

Biomining of dolomite by coralline algae

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Biomining of dolomite and magnesite discovered in tropical coralline algae: a biological solution to the geological dolomite problem

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Abstract

Dolomite is a magnesium-rich carbonate mineral abundant in fossil carbonate reef platforms but surprisingly rare in modern sedimentary environments, a conundrum known as the “Dolomite Problem”. Marine sedimentary dolomite has been interpreted to form by an unconfirmed, post-depositional diagenetic process, despite minimal experimental success at replicating this. Here we show that dolomite, accompanied by magnesite, forms within living crustose coralline alga, *Hydrolithon onkodes*, a prolific global tropical reef species. Chemical micro-analysis of the coralline skeleton reveals that not only are the cell walls calcitised, but that cell spaces are typically filled with magnesite, rimmed by dolomite, or both. Mineralogy was confirmed by X-ray diffraction. Thus there are at least three mineral phases present (magnesium calcite, dolomite and magnesite) rather than one or two (magnesium calcite and brucite) as previously thought. Our results are consistent with dolomite occurrences in coralline algae rich environments in fossil reefs. Instead of a theory of post-depositional dolomitisation, we present evidence revealing biomineralization that can account for the massive formations seen in the geologic record. Additionally, our findings imply that previously unrecognized dolomite and magnesite have formed throughout the Holocene. This discovery together with the scale of coralline algae dominance in past shallow carbonate environments raises the possibility that environmental factors driving this biological dolomitisation process have influenced the global marine magnesium/calcium cycle. Perhaps, most importantly, we reveal that what has been considered a geological process can be a biological process, having many implications for both disciplines.

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1 Introduction

1.1 Background on the “Dolomite Problem”

The “Dolomite Problem” has been of interest to geologists and carbonate chemists for more than a century and relates to the mystery surrounding the abundant presence of the mineral dolomite ($\text{Ca}_{0.5}\text{Mg}_{0.5}\text{CO}_3$) in fossil reefs (e.g., Daito-jima) and carbonate platform sediments (e.g. the Dolomites) and its apparent absence from equivalent modern reef environments (e.g., Ohde and Kitano, 1981; McKenzie and Vasconcelos, 2009; Budd, 1997). Sedimentary dolomite in the geological record is commonly found in formerly warm, shallow, high energy, platform or atoll margin environments (McKenzie and Vasconcelos, 2009; Ohde and Kitano, 1981; Budd, 1997; Schlanger, 1957) and is typically associated with coralline algae (Ohde and Kitano, 1981; Budd, 1997; Schlanger, 1957). In recent coral-algal reefs the primary marine carbonate minerals are low magnesium calcite (rhombohedral CaCO_3 with small amounts (< 5%) of magnesium substituting for calcium) and aragonite (orthorhombic CaCO_3). Yet in a Pleistocene fossil reef around the reef crest the dolomite content was found to be more than 70% (Ohde and Kitano, 1981). It has been considered that the inclusion of dolomite into sedimentary systems must be a post-depositional, diagenetic process, where magnesium replaces calcium in the existing carbonate crystal structures (“dolomitisation”) (e.g., Budd, 1997). This paradigm has been adhered to for at least half a century despite experimental studies failing to replicate the process (McKenzie and Vasconcelos, 2009). Many geochemical models and environmental reconstructions (e.g., Griffith et al., 2008; Bao et al., 2009) incorporate dolomitisation as a parameter even though the exact process has not been identified. While the discovery of dolomite forming in anoxic microbial environments points towards a microbial mediation (Vasconcelos and McKenzie, 1997), it does not explain the abundant dolomite found in relict coral-algal reefs.

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1.2 Background on coralline algae

Coralline algae are calcifying red algae and are major reef builders, occurring globally (Adey and Macintyre, 1973). While modern corallines have only been confirmed back to the Cretaceous (Aguirre et al., 2000), calcifying red algae have a long history in the geologic record back through the Paleozoic (Brooke and Riding, 1998; Aguirre et al., 2000) and possibly even the Neoproterozoic (Xiao et al., 2004) and Mesoproterozoic (Butterfield, 2000). They have a high magnesium calcite (Mg-calcite) skeleton, typically ranging from 10–20 mol % MgCO_3 (Moberly, 1970; Chave, 1952, 1954; Milliman et al., 1971) (mol % MgCO_3 is % of magnesium substituting for calcium), although there is some degree of uncertainty around these measurements as results vary depending on the method used (Milliman et al., 1971; Chave, 1954). This high magnesium calcite is meta-stable and prone to dissolution as pH declines (Morse et al., 2006). While modern coralline algae are composed of Mg-calcite, it has been shown that the incorporation of magnesium, as measured in the cell wall, decreases with declining magnesium/calcium (Mg/Ca) ratio of the ambient seawater (Ries, 2006; Stanley et al., 2002) and in low Mg/Ca ratios equalling calcite seas (1:1), coralline algae are able to continue growing albeit with a low Mg-calcite skeleton. Researchers in the late 19th and early 20th century proposed coralline algae contained dolomite as part of the magnesium enriched calcite skeleton, but were unable to prove this hypothesis (Chave, 1954). Later research identified magnesium enriched skeletal portions approaching dolomite composition, however the presence of dolomite was not confirmed (Moberly, 1970).

