

Benthic coral reef calcium carbonate dissolution in an acidifying ocean

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Changes in CaCO₃ dissolution due to ocean acidification are potentially more important than changes in calcification to the future accretion and survival of coral reef ecosystems. As most CaCO₃ in coral reefs is stored in old permeable sediments, increasing sediment dissolution due to ocean acidification will result in reef loss even if calcification remains unchanged. Previous studies indicate that CaCO₃ dissolution could be more sensitive to ocean acidification than calcification by reef organisms. Observed changes in net ecosystem calcification owing to ocean acidification could therefore be due mainly to increased dissolution rather than decreased calcification. In addition, biologically mediated calcification could potentially adapt, at least partially, to future ocean acidification, while dissolution, which is mostly a geochemical response to changes in seawater chemistry, will not adapt. Here, we review the current knowledge of shallow-water CaCO₃ dissolution and demonstrate that dissolution in the context of ocean acidification has been largely overlooked compared with calcification.

Coral reefs have high biological diversity and provide a myriad of ecosystem services to humans, such as fisheries and tourism^{1,2}. The CaCO₃ coral reef structure provides habitat for a large number of species. Reef structures are formed through the growth and build up of coral aragonite skeletons, red and green calcareous macroalgae, and other calcareous organisms, such as bryozoans, echinoderms and foraminifera. However, for a whole coral reef to be in a state of net accretion, CaCO₃ production (and any external sediment supply) must exceed its loss through physical, chemical and biological erosion and transport and dissolution as follows:

$$\text{CaCO}_3 \text{ accretion} = \text{CaCO}_3 \text{ production} - \text{physical loss of CaCO}_3 - \text{CaCO}_3 \text{ dissolution}$$

Ocean acidification (OA) generally refers to the lowering of the ocean's pH due to the uptake of anthropogenic CO₂ from the atmosphere. When CO₂ dissolves in sea water it forms H₂CO₃ (carbonic acid), which rapidly dissociates into HCO₃⁻ (bicarbonate ion) and H⁺ (hydrogen ion)³. Some of the excess H⁺ combines with CO₃²⁻ (carbonate ion) to form HCO₃⁻ and the remaining H⁺ lowers the seawater pH (pH = -log [H⁺]) (Fig. 1). The effect of OA on the decreased production of coral reef CaCO₃ (calcification) is well documented; see, for example, refs 4–6. However, CaCO₃ production is only part of the equation determining coral reef accretion, and much less is known about the effects of OA on physical, chemical and biological erosion and transport (loss) and dissolution. In particular, the dissolution of coral reef CaCO₃ sediments has largely been neglected by the research community. For example, dissolution is often excluded from coral reef carbonate budgets developed by geologists (see, for example, refs 7,8), while biologists mainly focus on calcification (see, for example, ref. 9). In addition, unlike biologically mediated calcification that could potentially adapt to OA^{10,11} (but see ref. 12), increasing CaCO₃ dissolution is mostly a geochemical response to changes in seawater chemistry and will increase according to thermodynamic and kinetic constraints^{13,14}, which cannot adapt to changing carbonate chemistries.

CaCO₃ budgets

Coral reefs are self-perpetuating ecosystems, with CaCO₃ formation and accretion providing the structural complexity necessary to support their high functional and biological diversity. To predict the accretion of coral reefs under future-ocean carbonate chemistries, it is necessary to determine the balance between CaCO₃ production and destruction processes and the impact of seawater carbonate chemistries on these processes. CaCO₃ stock in coral reefs can be roughly divided into two main pools; coral framework and CaCO₃ sediments. Coral framework refers to what is generally thought of as the reef structure and is where the highest rates of calcification (that is, CaCO₃ production) take place. Living corals can be thought of as a thin veneer of living tissue growing vertically and horizontally through the water column on top of their deposited CaCO₃ skeleton framework. After deposition, these skeletons can undergo diagenetic processes that modify the CaCO₃ minerals over geological timescales, eventually forming sedimentary limestones¹⁵. The coral framework is also subjected to physical and mechanical, chemical and biological breakdown processes that give rise to the formation of permeable CaCO₃ sediments (Fig. 1). Permeable sediments make up the majority of CaCO₃ stored in coral reef ecosystems, accounting for up to 95% of areal benthic coverage¹⁶. Sediments represent the storage of reef-derived CaCO₃ over thousands of years¹⁷ and are important in the development of other geological reef structures by acting as infill¹⁸.

Lateral growth of coral reefs is due to high rates of calcification on the fore reef that generate a constant supply of CaCO₃ material, which is eventually broken down and transported reefward in the direction of the prevailing wind, waves and currents^{19,20} (Fig. 2). This transported CaCO₃ is then subjected to further breakdown processes, leading to the formation of shallow reef habitats (for example, reef flats and lagoons) as sediment accumulates during times of stationary or low sea-level rise (SLR)^{21,22}. Besides production via the breakdown and transport of the coral reef framework, sediment can also be formed directly through infaunal CaCO₃ production by organisms such as foraminifera, coralline algae and molluscs^{23,24}. Once produced, this sediment can be stored within the coral reef

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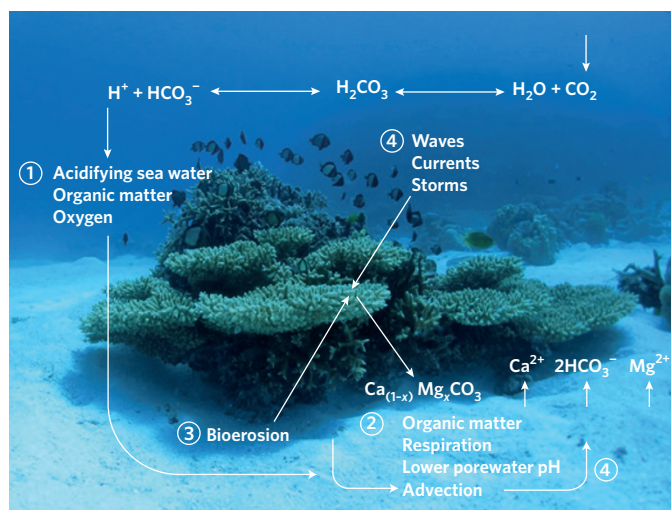


Figure 1 | Conceptual model of factors controlling CaCO_3 sediment dissolution. The numbers refer to the processes that break down permeable coral reef sediments: (1) environmental dissolution, or dissolution caused by the properties of sea water; (2) metabolic dissolution, which is induced through respiration and other metabolic processes occurring in sediment pore waters; (3) bioerosion, which can enhance dissolution through the physical and chemical actions of marine organisms; and (4) physical processes in coral reef sediments that interact with chemical and biological dissolution. Photo: © Ray Berkelman, AIMS.

ecosystem, lost through dissolution or transported offshore, where it either accumulates as sand banks or beach faces, or is deposited in the deep sea^{7,25}. Within reef flats and lagoons, sediment can be focused by currents and wave patterns, leading to the formation of low-lying land structures called sand or coral cays²⁶. Therefore, it is important to address how OA will affect all processes (for example, CaCO_3 production, dissolution (including bioerosion) and transport) that lead to the formation of reef habitat, both below and above the high tide mark.

