on calcification could potentially also vary with the level of oversaturation in the coral calcifying fluid.

Furthermore, density bands in coral skeletons suggest a layered growth (Cuif et al. 2012) that could be controlled by the exudation of organic molecules into the calcifying space (Cuif and Dauphin 2005). However, SOM are continually incorporated into the growing skeleton and the

early mineralization centers in coral skeletons contain only 1 weight percent of SOM, whereas the whole skeleton contains on average 3 weight percent (Falini et al. 2015). This suggests that the concentration of organic molecules is lower in the calcifying fluid during the "initiation" of coral calcification and that enhanced ion transport rather than organic matter release induces mineralization in corals. The neglect of a potential effect of organic molecules on the calcification rate in mathematical models of coral calcification (Hohn and Merico 2012, 2015; Nakamura et al. 2013; Galli and Solidoro 2018), therefore, seems to be justified because the calcification rate is apparently much more dependent on the ion composition of the calcifying fluid. But if SOM do not facilitate calcification (Marin et al. 1996; Sancho-Tomás et al. 2014) then why are these molecules released into the subcalicoblastic space?

Coral mucus and SOM

Organic molecules are released by specific gland cells, called mucocytes, that are present in all layers of the coral tissue (Marshall and Wright 1993). In the calicoblastic ectoderm of hermatypic, i.e., reef-forming, corals, mucocytes are not very abundant but cumulate toward the growing tips of the coral septae (Brown and Bythell 2005). This correlation may again suggest a connection between mucus release and calcification; however, in the calicoblastic epithelium of the ahermatypic, i.e., non-reef-forming, coral *Tubastrea faulkneri*, mucocytes are relatively abundant (Marshall and Wright 1993), yet the calcification rate does not differ from the morphologically very similar hermatypic coral *G. fascicularis* (Marshall 1996). The release of organic molecules into the subcalicoblastic space may, therefore, have other reasons than to influence calcification although the hypothesis that organic molecules protect the coral tissue against overcrusting by calcium carbonate in highly supersaturated waters (Marin et al. 1996) also remains plausible.

The identification of the molecular composition of SOM (Watanabe et al. 2003; Puverel et al. 2005; Drake et al. 2013; Ramos-Silva et al. 2014) revealed that the majority of glycoproteins in SOM are associated to adhesion and structure (Drake et al. 2013) and a strong resemblance to coral mucus (Ramos-Silva et al. 2014) suggests a common origin of CM and SOM (Marin et al. 1996) that agrees well with the observation that coral planula larvae use mucus to adhere to the substrate (Harii and Kayanne 2003; Brown and Bythell 2005) before transforming into the primary polyp. We therefore tested if the chemical similarity between CM and SOM depicts a functional similarity with respect to the crystallization process. As mentioned above, neither CM nor SOM altered the precipitation rate (Fig. 1). Nevertheless, the crystal polymorphs differed slightly between the incubations with CM and those with SOM (Fig. 2). Small amounts of calcite were present on the crystals in the CM incubations that were absent in the presence of SOM (Fig. 2). Despite the resemblance between CM and SOM, there are still differences in the chemical composition (Ramos-Silva et al. 2014) that could explain the observed differences in crystal morphologies. However, the term mucus is a generic term that comprises a mixture of various mucoid substances and the composition of mucus can vary over time and with different environmental conditions (Crossland 1987; Brown and Bythell 2005). Depending on its composition, mucus can fulfill a variety of different functions from desiccation resistance and sunscreen protection to feeding and chemical defense (Goldberg 2002; Brown and Bythell 2005; Wijgerde et al. 2011). Extracellular digestion, for example, is a function not required below the coral tissue, and the absence of digestive enzymes may already lead to a compositional and therefore functional difference between CM and SOM in the crystallization process.

The composition of mucus can also vary between species (Meikle et al. 1988), and the mucus used in this study was obtained from solitary *Fungia* spp. corals, whereas the SOM was isolated from skeleton fragments of the branching coral *Stylophora pistillata*. The precipitation of small amounts of calcite could, therefore, be specific for *Fungia* but not for *Stylophora*. However, calcite has not been found in *Fungia* skeletons (Dahan et al. 2003). Two solitary corals from the Mediterranean and several other tropical corals such as *Porites lobata* do exhibit small amounts of calcite in their skeletons (Goffredo et al. 2012). Newly settled larvae of *Pocillopora damicornis* precipitate small amounts of calcite during basal plate formation of the primary polyp that later disappear with aging (Vandermeulen and Watabe 1973; Gilis et al. 2014). This suggests that also the chemical composition of SOM may vary over time or that SOM directly originate from CM.

Evolutionary origin of SOM

Based on our finding that the potential to influence the crystal polymorph is already inherent in CM and the fact that basal plate formation in primary polyps involves precipitation of calcite besides aragonite (Goffredo et al. 2012), we propose a conceptual model to explain the evolutionary origin of SOM in coral skeletons by applying recapitulation theory (Shumway 1932): All metazoans trace back to the cell lineage of opisthokonta choanoflagellates (Knoll 2003; Read et al. 2013; Arendt et al. 2015). Choanoflagellates can be solitary or colony-forming, and both forms can be sessile or free floating (Nielsen 2008). Cells in colony are held together by a gelatinous extracellular matrix (Nielsen 2008). The adhesiveness of the