Here we present evidence that dolomite and magnesite (MgCO_3) form inside living coralline algae and thus must be influenced, if not caused, by biological processes. The intimate association between dolomite and coralline algae suggested by our findings is consistent with the predominant occurrence of sedimentary dolomite in fossil carbonate reef environments (McKenzie and Vasconcelos, 2009; Budd, 1997; Ohde and Kitano, 1981), typically in coralline algae facies (Saller, 1984; Schlanger, 1957; Budd, 1997; McKenzie and Vasconcelos, 2009; Ohde and Kitano, 1981).

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Note that we limit our discussion to marine sedimentary dolomite, excluding that of metamorphic origin. While the stoichiometric composition of dolomite is $\text{Ca}_{0.5}\text{Mg}_{0.5}\text{CO}_3$, sedimentary dolomite typically deviates from this (38–50 mol% MgCO_3 , Budd, 1997), is imperfectly ordered, and is commonly referred to as “protodolomite” (Ohde and Kitano, 1981). We use the term protodolomite to reflect the sedimentary nature of the dolomite in our study.

2 Materials and methods

2.1 Sample collection and preparation

Samples of living crustose coralline algae were collected under permit G09/29996.1 from between 3–5 m depth below mean low tide, along a 150 metre transect on the north reef front of Heron Island (transect headed east from 23.433285° S 151.929648° E), southern Great Barrier Reef in December 2009. Photosynthetic activity was confirmed using a pulse amplitude modulated (PAM) fluorometer (Russell et al., 2009). Samples were 2–10 mm thick, not subjected to any chemical cleaning process and were sun-dried. *Hydrolithon onkodes* (Penrose and Woelkering, 1992) were identified in SEM-EDS by anatomy of reproductive conceptacles and thallus containing horizontal rows of trichocytes (Ringeltaube and Harvey, 2000).

2.2 X-ray diffraction

Powder X-ray diffraction was carried out with a SIEMENS D501 Bragg-Brentano diffractometer equipped with a graphite monochromator and scintillation detector, using $\text{CuK}\alpha$ radiation. Samples were milled by hand in acetone in an agate mortar, some with fluorite added as an internal standard, and suspended on quartz-low background holders. Scan range was 2 to 70° 2 theta, step size 0.02° 2 theta, and scan speeds varied from 1° min⁻¹ to 7° min⁻¹. The results were interpreted using the SIEMENS software

package, Diffracplus Eva 10 with ICDD database PDF-2 for identification, and RIET-ICA (Hunter, 1998) for modelling. Parameters refined in the Rietveld modelling using a Pseudo-Voigt function included six background parameters, zero correction, scale parameters of all phases (calcite, dolomite, magnesite, aragonite), up to three peak shape parameters per phase, a preferred orientation parameter for calcite, and unit cell parameters of calcite and magnesite. Two different calcite compositions were refined (17.5 mol % and 24 mol %) as they best account for peak asymmetry. The Mg-content of calcite was calculated from the (104) peak position (Goldsmith et al., 1955).

2.3 Scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS) and inductively coupled plasma – atomic emission spectroscopy (ICP-AES)

The SEM-EDS was carried out using a Hitachi 4300 SE, equipped with an integrated Oxford X-Max element detector, operated at 15.0 kV, 25 mm working distance, current 0.6 nano ampere, beam width and penetration approximately 3 μm . Samples were carbon coated and held in with carbon tape, a session was undertaken using a platinum coating. ICP-AES was carried out using a Varian Vista Pro Axial CCD simultaneous ICP-AES, power 1.30 kW, plasma flow 15.0 l min⁻¹, auxillary flow 1.50 l min⁻¹, nebulizer flow 0.70 l min⁻¹, replicate read time 5.00 s, instrument stabilisation delay 15 s, and 5 replicates. AccuTrace reference standards were used. 3 mg of sample was digested in 10 ml of 10 % nitric acid. A check standard was run every third analysis.

3 Results

3.1 SEM-EDS

We found substantial amounts of protodolomite and magnesite within the Mg-calcite skeleton of the coralline algae *H. onkodes* (Fig. 1). A detailed analysis using SEM-EDS reveals that protodolomite is pervasively present within the honeycomb-like cell

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5 wall structure as rims surrounding cells that are in-filled to various degrees by magnesite. SEM spot analyses (Table 1 in the Supplement) show that the protodolomite rims (2–4 μm thickness) range in composition from 38–62 mol % MgCO_3 ($n = 37$), thus exceeding previously reported protodolomite ranges of 38–50 mol % MgCO_3 (Budd, 1997). Cell walls have 8–25 mol % MgCO_3 , ($n = 57$). Cells (5–15 μm) are partially filled by magnesite with 95–99.5 mol % MgCO_3 , ($n = 18$). Concentric zonations are apparent around some cells, extending into the cell wall and could reflect organic material or varying magnesium contents, however as the SEM-EDS weight % results were generally higher than the organic rich cell spaces and there were no voids associated with these bands, we consider it unlikely these zonations are organic matter and therefore a varying magnesium content is the probable explanation. An SEM cross section of a reproductive conceptacle (Fig. 2) shows larger scale dolomite and magnesite in-fill. It seems the distribution of magnesite within the conceptacle is constrained by the precursor organic fabric. Most striking about these textural features (and Figs. 3, 4) is the similarity to those characterised in Cenozoic island dolomites (Budd, 1997; Land, 1973; Ward and Halley, 1985), which show pronounced dolomite rims, concentric zonation, inclusions within cells and vuggy textures (Ward and Halley, 1985).