CaCO_3 budgets determine the net accretion of coral reefs by quantifying the overall contribution of constructive (for example calcification, external supply of sediment) and destructive (for example dissolution and transport) processes. A common type of partial budget quantifies net accretion as the difference between framework carbonate production and loss due to bioerosion (for example, ref. 27). However, this type of budget does not include dissolution of the framework, or processes in the CaCO_3 sediments where much of the dissolution occurs. Whole coral reef ecosystem budgets quantify net accretion as the difference between carbonate production within the framework and in the CaCO_3 sediments, and loss due to CaCO_3 sediment export off the reef. For example, a budget of Cane Bay, St Croix showed that $0.71 \text{ kg m}^{-2} \text{ yr}^{-1}$ of CaCO_3 sediment was generated²⁸. It was estimated that $0.41 \text{ kg m}^{-2} \text{ yr}^{-1}$ of the sediment was reincorporated into the reef, whereas $0.13 \text{ kg m}^{-2} \text{ yr}^{-1}$ was exported off the reef as bed load, leaving a deficit of 24% ($0.17 \text{ kg m}^{-2} \text{ yr}^{-1}$) in annually produced sediment. This missing part of the budget was attributed to accumulation in channels and offshore export as suspended sediment loads; however, neither process was directly measured. A similar budget constructed for Kailua Bay, Hawaii estimated $0.53 \text{ kg m}^{-2} \text{ yr}^{-1}$ of CaCO_3 sediment was produced, with $0.33 \text{ kg m}^{-2} \text{ yr}^{-1}$ formed through erosion of the reef framework and $0.20 \text{ kg m}^{-2} \text{ yr}^{-1}$ produced directly within the sediments⁷. When compared with the geological accumulation of sediment over the past 5,000 years while Kailua Bay was inundated by SLR, there was a 25% ($0.13 \text{ kg m}^{-2} \text{ yr}^{-1}$) discrepancy between the modern budget and measured volume of sediment. This missing, destructive component of the budget was attributed to processes

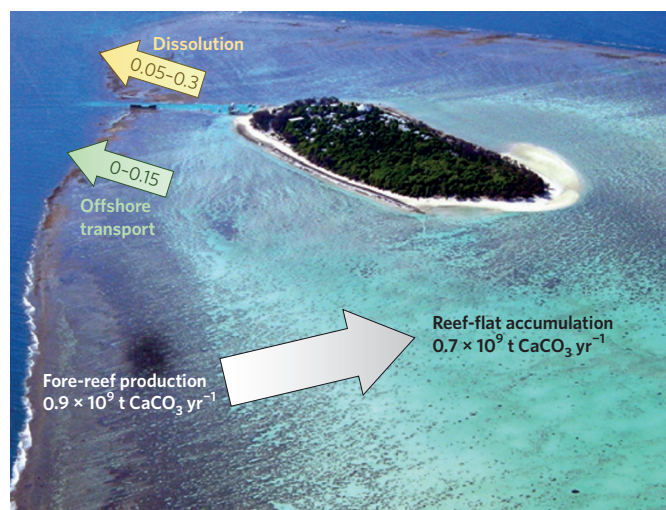


Figure 2 | Conceptual model illustrating the processes affecting whole coral reef accretion with global production and accumulation rates, adapted from ref. 31. Global production and accumulation values assume a global reef area of $0.6 \times 10^6 \text{ km}^2$ and all values are in $\times 10^9 \text{ t CaCO}_3 \text{ yr}^{-1}$. A previous study³¹ estimated that loss due to dissolution and offshore transport combined was ~20% of production ($0.2 \times 10^9 \text{ t CaCO}_3 \text{ yr}^{-1}$); however, measured values were not used to constrain this estimate. When the range of conservative net daily CaCO_3 dissolution rates for sediments ($0.09\text{--}0.50 \text{ kg m}^{-2} \text{ yr}^{-1}$; Table 1) are extrapolated to the global reef area ($0.05 \times 10^9\text{--}3.0 \times 10^9 \text{ t CaCO}_3 \text{ yr}^{-1}$) they could account for up to 167% of the total loss term estimated by this previous study³¹. Values for offshore transport were estimated based on the difference between the loss term estimated in ref. 31 and the conservative dissolution rates. Photo by Christian Wild; adapted with permission from ref. 65, © 2008 by the Association for the Sciences of Limnology and Oceanography, Inc.

such as offshore transport or dissolution, but neither process was measured.

Observed net CaCO_3 dissolution rates in a range of natural and experimental benthic coral reef habitats range from 0 to $21.9 \text{ kg m}^{-2} \text{ yr}^{-1}$, with most falling between 0.09 and $3.50 \text{ kg m}^{-2} \text{ yr}^{-1}$ (ref. 29). Most of these dissolution rates were derived from night or dark incubations and do not include the full diel cycle of CaCO_3 precipitation and dissolution occurring in shallow reef sediments³⁰. As the majority of CaCO_3 dissolution most likely occurs in the sediments and because dissolution rates can range from positive to negative (that is, calcification) in permeable sediments over a diel cycle, a more conservative range of net daily CaCO_3 dissolution rates is between 0.09 and $0.50 \text{ kg m}^{-2} \text{ yr}^{-1}$ ($0.24\text{--}1.38 \text{ g m}^{-2} \text{ d}^{-1}$; Table 1). This range of net daily sediment dissolution rates can account for 59 to 385% of the discrepancies in the carbonate budgets of previous studies^{7,28}. Furthermore, a global budget of coral reef CaCO_3 production showed that reefs produce $1.5 \text{ kg m}^{-2} \text{ yr}^{-1}$, with an estimated (not measured) 20% ($0.3 \text{ kg m}^{-2} \text{ yr}^{-1}$) lost to offshore transport or dissolution³¹ (Fig. 2). The range of the most conservative CaCO_3 dissolution rates ($0.09\text{--}0.50 \text{ kg m}^{-2} \text{ yr}^{-1}$) could account for 6 to 33% of the global production of CaCO_3 by coral reefs, enough to balance the loss terms estimated previously³¹. However, it is important to note that the budget in that study³¹ was constructed based on net ecosystem calcification rates, which may have already included dissolution.

Present estimates of CaCO_3 dissolution may balance the missing terms in many whole coral reef carbonate budgets, but how will OA influence loss terms such as dissolution and the associated accretion of coral reefs? A $0.4 \text{ kg m}^{-2} \text{ yr}^{-1}$ increase in the dissolution rate of CaCO_3 sediments was measured under a $400 \mu\text{atm}$ increase in surface seawater partial pressure of CO_2 ($p\text{CO}_2$) from present conditions³⁰, which is equivalent to an ~80% reduction in

sediment accretion rates by 2100^{7,28}. This could represent a large transformation in the way coral reef ecosystems process and accumulate CaCO₃ as sediment, and has important implications for the future development of reef habitat and framework. Permeable CaCO₃ sediments are the principal source material leading to the formation of coral reef lagoons, reef flats and coral cays, and an adequate supply is essential to keep up with SLR³². Therefore, if increased dissolution under OA decreases the supply of CaCO₃ sediments, the morphology of these habitats will change. Current rates of SLR (~3.26 mm yr⁻¹; ref. 33) already endanger low-lying coral cays³⁴, and SLR is expected to accelerate by the end of the century. Although coral reefs as CaCO₃ structures have historically kept up with much greater rates of SLR²², the formation of modern reef structures such as shallow reef flats and lagoons may not be able to keep up in an acidifying ocean³⁵. However, in reef ecosystems where coral growth is currently limited by sea level (for example, shallow reef flats)³⁶, moderate flooding due to rising sea levels may act to accelerate coral growth. Therefore, to better predict how modern reefs will respond to the combined effects of SLR and OA, it is necessary to determine how CaCO₃ dissolution will affect their formation from a whole-system, holistic perspective.

Whole-system responses

Studies investigating the calcification responses of whole coral reef communities to OA have generally shown a much stronger response and sensitivity to changes in the aragonite saturation state (Ω_{Ar}) than studies of individual organisms (see, for example, refs 6,37,38). On average, community calcification is predicted to decrease by 60% per unit decrease in Ω_{Ar} , but estimates range from 10 to >100%, that is, net dissolution^{39,40}. The greater sensitivity is most likely the result of the combined effect of decreasing organism calcification rates and increasing CaCO₃ dissolution rates in sediments and micro-environments^{10,38}. Evidence of net CaCO₃ dissolution is commonly observed at night in the water column in many coral reef environments^{40–42} and at any time in carbonate sediment pore waters owing to the metabolic processes driving dissolution^{43,44}.