extracellular matrix depends on the calcium concentration (Deman et al. 1974; Chan 1976; Kretsinger 1976; Kaźmierczak et al. 1985; Helman et al. 2008), and it is assumed that rising oceanic calcium concentrations in the Precambrian ocean due to enhanced weathering (Kaźmierczak and Kempe 2004) led to the emergence of metazoans (Kaźmierczak et al. 1985). The first metazoans were sphere-shaped blasteas that fed via extracellular digestion and/or endocytosis (Arendt et al. 2015). These blasteas eventually invaginated and developed a gastric cavity that improved the efficiency of the extracellular digestion because food particles could become entrapped in the gastric pouch from where the nutrients are taken up by the inner epithelium (Arendt et al. 2015). The coral body plan, in fact, never developed beyond the simple organization of a sessile gastrula (Galloway et al. 2007; Tambutté et al. 2011), and the whole evolutionary development is optimized and repeated (Fig. 4) during the coral life cycle (Gleason and Hofmann 2011). The development of metazoans allowed the specialization of cells and the development of specific cell types (Arendt et al. 2015), one of which are the mucus secreting gland cells or mucocytes. Coral planula as well as adult polyps perform muco-ciliary feeding (Goldberg 2002) and extracoelenteric digestion (Wijgerde et al. 2011). The whole planula is therefore covered by a mucus layer (Fig. 4). When the coral planula sinks down from the water column to the benthos, it eventually adheres to a hard substrate and transforms into a primary polyp (Gleason and Hofmann 2011; Edmunds et al. 2013). The isolation of a medium below the coral polyp from the surrounding seawater and continuous calcium excretion into this space (Al-Horani et al. 2003a; Allemand et al. 2004) due to the cellular requirement to regulate intracellular calcium concentrations (Carafoli 1987; Case et al. 2007) initiate calcification (Gilis et al. 2014). At this stage, the mucus that was used to adhere the coral to the substratum becomes incorporated into the growing skeleton, known as SOM.

However, since these molecules are highly adhesive, the incorporation into the skeleton increases the stability (Okumura and De Gennes 2001; Mayer and Sarikaya 2002; Meyers et al. 2008) and allows corals to withstand greater physical stress. The adhesive properties of mucus would therefore become stabilized in evolutionary terms (Kauffman 1992). Stronger adhesion would allow coral larvae to colonize environments with higher flow rates (Harii and Kayanne 1996) and adult colonies to reach out further into the currents, which is advantageous for suspension feeders (Sebens et al. 1996, 1998; Houlbrèque and Ferrier-Pagès 2009) and coral growth (Sebens 1984; Fabricius et al. 1995; Mass et al. 2010).

The role of the SOM for coral calcification remains enigmatic, presumably because a function is imposed that cannot be proved. If the primary function of SOM is to influence the crystal polymorph then this function is already inherent to CM. If the function of SOM is to act as

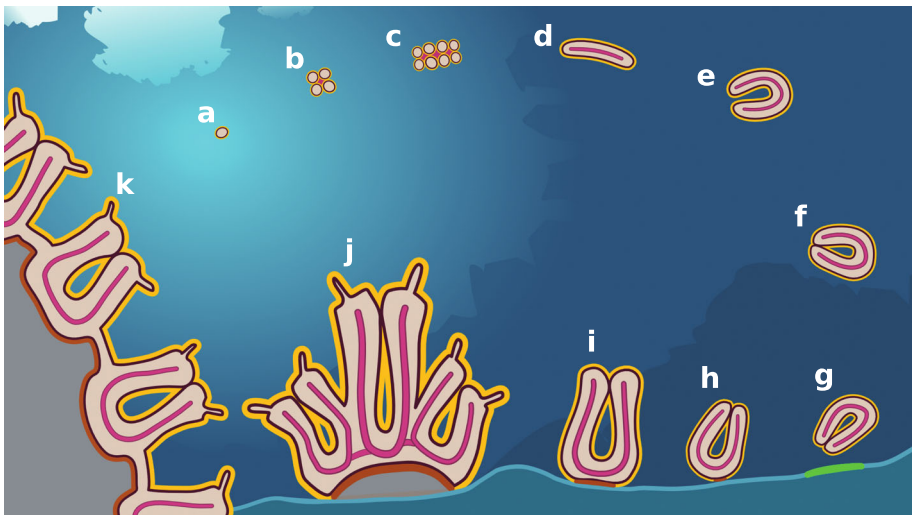

Fig. 4 Coral ontogeny: (a) egg cell or zygote, (b) 4 cell cleavage stadium, (c) 8 cell cleavage stadium, (d) flattened blastula (prawn chip), (e) gastrula, (f) pelagic planula larvae, (g) sinking planula, (h) settling planula, (i) primary polyp, (j) juvenile coral, (k) adult coral (Jones et al. 2015a, b). The yellow coating depicts the mucus layer on the surface of all stages during the coral life cycle (Brown and Bythell 2005). The glutinous constituents of mucus cause cell-to-cell adhesion (Kaźmierczak et al. 1985), and the mucus between the two developing cell layers becomes the collagenous mesoglea (Young 1973) (drawn in pink). The adhesive properties of mucus (Brown and Bythell 2005; Drake et al. 2013) also allow the sinking planula to attach to the substratum (Harii and Kayanne 1996) where it transforms into a primary polyp (Gleason and Hofmann 2011; Edmunds et al. 2013). At this stage, i.e., when the primary polyp starts to lay down its skeleton (Gilis et al. 2014) (gray), the mucus layer facing the substratum becomes what we call skeletal organic molecules (drawn in orange)

a glue to create a more stable composite material, then this function is fulfilled by adhesive molecules that are not unique to SOM but are also present in CM and the mesoglea. Lastly, a facilitating function to overcome kinetic barriers for skeleton formation cannot be confirmed. The origin of SOM may therefore be a remnant of early ontogeny and the role of CM for adhesion.

Compliance with ethical standards

Conflict of interest The authors declare no conflict of interest.

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