10 Although the time frame over which dolomitisation of sedimentary carbonates takes place has not been precisely identified, it is generally thought to form over time scales of up to millions of years (Saller, 1984). We note that while the cells in the top photosynthetically active layers of the coralline algae are mostly void (Fig. 5) small amounts of magnesite in-fill were observed. Protodolomite rims occur within 1 mm of these top layers, clearly within the living tissue. There is a noticeable, though not always consistent, increase in the amount of magnesite and protodolomite towards the base (2–10 mm from surface) (Fig. 6). Thus, in contrast to existing theories, protodolomite and magnesite precipitation are contemporaneous with organism growth.

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3.2 XRD

The presence of protodolomite and magnesite was confirmed with XRD analyses (Fig. 7). The typically very broad protodolomite (Zhang, 2010) and magnesite (Graf et al., 1961) reflections were observed in 10 out of 19 samples as a continuous shoulder on the (104) calcite peak, sometimes ending in a distinct magnesite maximum. The remaining 9 samples displayed a strong asymmetry of the calcite peak towards higher 2θ angles (Fig. 8). While such an asymmetry is generally interpreted to represent Mg-calcite that is more Mg-rich than the average (Milliman et al., 1971) we note that it could also represent protodolomite. Ca-Mg disorder in the dolomite structure increases the unit cell size (Zhang, 2010) thus shifting the XRD peaks of Mg-calcite and protodolomite even closer together, so that the peak range for protodolomite with compositions of 38–50 mol % MgCO_3 (Zhang, 2010) actually sits in the same peak range as 30–37 mol % MgCO_3 calculated using a standard Mg-calcite correlation curve (Goldsmith et al., 1955). Indeed, when investigating one of the samples with such asymmetry using SEM-EDS, similarly to the magnesite rich samples no clear compositions in the range 28–36 mol % MgCO_3 were found, however protodolomite composition of 38–40 mol % MgCO_3 was measured (Table 2 in the Supplement), suggesting that its presence contributes to the calcite peak asymmetry in this case. This opens up the possibility that previous studies noting similar asymmetry (Milliman et al., 1971), without the advantage of recent research on disordered dolomite cell size (Zhang, 2010) may have overlooked the presence of protodolomite when basing their findings solely on XRD results. Aragonite was identified by XRD in 12 of the 19 samples (Table 3 in the Supplement) and is seen as rims in Fig 3. As SEM was not done on all the samples it is not known whether all aragonite is present as rims or may be remnants of coral overgrown by the coralline algae.

Applying the standard method of calculating the average Mg-calcite composition based on peak position (Goldsmith et al., 1955) the samples with dolomite and magnesite peaks returned a composition of 17.45 mol % MgCO_3 (Table 3 in the Supplement)

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and the remaining samples an average of 16.78 mol% MgCO_3 . Using ICP-AES to measure bulk magnesium concentration, results ranged from 22.60 to 33.70 mol% MgCO_3 (Table 3 in the Supplement), significantly higher than those returned by XRD, reflecting the presence of the protodolomite and magnesium phases. This discrepancy has been well recognized in previous research (Chave, 1954) where it was attributed to either Mg-calcite with up to 30 mol% MgCO_3 , problems with the peak modeling curve (Chave, 1954), or to the presence of amorphous brucite ($\text{Mg}(\text{OH})_2$) (Milliman et al., 1971).

4 Discussion

4.1 Results compared to previous work on coralline algae

While the composition of the cell wall structure measured by SEM-EDS is in agreement with previous studies of tropical coralline algae (Stanley et al., 2002; Moberly, 1970) the presence of protodolomite has not previously been confirmed (Moberly, 1970). Other than a miniscule amount of magnesite composition (mineralogy not confirmed by XRD) in one cell of a fresh coralline alga, *Hydrolithon gardineri*, (Marshall Islands) (Moberly, 1970), we could find no previous record of magnesite in coralline algae. We propose that the standard method of bleaching prior to analysis (Bischoff, 1983), which is noted to reduce the bulk magnesium measured (Milliman et al., 1971), may not only remove the cell organic material but also the magnesite within the cell space. Moberly (1970) also identified magnesium enriched cell rims (2 μm wide) and measured compositions approaching dolomite yet rejected the presence of dolomite. We note, however, that their analytical beam was 6 μm wide and therefore measuring an average of the rim and surrounding cell walls, which have 12–17 mol% MgCO_3 , indicating that the rims themselves were likely to have dolomite and/or magnesite composition.

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We could find no published or unpublished mineralogical analyses of *H. onkodes* and this may explain why this abundant protodolomite and magnesite has not previously been discovered. Given the difficulty in identifying protodolomite by XRD without the benefit of detailed SEM-EDS or the recent work identifying the shift in protodolomite peak position (Zhang, 2010) to that of high Mg-calcite, from the common reporting of XRD curve asymmetry and discrepancies with bulk magnesium (Milliman et al., 1971; Chave, 1952; Moberly, 1970) it seems probable that protodolomite in coralline algae has been measured many times in past studies but was not able to be identified or confirmed. Moreover, these reports have included various genera and species collected from diverse locations outside of the tropical environment, indicating the occurrence of protodolomite is not restricted to our sample locations and may be widespread.