Mesocosm or enclosure experiments, the Biosphere II artificial reef community and measurements from natural coral reef

environments have all shown that CaCO₃ dissolution will increase in response to rising seawater CO₂ and decreasing pH and Ω_{Ar} (for example, refs 6,38–40,45). Some of these results suggest that the process of CaCO₃ dissolution could be an order of magnitude more sensitive to OA than calcification in individual organisms³⁸, but despite this observation, few studies have attempted to quantify the relative contributions of these processes. This is partly due to the fact that our present measurement techniques only measure the net effect of these processes, and thus, it is challenging to quantify gross calcification and dissolution. Nevertheless, separation in time (for example, night net dissolution) and space (most dissolution probably occurs in the sediments) provide initial constraints and a conservative estimate of gross CaCO₃ dissolution rates^{40,44}.

Drivers of coral reef CaCO₃ sediment dissolution

Based on over 50 years of research (Fig. 3), the dissolution of permeable reef sediments can be grouped under three processes: (1) environmental dissolution, or dissolution caused by the properties of the bulk sea water^{29,46}; (2) metabolic dissolution, which is induced through respiration and other metabolic processes occurring in sediment pore waters^{44,47}; and (3) bioerosion, which can enhance dissolution through the physical and chemical actions of marine organisms^{48,49} (Fig. 1). Environmental and metabolic dissolution can largely be grouped under the broader term of chemical dissolution, whereas biological dissolution or bioerosion can occur via physical and chemical processes. In addition, a number of physical processes (for example, wave action, currents, advective porewater flow) in coral reef sediments can interact with chemical and biological dissolution. As such, it is difficult to separate out the long-term physical, chemical and biological drivers of coral reef CaCO₃ sediment dissolution because they act synergistically (Fig. 1).

Environmental dissolution. Environmental dissolution refers to dissolution of CaCO₃ substrates immersed in water that is undersaturated with respect to the dissolving mineral phase. For example, as CaCO₃ substrates sink through the water column of the open ocean, at some depth they will cross the saturation horizon ($\Omega = 1$) and undergo environmental dissolution. Although seawater saturation

Table 1 | CaCO₃ dissolution rates measured in shallow permeable coral reef sediments.

Location	CO ₂ level	Dark dissolution (g CaCO ₃ m ⁻² h ⁻¹)	Net dissolution (g CaCO ₃ m ⁻² d ⁻¹)	Method	Ref.
Bermuda	Ambient		0.66*	Bell jar incubations	93
Bermuda	Ambient		0.48 to 1.92*	Vertical eddy diffusion	75
Florida	Ambient	0.03	-0.11	<i>In situ</i> chamber incubations	94
Hawaii	Ambient	0.03	0.31	<i>In situ</i> chamber incubations	94
Heron Island, Great Barrier Reef	Ambient	0.26		<i>Ex situ</i> flume incubations	95
Heron Island, Great Barrier Reef	-2× ambient	0.31 to 0.57		<i>Ex situ</i> flume incubations	95
Heron Island, Great Barrier Reef	Ambient	0.03 to 0.28	0.26 to 0.44	<i>In situ</i> advective chamber incubations	44
Heron Island, Great Barrier Reef	Ambient	0.09 to 0.1	-0.06 to -0.23	<i>In situ</i> advective chamber incubations	30
Heron Island, Great Barrier Reef	-2× ambient	0.13 to 0.15	0.36 to 0.9	<i>In situ</i> advective chamber incubations	30
Heron Island, Great Barrier Reef	Ambient	0.03 to 0.10	-0.27 to 1.38	<i>In situ</i> advective chamber incubations	96
Monaco	Ambient	0.08		Mesocosm incubations	97
Moorea	Ambient	0.08	0.24	<i>In situ</i> chamber incubations	98

Negative rates indicate precipitation. Ambient CO₂ level refers to incubations done without manipulating the carbonate chemistry. Dark dissolution rates are hourly rates measured under dark conditions, while net dissolution rates are estimated over an entire diel cycle and include any daytime precipitation occurring in the sediments. *pCO₂ at this site was naturally elevated, and therefore it was excluded from the range of net daily dissolution rates used in the main text.

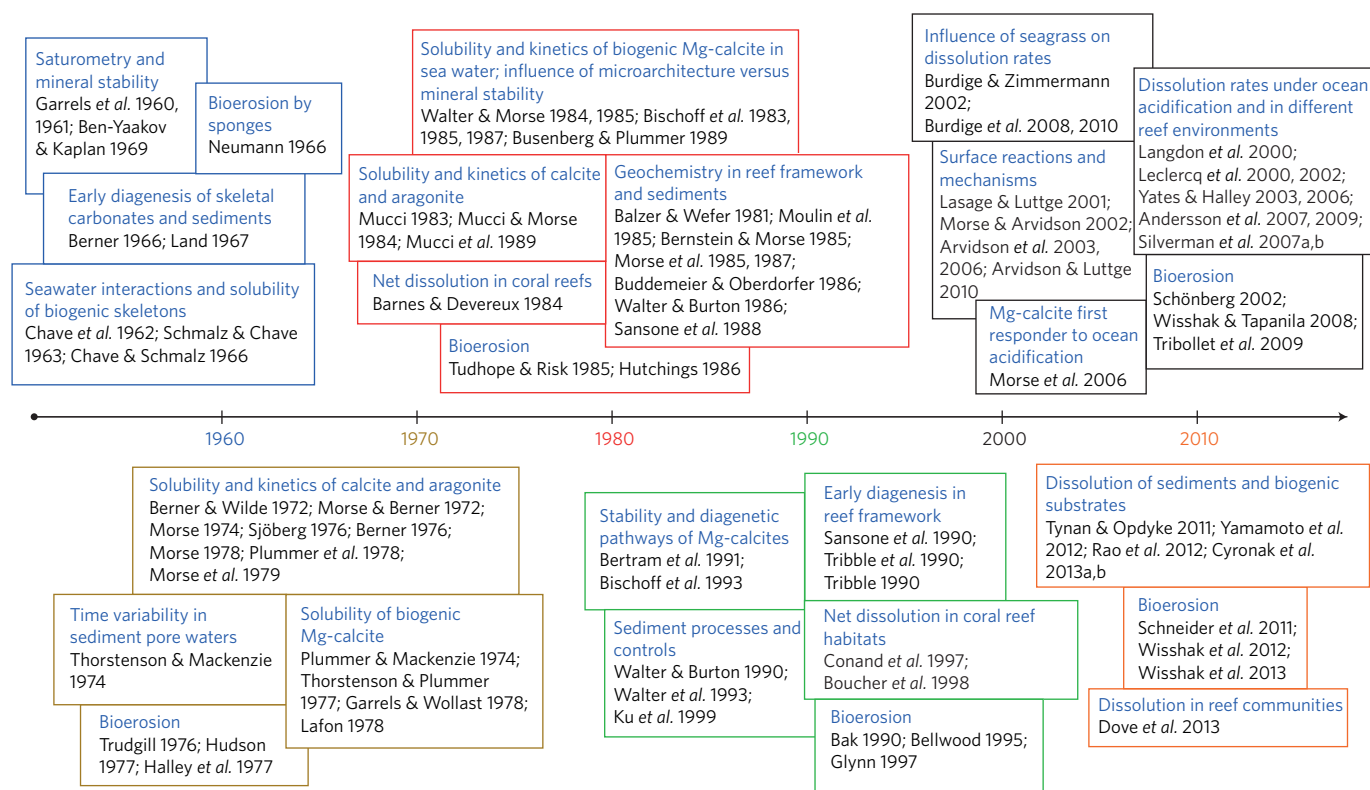


Figure 3 | Timeline of studies addressing various aspects of carbonate dissolution from the 1960s until present. This is by no means a comprehensive list, but rather an overview of the work that has been done over the past several decades. There are many additional important studies that deserve recognition. References are provided in the Supplementary Information.

with respect to aragonite on coral reefs will remain well above 1 as a result of OA⁵⁰, a significant proportion of CaCO₃ sediments, cements and reef framework are composed of Mg-calcite minerals, which are more soluble than aragonite. As much as 50% of bulk coral reef sediments can be composed of Mg-calcite^{23,51}. As seawater pH and Ω decrease, an increasing proportion of these mineral phases will be immersed in undersaturated sea water and undergo dissolution. However, at this time, we have limited understanding of the solubilities and the reaction kinetics of these phases; that is, when and how fast will these mineral phases dissolve in response to OA. To date, only one study has rigorously evaluated the rate of dissolution of shallow-water Mg-calcite minerals in sea water¹⁴ and then only under limited chemical conditions. Determination of absolute rates is further complicated by the presence of impurities and mixed mineralogies, including, for example, dolomite, which has been reported for some crustose coralline algae⁵². However, it can be concluded that an increasing proportion of these mineral phases will undergo dissolution in response to OA and the rate of dissolution will also increase^{13,14}.

Metabolic dissolution. Metabolic CaCO₃ dissolution is driven by aerobic respiration that generates CO₂ and carbonic acid in the sediment pore water or other microenvironments. The amount of dissolution from CO₂ and carbonic acid generation is proportional to the rate of organic matter decomposition, which in turn is controlled by the supply of organic matter, its reactivity and the availability of oxygen^{53,54}. In addition, oxidation of reduced metabolites such as FeS, Mn²⁺ and NH₄⁺ can also result in CaCO₃ dissolution⁵⁵ when either O₂ is transported down to the anaerobic zone or reduced metabolites are transported upwards to the aerobic zone. Organic matter oxidation can also occur anaerobically via sulphate reduction, and in some reefs this may be the dominant pathway⁵⁶. The alkalinity that is produced when organic matter is oxidized via

sulphate reduction may increase the porewater saturation state with respect to carbonate minerals, resulting in carbonate precipitation⁵⁷. However, the geochemistry is complex, with H₂S produced in the initial stages of sulphate reduction in low Fe sediments resulting in dissolution⁵⁸.

Other pathways of organic matter oxidation such as NO₃⁻, MnO₂ and Fe reduction and methanogenesis are usually considered to be only minor in reefs (for example, ref. 56). However, recent work^{59,60} suggests NO₃⁻ reduction (denitrification) in permeable coral reef CaCO₃ sediments may be more important than previously thought, although there is only net production of alkalinity if the NO₃⁻ is sourced from the water column (that is, not from coupled nitrification–denitrification)⁶¹. MnO₂ reduction and porewater alkalinity production may be more important in reef channels where strong tidal currents maintain a higher level of reactive manganese⁶². It has recently been suggested that this traditional cascade of biogeochemical reactions coupled to carbonate dissolution and precipitation can be reversed in quartz muds and fine sands due to long-distance electron transport^{63,64}, but it is unknown if this reversal occurs in permeable CaCO₃ sediments.

In shallow coral reef environments, light reaches the sediments, allowing microphytobenthos (and macroalgae) to grow, and as such, the sediments are subject to diel cycles of productivity and respiration⁶⁵. The sediments and framework also experience strong diel cycles in the overlying water, driven by coral respiration and productivity. Net CaCO₃ dissolution mostly occurs in the dark, but rates are not necessarily constant over the dark part of the diel cycle⁴⁴. During the day, photosynthetic organisms calcify and the consumption of CO₂ reduces the production of carbonic acid and associated dissolution, typically resulting in net calcification and precipitation³⁷. Net dissolution can still occur in the early stages of the light cycle⁴⁴ and during the day in response to cloud cover, turbidity and hypersalinity³⁷. As such, the amount of light reaching

the sediment surface, and the associated benthic productivity, is an important control on whether sediments are net calcifying and precipitating or net dissolving. Because depth is an important control on the amount of light reaching the bottom, deeper sediments are likely to have higher rates of dissolution than shallow sediments⁴⁴. However, the net amount of calcification and precipitation is not only proportional to the amount of light but also depends on the time of day. This hysteretic trend is most likely due to a lowering of the porewater Ω_{Ar} during the night, which results in lower rates of calcification and precipitation in the morning than in the afternoon for the same amount of light reaching the sediments⁴⁴.

Interaction of environmental and metabolic dissolution. Although benthic metabolism is clearly an important control on CaCO_3 sediment dissolution in coral reef sediments, a number of recent laboratory and *in situ* field experiments suggest that dissolution will be enhanced by OA due to lowered pH in the water column. For example, a recent mesocosm experiment with lowered pH and increased temperature showed no change in benthic coral reef community productivity and respiration, but a reduction in CaCO_3 sediment grain size, which the authors of this study attributed to enhanced CaCO_3 sediment dissolution⁶. However, it is unknown whether respiration in the sediment component of the coral reef community remained unchanged under lowered pH. A recent laboratory flume study found enhanced CaCO_3 sediment dissolution under high water flow and lowered pH (Table 1), despite decreases in benthic respiration⁶⁶. Similarly, recent *in situ* field manipulations with lowered pH showed a small change in benthic productivity, no change in respiration and enhanced CaCO_3 sediment dissolution³⁰. In addition, advective flow stimulated a twofold increase in CaCO_3 sediment dissolution in the low pH treatment³⁰. The acidity of the low pH water could have further decreased when advected through the sediments due to metabolic CO_2 release during benthic respiration.

Bioerosion. Biological destruction of CaCO_3 is collectively referred to as bioerosion, but the mechanisms organisms use to chemically dissolve or mechanically erode carbonate substrates vary. Physical bioerosion results from grazing of algae by fish, echinoderms, limpets, snails and chitons⁴⁸. In contrast, euendolithic microorganisms colonize and actively penetrate carbonate substrates by releasing acids⁶⁷, whereas sponges use a combination of chemical and mechanical erosion⁶⁸. Holothurians dissolve CaCO_3 in their digestive systems as they process sediments for organic detritus⁶⁹. It is important to note that physical and chemical bioerosion may just recycle much of the carbonate material (for example, ~71%; ref. 28) resulting in only a small net loss of CaCO_3 from the reef; however, it may make this material more susceptible to loss via dissolution.

As a result of OA, bioerosion could potentially increase due to a number of factors. For example, biogenic CaCO_3 substrates and structures may become weaker and more vulnerable to both mechanical and chemical erosion, and chemical eroders will need to release less acid to initiate seawater undersaturation and CaCO_3 dissolution. Experiments to date show consistent increases in bioerosion rates under increased CO_2 conditions. For example, increased rates of penetration and CaCO_3 dissolution (+48%) by euendolithic algae have been shown for *Porites* blocks exposed to seawater $p\text{CO}_2$ of 750 μatm compared with blocks exposed to 400 μatm (refs 67,70). Significant increases in the rate of bioerosion under increased CO_2 have also been observed for the sponge *Cliona orientalis* in controlled experiments⁷¹.

Physical processes. In addition to the constant erosion by waves, currents and bioerosion, coral reef structures also experience episodic storm events that can cause a large amount of structural damage. Combined, these physical processes of erosion over time break down CaCO_3 material into increasingly smaller grain sizes.

Dissolution of CaCO_3 material is inversely related to grain size and surface microstructure, with smaller grain sizes dissolving more rapidly¹³. Similarly, the dissolution of perforate corals was directly proportional to their surface area, but the relationship was less predictable for imperforate corals⁷². However, in both these experimental studies, the water was maintained at a constant saturation state and may not reflect *in situ* natural conditions. For example, smaller grain sizes would restrict the advective flow of undersaturated water that may drive dissolution, allowing the build up of saturated water and limiting dissolution¹³.