4.2 Applying results to interpret fossil dolomite formation

Assuming that the processes taking place to create the observed mineral phases have persisted through time, we apply our findings to interpret protodolomite formations in an emerged Pleistocene reef (Ohde and Kitano, 1981). To establish whether there is sufficient magnesium present within the coralline algae to form the quantity of dolomite observed in fossil coral reefs, we assumed a closed system and used a mass balance approach (Lohmann and Meyers, 1977) to calculate potential yield of dolomite. We calculated that 66 mol% of the magnesite bearing algal carbonate of this study can potentially form protodolomite assuming an average composition for sedimentary protodolomite of 44 mol% MgCO_3 (Ohde and Kitano, 1981) and 17.45 mol% MgCO_3 for Mg-calcite. Carbonate rock from reef crest zones of the emerged Pleistocene reef contains approximately 73 wt% protodolomite and 27 wt% low Mg-calcite (4 mol% MgCO_3). If all the magnesium in our dolomite and magnesite rich coralline algae samples were to convert to this low Mg-calcite and protodolomite, then the final equilibrium phase would comprise 72 wt% protodolomite and 28 wt% low Mg-calcite, showing there is sufficient magnesium within the living phase to provide the final mineral proportions as measured in this Pleistocene reef. The samples without the magnesite

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shoulder return 47–57% potential protodolomite, however based on the visible high porosity, presence of prolific borings and high degree of friability of these samples, we consider it unlikely that they remain a part of the reef structure and instead break apart, perhaps providing micron scale dolomite crystals to proximal sediment.

5 The total magnesium contained in our most magnesium-rich samples can provide an elegant mass balance for the final dolomite proportions in the fossil reef. The locations of protodolomite in the Pleistocene reef (Ohde and Kitano, 1981) are consistently restricted to the same areas that coralline algal crusts, particularly of *H. onkodes*, form prolifically in modern reefs, i.e. shallow, high energy zones of tropical coral-algal reefs (Rasser and Piller, 1997; Ringeltaube and Harvey, 2000). With this in mind, we can extend this intimate association of coralline algae and dolomite to examples of other occurrences of dolomite in the geological record. Dolomitised coralline algae are ubiquitous in Cenozoic island dolomites and is, in fact, the fabric most likely to be dolomitised (Budd, 1997). The mid Miocene saw a shift in coral reef formation, with extensive development of coralline algal facies replacing corals as the dominant carbonate producer (Halfar and Mutti, 2005) and this may well explain the formation of massive dolomite occurrences during that time (Budd, 1997). In Eocene sections of a core from Enewetak atoll, dolomite appeared only in association with coralline algae and displayed crystal growth which appeared to be constrained by the shape of the coralline algae (Schlanger, 1957). Triassic “Dolomites” in the Italian Alps are dominantly composed of coralline algae (and echinoderms) (McKenzie and Vasconcelos, 2009). Predecessor calcifying red algae species have been found in the geologic record back to the Silurian (Brooke and Riding, 1998) and it is likely that a similar dolomite biomineralization had been taking place over this time as environmental conditions allowed. We can speculate that this type of biomineralization had been taking place throughout the Precambrian in less complex organisms prior to the time of the first confirmed red algae.

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4.3 Dolomite and the Mg/Ca cycle

Dolomite formation is thought to control the history of Mg/Ca ratio in the ocean throughout the Phanerozoic (Holland, 2005; Wilkinson and Algeo, 1989). If a volumetrically significant proportion of the dolomite has a biological origin then previously unrecognized environmental factors would have affected the dolomite formation. Defining both the environmental factors and the mass of this sedimentary dolomite through time will improve our understanding of the Mg/Ca cycle. Furthermore, the observation of significant protodolomite within coralline algal facies implies the amount of protodolomite in modern carbonates has been dramatically underestimated and may represent a modern flux of up to 25 % of modern reef carbonate or 2.25×10^{12} moles yr^{-1} Mg if the long term flux of carbonate to shallow water environments is 9×10^{12} moles yr^{-1} (Opdyke and Wilkinson, 1988).

4.4 Possible processes taking place

Future studies should aim at identifying the exact formation processes of the observed magnesite and protodolomite, whether they are biologically induced or biologically controlled by the coralline algae. At this stage we can only speculate as to the processes taking place. As the magnesite in-fill within cells is pervasive but not consistent, this suggests a biologically induced rather than controlled reaction. This may be mineralization resulting from a supersaturation of magnesium relative to calcium in the cell space as cell wall calcification takes place. Noting that there is an apparent increase in protodolomite towards the base layers of the coralline algae (sample 47), and that protodolomite appears almost exclusively as cell rims, this implies that over time a reaction takes place between the magnesite and cell wall to form the primary dolomite. The actual mechanisms that induce this reaction may include internal changes of pH from photosynthesis and respiration (Chisholm et al., 1990; de Vrind-de Jong and de Vrind, 1997) and metabolic activity (Pueschel et al., 2005) that lead to localised dissolution and re-precipitation of the carbonate minerals.