Porewater advection is also an important control on dissolution in permeable CaCO_3 sediments as it transports O_2 into the sediment matrix⁶⁵, which stimulates aerobic respiration and enhances dissolution⁴⁴. O_2 transported into permeable sediments by advection would also decrease sulphate reduction in the surface layers by pushing the oxic/anoxic interface deeper. A deeper oxic/anoxic interface reduces the production of alkalinity from sulphate reduction, decreasing the porewater Ω_{Ar} and potentially enhancing CaCO_3 dissolution. Reduced metabolites would also be reoxidized as O_2 is transported deeper into the sediments resulting in CaCO_3 dissolution⁵⁵. O_2 is also transported into sediment pore waters via bioturbation and bioirrigation⁶⁵, and seagrasses also release O_2 through their rhizomes, which can enhance CaCO_3 dissolution⁴⁷. Similarly, *in situ* advection of low pH sea water through CaCO_3 sediments stimulated a twofold increase in sediment dissolution (environmental dissolution), compared with sediments exposed to low pH sea water only via diffusion³⁰. This most likely reflects the delivery of undersaturated water further into the sediment microstructure where water under diffusive flow cannot penetrate.

Naturally high CO_2 environments

There are at present many marine environments that already experience seawater CO_2 and pH levels similar or even more extreme than those levels anticipated as a result of oceanic uptake of anthropogenic CO_2 over this and the next century. The distribution and composition of different CaCO_3 mineral phases in these environments provide important clues in terms of the potential response to future OA, although extensive uncertainty still exists with respect to mineral solubility and kinetics. Consequently, the timing of critical thresholds (for example, when a coral reef ecosystem will be net dissolving) and rates of dissolution on relevant timescales of ongoing anthropogenic OA are major gaps in our knowledge. However, in general we have a good understanding of how CaCO_3 minerals respond to rising CO_2 and lower pH and Ω . For example, the CaCO_3 content of sediments becomes increasingly scarce as a function of depth and changes successively according to mineral stability. Similarly, we know that the rate of dissolution increases as a function of increasing seawater undersaturation^{73,74}. Selective dissolution according to mineral stability has been reported for a seasonally stratified environment in Bermuda exposed to high CO_2 and low pH conditions during summer⁷⁵. Observations from the eastern tropical Pacific, which naturally experiences high CO_2 , low pH and low Ω owing to upwelling, show high rates of bioerosion, low reef cementation and poorly developed reefs under these conditions (see, for example, ref. 76). Furthermore, observations from the volcanic CO_2 vent sites in Italy and Papua New Guinea have shown evidence of dissolution of individual calcifiers, both live and dead^{77,78}. In Papua New Guinea, no positive reef accretion occurred below an average seawater pH of 7.7 (ref. 77).

Interaction of other coral reef stressors

Coral reefs are subject to many anthropogenic stressors, such as nutrient over-enrichment (eutrophication), climate change (for example, bleaching due to rising temperatures and increases in the intensity of tropical cyclones), overfishing, sedimentation, disease and pollution that may act synergistically with OA to enhance

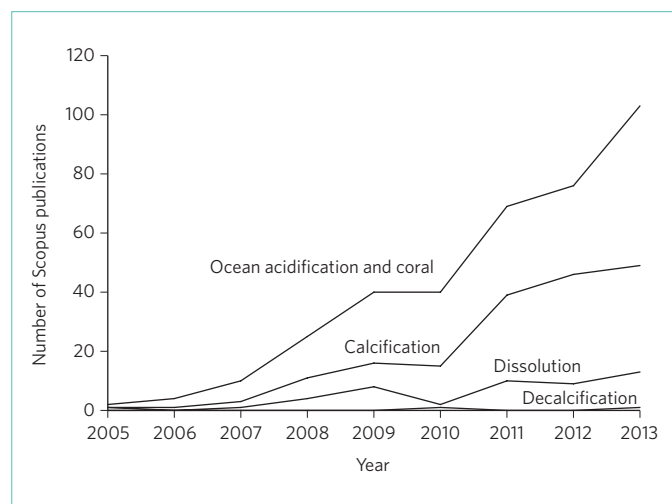


Figure 4 | Number of publications per year from a Scopus search of ‘ocean acidification’ and ‘coral’ in the title, abstract and keywords between 2005 and 2013. Of the ‘ocean acidification’ and ‘coral’ publications, the number per year that included ‘calcification’, ‘dissolution’ or ‘decalcification’ are also shown.

CaCO₃ sediment dissolution. Excess terrestrially derived nitrogen and phosphorus and organic matter are delivered to coral reefs via river runoff, groundwater and atmospheric deposition⁷⁹. Increased nitrogen and phosphorus loads could enhance reef primary production and net autotrophy, which could lead to enhanced bioerosion⁸⁰. However, high concentrations of PO₄³⁻ may inhibit CaCO₃ sediment dissolution⁸¹. If nutrients are delivered during the spawning season of the crown of thorn starfish, their numbers may also be enhanced⁸², potentially leading to increased bioerosion due to exposed coral skeletons.

Increased dissolved and particulate organic matter loads would enhance benthic respiration and net heterotrophy, increasing average coral reef water column *p*CO₂ (ref. 83), which together could enhance CaCO₃ sediment dissolution. Similarly, increased bleaching-induced stress and respiration due to climate change⁸⁴ may also increase the *p*CO₂ of coral reef waters, most likely due to the release of high amounts of organic matter⁸⁵. Increased cyclone activity due to climate change⁸⁶ may lead to more erosion and physical loss of reef CaCO₃ and increased resuspension of fine CaCO₃ sediment in more acidic water due to more frequent and larger storms could result in enhanced dissolution. In the aftermath of cyclones, increased seawater *p*CO₂ and suppressed Ω_{Ar} of reefs have been observed for short periods of time^{87,88}, potentially leading to the increased dissolution of any suspended and *in situ* CaCO₃ sediments. Changes in the benthic community structure of coral reefs towards more fleshy taxa due to a combination of OA and other anthropogenic impacts, such as overfishing⁸⁹, may also increase benthic respiration and associated CaCO₃ sediment dissolution. This is also relevant for the proposed management of OA on coral reefs where it has been suggested that fleshy taxa may provide a buffering that would enhance calcification^{90,91}. However, fleshy taxa may also enhance dissolution owing to enhanced respiration and offset any benefits associated with enhanced calcification, but the issue is complex, and, depending on the separation of processes in time and space, could result in either a net positive or negative outcome.

Publication bias

Clearly, changes in dissolution in an acidifying ocean are just as, or maybe more, important than calcification to the survival and accretion of coral reefs. However, despite the importance of coral reef

sediment dissolution, recent publications demonstrate that there has been much less interest in dissolution than calcification. A Scopus search of ‘ocean acidification’ and ‘coral’ in the title, abstract and keywords returned 370 publications between 2005 and 2013 (Fig. 4). Of these, 182 (49.3%) included ‘calcification’, but only 52 (13.8%) included ‘dissolution’. Two of the latter publications used ‘decalcification’ to refer to a state when net ecosystem calcification is <0, which is equivalent to net dissolution, and one uses ‘decalcification’ interchangeably with dissolution, so they were included with the dissolution publications. Only 15 of the 370 publications (4.1%) measured or estimated net CaCO₃ dissolution compared with 105 of the 370 publications (28.4%) that measured or estimated net calcification. This is seven times as many published calcification measurements or estimates compared with dissolution measurements or estimates from coral reefs. The bias towards calcification, compared with dissolution, may simply reflect the number of biologists, compared with geochemists, working on coral reefs. But irrespective of the reason why, and despite changes in CaCO₃ sediment dissolution in an acidifying ocean being potentially more important than changes in calcification to the future accretion and survival of coral reef ecosystems, there are clearly far fewer publications devoted to dissolution than calcification.

Future directions

We clearly need a better understanding of how porewater chemistries change, and the associated effect on CaCO₃ sediment dissolution, as OA changes the overlying water column. A combination of O₂, *p*CO₂ and pH planar optodes and flume studies may be useful for studying the subsurface carbonate chemistry around permeable sediment microstructures under conditions of natural advective flow.

We also need a better understanding of the interactions between environmental and metabolic dissolution in shallow permeable sediments and how dissolution rates relate to sediment properties such as grain size, mineralogy, organic matter content and hydrology. Insights could be gained using *in situ* manipulations of respiration (light, organic matter), water column *p*CO₂ and advective flow while measuring CaCO₃ dissolution in a range of sediment types. In addition, the relative importance of changes in benthic productivity and respiration due to other stressors on coral reefs, such as nutrient enrichment versus changes in the pH of the overlying water (OA) on CaCO₃ sediment dissolution, also needs to be determined.

It is not yet clear how OA will affect the loss terms (dissolution, transport) of CaCO₃ budgets for whole coral reef systems. Increased bioerosion may result in more sediment production. Sediment and framework dissolution will increase, but what this will mean for CaCO₃ budgets of whole coral reef systems remains to be established. Similarly, we do not know how transport terms will be affected by the suspension of sediment in more corrosive sea water. Other open questions include how the CaCO₃ budgets of whole coral reef systems will be affected by the interaction of other stressors with OA, and what impact changes in the loss terms will have on reef structure and the habitats they provide. Furthermore, more complete CaCO₃ budgets that include dissolution need to be constructed for different types of whole coral reef systems, under different states of stress.

The stability and dissolution kinetics of biogenic skeletal carbonates under natural environmental conditions near equilibrium need to be better understood. One of the big challenges we are facing is how to bridge our current understanding of CaCO₃ dissolution based on controlled laboratory experiments to natural systems. This will require a holistic approach combining laboratory, field and numerical modelling studies.

Finally we need to tease apart gross dissolution terms from net ecosystem calcification, as detailed in ref. 92.

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References

- Hoegh-Guldberg, O. Climate change, coral bleaching and the future of the world's coral reefs. *Mar. Freshwat. Res.* **50**, 839–866 (1999).
- Harrison, P. & Booth, D. in *Marine Ecology* Vol. 1 (eds Connell, S. D. & Gillanders, B. M.) Ch. 13, 316–377 (Oxford Univ. Press, 2007).
- Fabry, V. J., Seibel, B. A., Feely, R. A. & Orr, J. C. Impacts of ocean acidification on marine fauna and ecosystem processes. *ICES J. Mar. Sci.* **65**, 414–432 (2008).
- Gattuso, J.-P., Allemand, D. & Frankignoulle, M. Photosynthesis and calcification at cellular, organismal and community levels in coral reefs: a review on interactions and control by carbonate chemistry. *Am. Zool.* **39**, 160–183 (1999).
- Langdon, C. & Atkinson, M. J. Effect of elevated pCO₂ on photosynthesis and calcification of corals and interactions with seasonal change in temperature/irradiance and nutrient enrichment. *J. Geophys. Res. Oceans* **110**, 1–16 (2005).
- Dove, S. G. *et al.* Future reef decalcification under a business-as-usual CO₂ emission scenario. *Proc. Natl Acad. Sci. USA* **110**, 15342–15347 (2013).
- Harney, J. N. III & Fletcher, C. H. A budget of carbonate framework and sediment production, Kailua Bay, Oahu, Hawaii. *J. Sediment. Res.* **73**, 856–868 (2003).
- Mallela, J. & Perry, C. T. Calcium carbonate budgets for two coral reefs affected by different terrestrial runoff regimes, Rio Bueno, Jamaica. *Coral Reefs* **26**, 129–145 (2007).
- Schneider, K. & Erez, J. The effect of carbonate chemistry on calcification and photosynthesis in the hermatypic coral *Acropora eurystoma*. *Limnol. Oceanogr.* **51**, 1284–1293 (2006).
- Pandolfi, J. M., Connolly, S. R., Marshall, D. J. & Cohen, A. L. Projecting coral reef futures under global warming and ocean acidification. *Science* **333**, 418–422 (2011).
- Holcomb, M. *et al.* Coral calcifying fluid pH dictates response to ocean acidification. *Sci. Rep.* **4**, 5207 (2014).
- Hoegh-Guldberg, O. Coral reef sustainability through adaptation: Glimmer of hope or persistent mirage? *Curr. Opin. Environ. Sust.* **7**, 127–133 (2014).
- Walter, L. M. & Morse, J. W. Reactive surface area of skeletal carbonates during dissolution: effect of grain size. *J. Sediment. Res.* **54**, 1081–1090 (1984).
- Walter, L. M. & Morse, J. W. The dissolution kinetics of shallow marine carbonates in seawater: a laboratory study. *Geochim. Cosmochim. Acta* **49**, 1503–1513 (1985).
- A comprehensive study of dissolution kinetics of biogenic carbonate substrates in sea water showing that microarchitecture can sometimes override thermodynamic mineral stability as a control of dissolution rates.**
- Sanders, D. Syndepositional dissolution of calcium carbonate in neritic carbonate environments: geological recognition, processes, potential significance. *J. Afr. Earth Sci.* **36**, 99–134 (2003).
- Gattuso, J., Frankignoulle, M. & Wollast, R. Carbon and carbonate metabolism in coastal aquatic ecosystems. *Annu. Rev. Ecol. Syst.* **29**, 405–434 (1998).
- Smith, B. T., Frankel, E. & Jell, J. S. in *Reefs and Carbonate Platforms in the Pacific and Indian Oceans* 279–294 (Blackwell Publishing, 2009).
- Hubbard, D. K., Burke, R. B. & Gill, I. P. Where's the reef: the role of framework in the Holocene. *Carbonate. Evaporite.* **13**, 3–9 (1998).
- Davies, P. & Kinsey, D. Holocene reef growth — One Tree Island, Great Barrier Reef. *Mar. Geol.* **24**, M1–M11 (1977).