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5 Conclusions

This study presents empirical evidence that formation of protodolomite can be biologically mediated, and occurs in an organism that has at times in geological history dominated global carbonate reef development (Aguirre et al., 2000; Adey and Macintyre, 1973). While it is true diagenesis has an important role to play in the reorganization of magnesium in carbonates (Lohmann and Meyers, 1977), this biological mechanism taking place in living calcifying algae could be the key to understanding how the magnesium arrives in such high concentrations in the first place. In the absence of any demonstrated and verified diagenetic processes that could account for initial dolomite formation in fossil reefs, it must be considered likely that all past shallow reef sedimentary dolomite formation has had a similar origin whether by predecessors of the coralline species investigated here, or by earlier unidentified organisms employing similar physiological processes. Regardless of the exact species involved, biological vital effects may play an important role in the fractionation of stable isotopes in dolomite, meaning that models and studies that rely on these isotopic data, and assume that dolomite formation is diagenetic, will need to be revisited (e.g. Bao et al., 2009; Budd, 1997; Saller, 1984). Further, reconstruction of past environments of dolomite deposition will be aided by considering the conditions needed for the development of coralline algal dominated reefs. Finally, our discovery that a major geological process is in fact biologically mediated will have implications for many areas of both geology and marine biology.

Supplementary material related to this article is available online at:
[http://www.biogeosciences-discuss.net/8/5881/2011/
bgd-8-5881-2011-supplement.pdf](http://www.biogeosciences-discuss.net/8/5881/2011/bgd-8-5881-2011-supplement.pdf).

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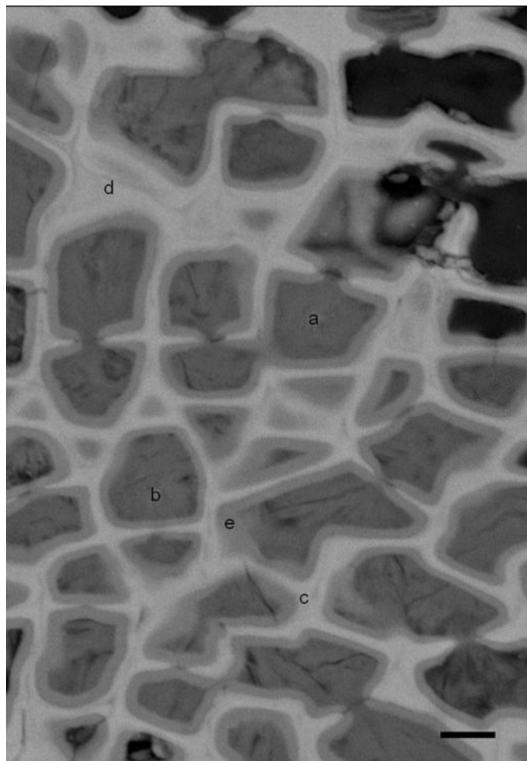


Fig. 1. SEM backscattered electron (BSE) image of coralline alga (sample 302) showing detail of magnesite cell infill (**a, b**) and protodolomite rims (**e**) within Mg-calcite cell wall structure (**d**). Black lines and textures within the cells are most likely voids or remnant organic structures. Above “d” micron scale bands of slightly darker grey within the cell walls indicate varying magnesium within the cell wall. Concentric zonation is seen around cells (top left). SEM-EDS spot analyses of labeled sites **a** = 99.22, **b** = 99.19, **c** = 23.9, **d** = 15.17, **e** = 45.75 mol % MgCO_3 . Scale bar = 5 μm . ■ Cell wall structure (Mg-calcite 8–25 mol % MgCO_3) ■ protodolomite (38–62 mol % MgCO_3), ■ magnesite (95–99.55 mol % MgCO_3), ■ void.

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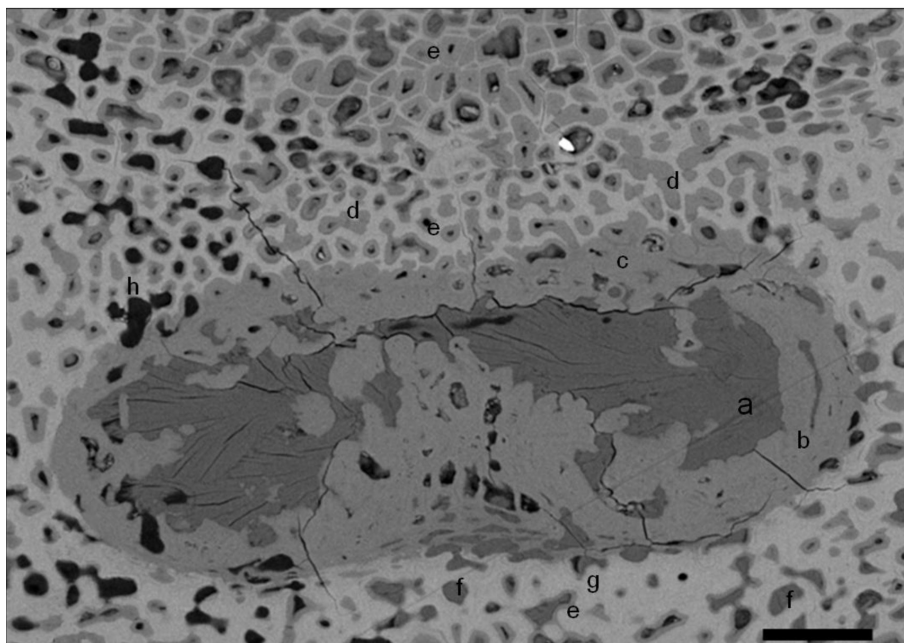