- Kinsey, D. & Davies, P. *Carbon Turnover, Calcification and Growth in Coral Reefs* (Elsevier, 1979).
- Marshall, J. F. & Davies, P. J. Internal structure and Holocene evolution of One Tree Reef, southern Great Barrier Reef. *Coral Reefs* **1**, 21–28 (1982).
- Montaggioni, L. F. History of Indo-Pacific coral reef systems since the last glaciation: Development patterns and controlling factors. *Earth Sci. Rev.* **71**, 1–75 (2005).
- Harney, J. N., Grossman, E. E., Richmond, B. M. & Fletcher, C. H. III Age and composition of carbonate shoreface sediments, Kailua Bay, Oahu, Hawaii. *Coral Reefs* **19**, 141–154 (2000).
- Yamano, H., Miyajima, T. & Koike, I. Importance of foraminifera for the formation and maintenance of a coral sand cay: Green Island, Australia. *Coral Reefs* **19**, 51–58 (2000).
- Ryan, D. A., Opdyke, B. N. & Jell, J. S. Holocene sediments of Wistari Reef: Towards a global quantification of coral reef related neritic sedimentation in the Holocene. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **175**, 173–184 (2001).
- Gourlay, M. in *Proc. 6th Int. Coral Reef Symp.* (eds Choat, J. H. *et al.*) 491–496 (1998).
- Kennedy, E. V. *et al.* Avoiding coral reef functional collapse requires local and global action. *Curr. Biol.* **23**, 1–7 (2013).
- Hubbard, D. K., Miller, A. I. & Scaturro, D. Production and cycling of calcium carbonate in a shelf-edge reef system (St. Croix, US Virgin Islands); Applications to the nature of reef systems in the fossil record. *J. Sediment. Res.* **60**, 335–360 (1990).
- Andersson, A. J. & Gledhill, D. Ocean acidification and coral reefs: effects on breakdown, dissolution, and net ecosystem calcification. *Annu. Rev. Mar. Sci.* **5**, 321–348 (2013).
- Cyronak, T., Santos, I. R. & Eyre, B. D. Permeable coral reef sediment dissolution driven by elevated pCO₂ and pore water advection. *Geophys. Res. Lett.* **40**, 4876–4881 (2013).
- First study to measure CaCO₃ sediment dissolution in situ over a diel cycle with advective flow and increased pCO₂ (ocean acidification scenarios).**
- Milliman, J. D. Production and accumulation of calcium carbonate in the ocean: Budget of a nonsteady state. *Glob. Biogeochem. Cycles* **7**, 927–957 (1993).
- Perry, C. T. *et al.* Implications of reef ecosystem change for the stability and maintenance of coral reef islands. *Glob. Change Biol.* **17**, 3679–3696 (2011).
- Nicholls, R. J. & Cazenave, A. Sea-level rise and its impact on coastal zones. *Science* **329**, 1517–1520 (2010).
- Woodroffe, C. D. Reef-island topography and the vulnerability of atolls to sea-level rise. *Glob. Planet. Change* **62**, 77–96 (2008).
- Smith, S. & Kinsey, D. Calcium carbonate production, coral reef growth, and sea level change. *Science* **194**, 937–939 (1976).
- Grigg, R. Holocene coral reef accretion in Hawaii: a function of wave exposure and sea level history. *Coral Reefs* **17**, 263–272 (1998).
- Yates, K. K. & Halley, R. B. Diurnal variation in rates of calcification and carbonate sediment dissolution in Florida Bay. *Estuar. Coast.* **29**, 24–39 (2006).
- Andersson, A. J. *et al.* Net loss of CaCO₃ from a subtropical calcifying community due to seawater acidification: mesocosm-scale experimental evidence. *Biogeosciences* **6**, 1811–1823 (2009).
- Yates, K. & Halley, R. CO₂⁻³ concentration and pCO₂ thresholds for calcification and dissolution on the Molokai reef flat, Hawaii. *Biogeosci. Discuss.* **3**, 123–154 (2006).
- Silverman, J., Lazar, B. & Erez, J. Effect of aragonite saturation, temperature, and nutrients on the community calcification rate of a coral reef. *J. Geophys. Res. Oceans* **112**, C05004 (2007).
- Barnes, D. & Devereux, M. Productivity and calcification on a coral reef: A survey using pH and oxygen electrode techniques. *J. Exp. Mar. Biol. Ecol.* **79**, 213–231 (1984).
- Shamberger, K. E. F. *et al.* Calcification and organic production on a Hawaiian coral reef. *Mar. Chem.* **127**, 64–75 (2011).
- Morse, J. W., Zullig, J. J., Bernstein, L. D., Millero, F. J. & Milne, P. J. Chemistry of calcium carbonate-rich shallow water sediments in the Bahamas. *Am. J. Sci.* **285**, 147–185 (1985).
- Cyronak, T., Santos, I. R., McMahon, A. & Eyre, B. D. Carbon cycling hysteresis in permeable carbonate sands over a diel cycle: implications for ocean acidification. *Limnol. Oceanogr.* **58**, 131–143 (2013).
- Langdon, C. *et al.* Effect of elevated CO₂ on the community metabolism of an experimental coral reef. *Glob. Biogeochem. Cycles* **17**, 1011 (2003).
- Morse, J. W. & Arvidson, R. S. The dissolution kinetics of major sedimentary carbonate minerals. *Earth Sci. Rev.* **58**, 51–84 (2002).
- Comprehensive review focused on the chemical kinetics controlling the rates of reaction between sedimentary carbonate minerals and solutions.**
- Burdige, D. J. & Zimmerman, R. C. Impact of sea grass density on carbonate dissolution in Bahamian sediments. *Limnol. Oceanogr.* **47**, 1751–1763 (2002).
- Glynn, P. W. in *Life and Death of Coral Reefs* (ed. Birkeland, C.) 68–95 (Chapman Hall, 1997).
- Comprehensive review of coral reef bioerosion.**
- Reyes-Nivia, C., Diaz-Pulido, G., Kline, D., Guldberg, O.-H. & Dove, S. Ocean acidification and warming scenarios increase microbioerosion of coral skeletons. *Glob. Change Biol.* **19**, 1919–1929 (2013).
- Orr, J. C. *et al.* Anthropogenic ocean acidification over the twenty-first century and its impact on calcifying organisms. *Nature* **437**, 681–686 (2005).
- Land, L. S. Diagenesis of skeletal carbonates. *J. Sediment. Res.* **37**, 914–930 (1967).
- Nash, M. C. *et al.* Dolomite-rich coralline algae in reefs resist dissolution in acidified conditions. *Nature Clim. Change* **3**, 268–272 (2013).
- Andersson, A. J., MacKenzie, F. T. & Lerman, A. Coastal ocean and carbonate systems in the high CO₂ world of the Anthropocene. *Am. J. Sci.* **305**, 875–918 (2005).
- Dissolution of Mg-calcite mineral phases as the 'first responders' to ocean acidification.**

54. Morse, J. W., Andersson, A. J. & Mackenzie, F. T. Initial responses of carbonate-rich shelf sediments to rising atmospheric $p\text{CO}_2$ and "ocean acidification": role of high Mg-calcites. *Geochim. Cosmochim. Acta* **70**, 5814–5830 (2006).
55. Green, M. & Aller, R. C. Early diagenesis of calcium carbonate in Long Island Sound sediments: benthic fluxes of Ca^{2+} and minor elements during seasonal periods of net dissolution. *J. Mar. Res.* **59**, 769–794 (2001).
56. Tribble, G. W., Sansone, F. J. & Smith, S. V. Stoichiometric modeling of carbon diagenesis within a coral reef framework. *Geochim. Cosmochim. Acta* **54**, 2439–2449 (1990).
- Extensive study of biogeochemical processes within a reef framework showing that aerobic and anaerobic oxidation of organic matter dominates early diagenesis in a reef framework.**
57. Morse, J. W. & Mackenzie, F. T. *Geochemistry of Sedimentary Carbonates* (Elsevier Science and Technology, 1990).
- Comprehensive book addressing all aspects of sedimentary carbonate geochemistry.**
58. Ku, T. C. W., Walter, L. M., Coleman, M. L., Blake, R. E. & Martini, A. M. Coupling between sulfur recycling and syndepositional carbonate dissolution: evidence from oxygen and sulfur isotope composition of pore water sulfate, South Florida Platform, U.S.A. *Geochim. Cosmochim. Acta* **63**, 2529–2546 (1999).
59. Eyre, B. D., Glud, R. N. & Patten, N. Mass coral spawning: a natural large scale nutrient addition experiment. *Limnol. Oceanogr.* **53**, 997–1013 (2008).
60. Eyre, B. D., Santos, I. R. & Maher, D. T. Seasonal, daily and diel N₂ effluxes in permeable carbonate sediments. *Biogeosciences* **10**, 2601–2615 (2013).
61. Hu, X. & Cai, W. J. An assessment of ocean margin anaerobic processes on oceanic alkalinity budget. *Glob. Biogeochem. Cycles* **25**, GB3003 (2011).
62. Alongi, D. M., Trott, L. A. & Möhl, M. Strong tidal currents and labile organic matter stimulate benthic decomposition and carbonate fluxes on the southern Great Barrier Reef shelf. *Cont. Shelf Res.* **31**, 1384–1395 (2011).
63. Risgaard-Petersen, N., Revil, A., Meister, P. & Nielsen, L. P. Sulphur, iron, and calcium cycling associated with natural electric currents running through marine sediment. *Geochim. Cosmochim. Acta* **92**, 1–13 (2012).
64. Rao, A. M. F., Malkin, S. Y., Montserrat, F. & Meysman, F. J. R. Alkalinity production in intertidal sands intensified by lugworm bioirrigation. *Estuar. Coast. Shelf Sci.* **148**, 36–47 (2014).
65. Glud, R. N., Eyre, B. D. & Patten, N. Biogeochemical responses to mass coral spawning at the Great Barrier Reef: effects on respiration and primary production. *Limnol. Oceanogr.* **53**, 1014–1024 (2008).
66. Anthony, K. R. N., Diaz-Pulido, G., Verlinden, N., Tilbrook, B. & Andersson, A. J. Benthic buffers and boosters of ocean acidification on coral reefs. *Biogeosciences* **10**, 4897–4909 (2013).
67. Tribollet, A. in *Current Developments in Bioerosion* (eds Wisshak, M. & Tapanila, L.) 67–94 (Erlangen Earth Conference Series, Springer, 2008).
68. Neumann, A. C. Observations on coastal erosion in Bermuda and measurements of the boring rate of the sponge, *Cliona lampa*. *Limnol. Oceanogr.* **11**, 92–108 (1966).
69. Schneider, K. *et al.* Potential influence of sea cucumbers on coral reef CaCO_3 budget: a case study at One Tree Reef. *J. Geophys. Res.* **116**, G04032 (2011).
70. Reyes-Nivia, C., Diaz-Pulido, G. & Dove, S. Relative roles of endolithic algae and carbonate chemistry variability in the skeletal dissolution of crustose coralline algae. *Biogeosci. Discuss.* **11**, 2993–3021 (2014).
71. Fang, J. K. H. *et al.* Sponge biomass and bioerosion rates increase under ocean warming and acidification. *Glob. Change Biol.* **19**, 3581–3591 (2013).
72. van Woesik, R., van Woesik, K., van Woesik, L. & van Woesik, S. Effects of ocean acidification on the dissolution rates of reef-coral skeletons. *PeerJ* **1**, e208 (2013).
73. Peterson, M. N. A. Calcite: rates of dissolution in a vertical profile in the Central Pacific. *Science* **154**, 1542–1544 (1966).
74. Milliman, J. D. Dissolution of aragonite, Mg-calcite, and calcite in the North Atlantic Ocean. *Geology* **3**, 461–462 (1975).
75. Andersson, A., Bates, N. & Mackenzie, F. Dissolution of carbonate sediments under rising $p\text{CO}_2$ and ocean acidification: observations from Devil's Hole, Bermuda. *Aquat. Geochem.* **13**, 237–264 (2007).
76. Manzello, D. P. *et al.* Poorly cemented coral reefs of the eastern tropical Pacific: Possible insights into reef development in a high- CO_2 world. *Proc. Natl Acad. Sci. USA* **105**, 10450–10455 (2008).
77. Fabricius, K. E. *et al.* Losers and winners in coral reefs acclimatized to elevated carbon dioxide concentrations. *Nature Clim. Change* **1**, 165–169 (2011).
78. Hall-Spencer, J. M. *et al.* Volcanic carbon dioxide vents show ecosystem effects of ocean acidification. *Nature* **454**, 96–99 (2008).
79. Fabricius, K. E. Effects of terrestrial runoff on the ecology of corals and coral reefs: Review and synthesis. *Mar. Pollut. Bull.* **50**, 125–146 (2005).
80. Silverman, J. *et al.* Carbon turnover rates in the One Tree Island reef: A 40-year perspective. *J. Geophys. Res. Biogeosci.* **117**, G03023 (2012).
81. Walter, L. M. & Burton, E. A. The effect of orthophosphate on carbonate mineral dissolution rates in seawater. *Chem. Geol.* **56**, 313–323 (1986).
82. Brodie, J., Fabricius, K., De'ath, G. & Okaji, K. Are increased nutrient inputs responsible for more outbreaks of crown-of-thorns starfish? An appraisal of the evidence. *Mar. Pollut. Bull.* **51**, 266–278 (2005).
83. Cyronak, T., Santos, I. R., Schulz, K. G. & Eyre, B. D. Enhanced coral reef acidification driven by regional biogeochemical feedbacks. *Geophys. Res. Lett.* **41**, 5538–5546 (2014).
84. Hoegh-Guldberg, O. *et al.* Coral reefs under rapid climate change and ocean acidification. *Science* **318**, 1737–1742 (2007).
85. Kayanne, H. *et al.* Seasonal and bleaching-induced changes in coral reef metabolism and CO_2 flux. *Glob. Biogeochem. Cycles* **19**, 1–11 (2005).
86. Holland, G. J. & Webster, P. J. Heightened tropical cyclone activity in the North Atlantic: Natural variability or climate trend? *Phil. Trans. R. Soc. A* **365**, 2695–2716 (2007).
87. Gray, S. E. C., DeGrandpre, M. D., Langdon, C. & Corredor, J. E. Short-term and seasonal pH, $p\text{CO}_2$ and saturation state variability in a coral-reef ecosystem. *Glob. Biogeochem. Cycles* **26**, GB3012 (2012).
88. Manzello, D., Enochs, I., Musielewicz, S., Carlton, R. & Gledhill, D. Tropical cyclones cause CaCO_3 undersaturation of coral reef seawater in a high- CO_2 world. *J. Geophys. Res. Oceans* **118**, 5312–5321 (2013).
89. Hughes, T. P., Graham, N. A. J., Jackson, J. B. C., Mumby, P. J. & Steneck, R. S. Rising to the challenge of sustaining coral reef resilience. *Trend. Ecol. Evol.* **25**, 633–642 (2010).
90. Kleypas, J. A., Anthony, K. R. N. & Gattuso, J.-P. Coral reefs modify their seawater carbon chemistry — case study from a barrier reef (Moorea, French Polynesia). *Glob. Change Biol.* **17**, 3667–3678 (2011).
91. Anthony, K. R. N., Kleypas, J. A. & Gattuso, J.-P. Coral reefs modify their seawater carbon chemistry — implications for impacts of ocean acidification. *Glob. Change Biol.* **17**, 3655–3666 (2011).
92. Andersson, A. J. & Mackenzie, F. T. Revisiting four scientific debates in ocean acidification research. *Biogeosciences* **9**, 893–905 (2012).
93. Balzer, W. & Wefer, G. Dissolution of carbonate minerals in a subtropical shallow marine environment. *Mar. Chem.* **10**, 545–558 (1981).
94. Yates, K. & Halley, R. Measuring coral reef community metabolism using new benthic chamber technology. *Coral Reefs* **22**, 247–255 (2003).
95. Anthony, K., Diaz-Pulido, G., Verlinden, N., Tilbrook, B. & Andersson, A. Benthic buffers and boosters of ocean acidification on coral reefs. *Biogeosci. Discuss.* **10**, 1831–1865 (2013).
96. Rao, A. M. F., Polerecky, L., Ionescu, D., Meysman, F. J. R. & de Beer, D. The influence of pore-water advection, benthic photosynthesis, and respiration on calcium carbonate dynamics in reef sands. *Limnol. Oceanogr.* **57**, 809–825 (2012).
97. Leclercq, N., Gattuso, J. P. & Jaubert, J. Primary production, respiration, and calcification of a coral reef mesocosm under increased CO_2 partial pressure. *Limnol. Oceanogr.* **47**, 558–564 (2002).
98. Boucher, G., Clavier, J., Hily, C. & Gattuso, J. Contribution of soft-bottoms to the community metabolism (primary production and calcification) of a barrier reef flat (Moorea, French Polynesia). *J. Exp. Biol. Ecol.* **225**, 269–283 (1998).

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Author contributions

B.D.E. and A.J.A. conceived the review. All authors contributed to the writing of the manuscript.

Additional information

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Competing financial interests

The authors declare no competing financial interests.