Fig. 2. SEM BSE image of coralline alga (sample 302) showing infilled cells within cell wall structure (top), and a large conceptacle (bottom) that is filled with magnesite (**a**) and protodolomite (**b**, **c**). SEM-EDS spot analyses of conceptacle mineralisation **a** = 99.55, **b** = 59.75, **c** = 61.67 mol% MgCO_3 . Original conceptacle fabric is ingrown by cells, now dolomitised, cell shapes are visible in dolomitic areas. Magnesite in-fill may be correlated with precursor organic content. Cells are either completely filled with protodolomite (**d**), rimmed by protodolomite and filled to various degrees by magnesite (**e**), or filled by only magnesite (**f**). From these images it appears that dolomitisation spreads out from the cells into the cell wall (**g**). Void cell (**h**). Increased dolomitisation can be seen at the top of the figure compared to the base. These areas of dominance of one mineral phase over another appear in patches throughout the section. Scale bar = 40 μm . Legend see Fig. 1.

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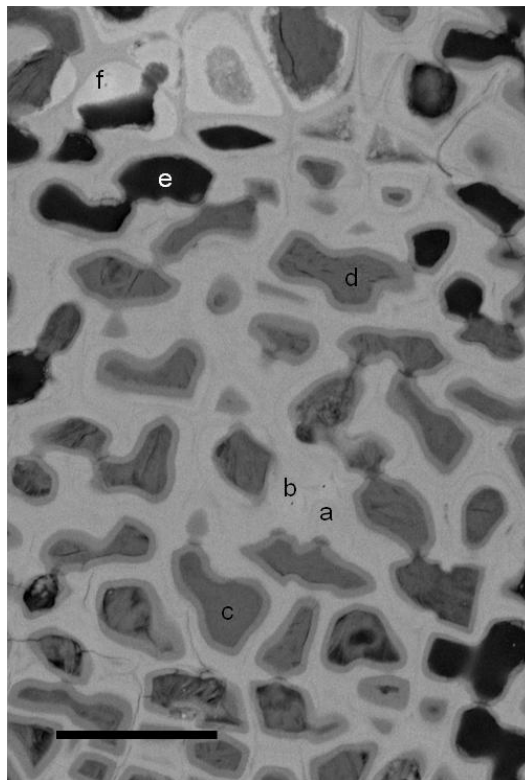


Fig. 3. SEM BSE (SE) image of aragonite-bearing coralline algae (Sample 302) showing the typical fabric of protodolomite rims around cells that are partially to completely filled with magnesite. White rims at the top (**f**) are aragonite. Textures within cells may represent organic material, or mineralization that was constrained by the organic fabric. Concentric zonations are seen within the cell wall material. SEM-EDS spot analyses of labeled sites, (**a**) = 11.32, (**b**) = 13.88, (**c**) = 98.44, (**d**) = 99.16 mol% MgCO_3 , (**e**) = hole, (**f**) = 0.67 (strontium = 1.69 wt% indicative of aragonite). Scale bar = 20 μm . Legend see Fig. 1.

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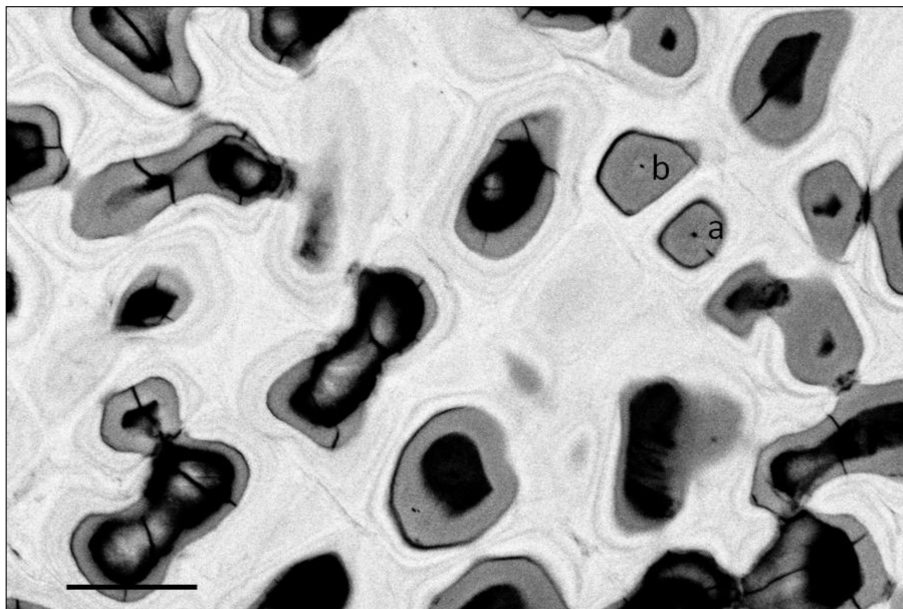


Fig. 4. SEM BSE image of coralline alga section (sample 47) taken with increased contrast to visualize the concentric zonations caused by different compositions of Mg-calcite in the cell wall. Black represents magnesite or void, grey is protodolomite and white to light-grey is Mg-calcite. **(a)**: protodolomite rim 50.65 mol % MgCO_3 **(b)**: protodolomite rim 55.29 mol % MgCO_3 . Black rims around a and b are not void and assumed to be magnesite, but are too narrow for accurate spot analysis. Scale bar = 10 μm .

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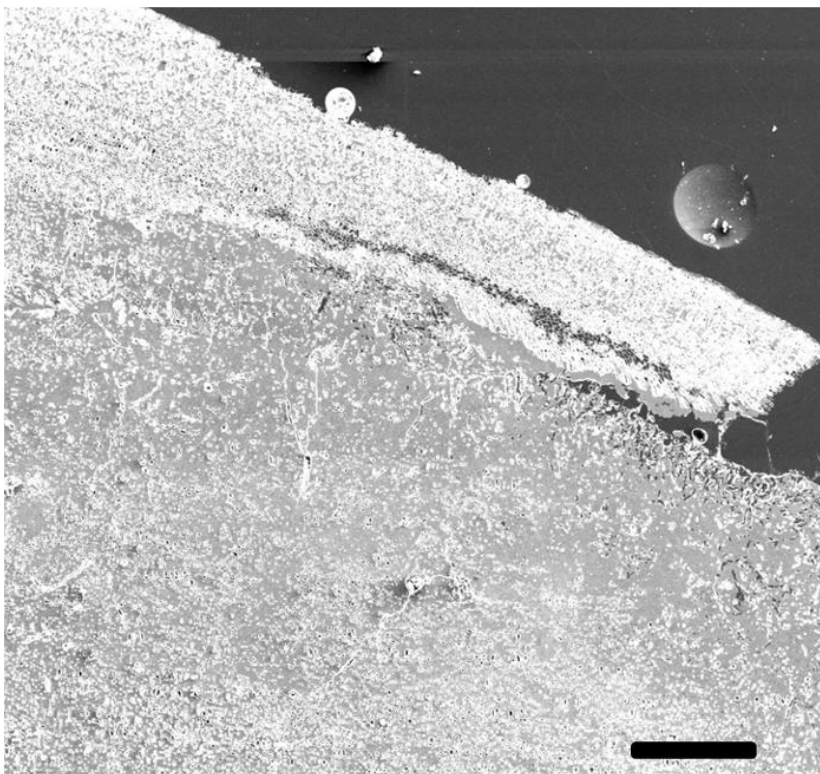


Fig. 5. SEM Secondary Electron image of coralline alga (sample 47), showing varying amounts of mineralisation in the top photosynthetically active layer and underlying crust. White indicates void space, grey is mineralised cell walls and in-filled cells, black is epoxy resin. Whilst the top layer clearly has less infill, it does contain some magnesite cell in-fill close to surface. Protodolomite is noticeably least present in the top layer compared to basal layers. Scale bar = 200 μm .

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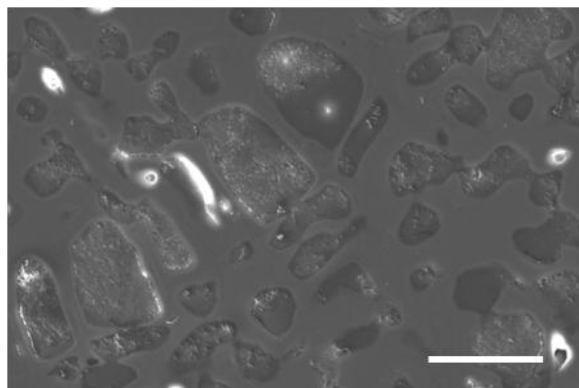
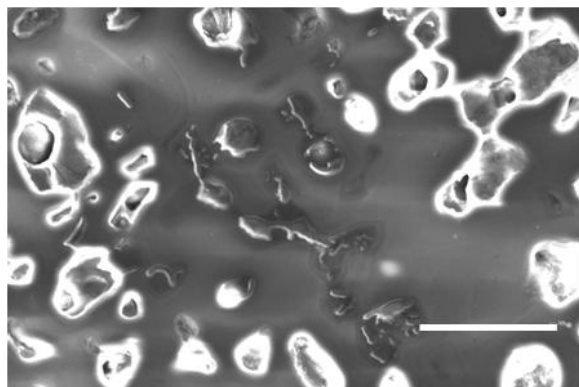


Fig. 6. SEM (SE) images showing the difference in cell infill between the top layers and the lower layers of coralline algae (sample 47). White indicates void (caused by charge build-up in sample) and shades of dark grey are in-fill. Top image taken at base of photosynthetically active layer, 0.5 mm from top of sample, showing that most cells are empty. Scale bar = 25 μ m. Bottom image taken at 4 mm depth, showing abundant cell in-fill. There was a general, although patchy trend for increasing cell in-fill towards the base.

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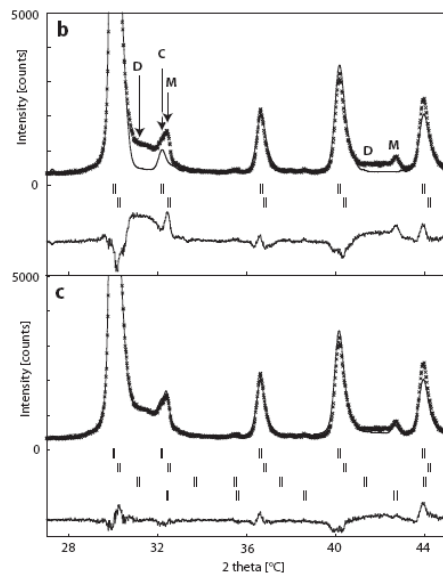
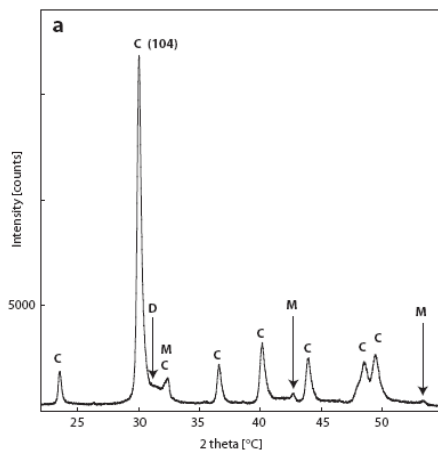
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Fig. 7. Powder X-ray diffraction pattern of coralline alga showing the main peaks of protodolomite (D), magnesite (M) and Mg-calcite (C). **(a)** The XRD pattern is dominated by peaks of the Mg-calcite of the cell walls. These peaks are unusually asymmetrical and have high shoulders towards higher 2θ angles (ie. towards smaller unit cell sizes), overlapping with the wide peaks of protodolomite and magnesite; see for example peak C (104). In order to resolve these peaks, profile fitting with the Rietveld method was carried out. **(b)** Rietveld refinement using Mg-calcite as the only phase resulted in significant misfits in the areas of protodolomite and magnesite ($R_p = 12.53$, $R_{wp} = 18.50$). To account for peak asymmetry two calcite compositions were refined (17.5 and 24 mol % MgCO_3). Crosses: observed trace; upper line: calculated trace; lower line: difference pattern; vertical bars from top to bottom: peak positions of calcite-I (17.5 mol % MgCO_3), calcite-II (24 mol % MgCO_3), dolomite, magnesite. **(c)** Rietveld refinement including dolomite and magnesite in addition to calcite results in a good fit ($R_p = 5.96$, $R_{wp} = 8.11$). The significant width of the dolomite XRD maxima suggests that the dolomite is very finely grained and not well crystallized, probably disordered (Zhang, 2010), and possibly bordering on amorphous. Moreover, we know that this protodolomite has a range of compositions and thus unit cell dimensions, also contributing to peak width. This made refinement of the unit cell impossible, and it was fixed to stoichiometric dolomite. The refined magnesite unit cell dimensions are $a = 4.678(1)$ Å and $c = 15.192(1)$ and thus about 1 % larger than ideal magnesite, which is typical for sedimentary magnesite (Graf et al., 1961).

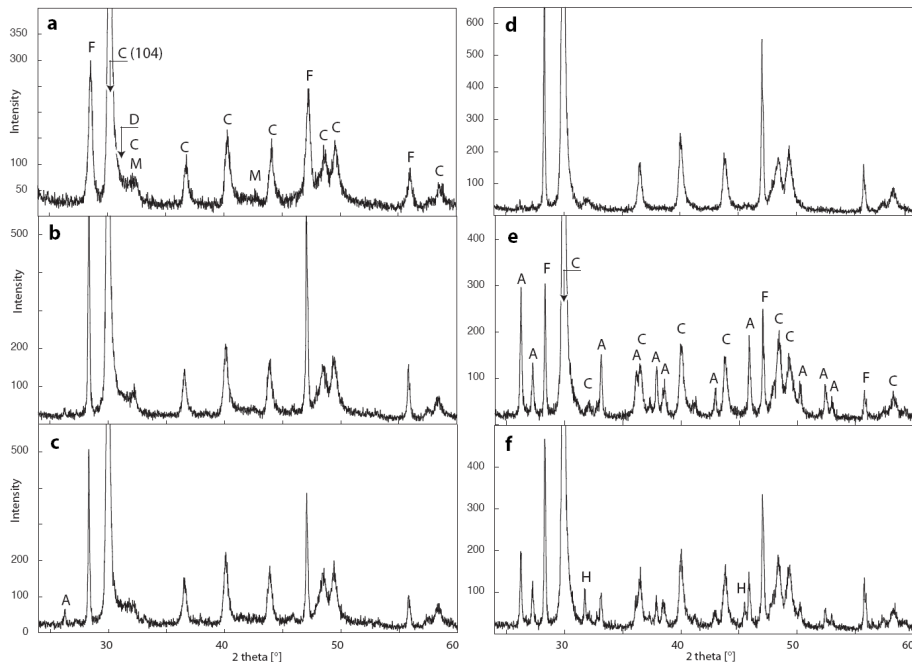


Fig. 8. Powder X-ray diffraction patterns of coralline algae, demonstrating how the presence of protodolomite and magnesite manifests itself in XRD analyses. In examples **(a–c)**, the calcite 104 reflection has a broad shoulder towards higher angles 2-theta, indicative of the presence of significant amounts of protodolomite and magnesite. This is consistent with the high Mg-contents of these samples (26.17–33.33 mol% Mg by ICP-AES). In **(d–f)**, the calcite 104 reflection has no significant shoulder, but displays a strong asymmetry that is typical for biogenic Mg-rich calcite (Milliman et al., 1971). This could mask the presence of protodolomite. For easier viewing reflections are labelled in selected scans only: Mg-rich calcite (C), dolomite (D), magnesite (M), fluorite (F), aragonite (A), halite (H).