

Millennial-scale ocean acidification and late Quaternary decline of cryptic bacterial crusts in tropical reefs

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ABSTRACT

Ocean acidification by atmospheric carbon dioxide has increased almost continuously since the last glacial maximum (LGM), 21 000 years ago. It is expected to impair tropical reef development, but effects on reefs at the present day and in the recent past have proved difficult to evaluate. We present evidence that acidification has already significantly reduced the formation of calcified bacterial crusts in tropical reefs. Unlike major reef builders such as coralline algae and corals that more closely control their calcification, bacterial calcification is very sensitive to ambient changes in carbonate chemistry. Bacterial crusts in reef cavities have declined in thickness over the past 14 000 years with largest reduction occurring 12 000–10 000 years ago. We interpret this as an early effect of deglacial ocean acidification on reef calcification and infer that similar crusts were likely to have been thicker when seawater carbonate saturation was increased during earlier glacial intervals, and thinner during interglacials. These changes in crust thickness could have substantially affected reef development over glacial cycles, as rigid crusts significantly strengthen framework and their reduction would have increased the susceptibility of reefs to biological and physical erosion. Bacterial crust decline reveals previously unrecognized millennial-scale acidification effects on tropical reefs. This directs attention to the role of crusts in reef formation and the ability of bioinduced calcification to reflect changes in seawater chemistry. It also provides a long-term context for assessing anticipated anthropogenic effects.

Received 25 January 2014; accepted 17 June 2014

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INTRODUCTION

Carbon dioxide (CO₂) released to the atmosphere can raise global temperature and increase ocean acidification (Doney *et al.*, 2009). Acidification occurs as atmospheric CO₂ dissolves in surface seawater (Raven *et al.*, 2005). As this increases the solubility of CaCO₃ minerals, it could influence biocalcification in marine organisms (Gattuso *et al.*, 1995; Feely *et al.*, 2004; Andersson *et al.*, 2011), including tropical reef formation (Kleypas *et al.*, 1999, 2006; Langdon *et al.*, 2000; Hoegh-Guldberg *et al.*, 2007; Pandolfi *et al.*, 2011; Andersson & Gledhill, 2013). However, evaluating these effects has proved to be challenging. The responses of calcifying organisms to increased CO₂ and lower pH are often complex (Delille *et al.*, 2005; Langer *et al.*, 2006; Anthony *et al.*, 2008; Ries *et al.*, 2009; Erez *et al.*, 2011; McCulloch *et al.*, 2012; Andersson &

Gledhill, 2013; Venn *et al.*, 2013) and can be difficult to evaluate with confidence (De'ath *et al.*, 2009), especially in relatively short-term experiments and mesoscale studies (Boyd & Doney, 2002; Andersson & Mackenzie, 2011; Andersson *et al.*, 2011). The responses of calcified organisms to acidification in part reflect differences in biocalcification processes, particularly the degree of control that the organisms exert. Whereas dominant framebuilders in present-day tropical reefs, such as scleractinian corals and crustose coralline red algae can closely direct the precipitation of their skeletons, less controlled bioinduced calcification, for example, in bacteria, is much more susceptible to environmental influence. Progressive acidification should therefore affect bioinduced calcification sooner than more controlled calcification, providing an early indicator of long-term change in seawater chemistry (Riding *et al.*, 2011). To explore this, we examined heavily calcified

bacterial crusts (Fig. 1) in tropical coral reefs and compared changes in their thickness over the past 14.5 thousand years (ka) with computed changes in surface tropical ocean pH for the same period. Our results show that bacterial crusts in reef cavities have declined significantly in thickness since ~12 ka ago. We attribute this decline to millennial-scale ‘natural’ ocean acidification. In contrast, acidification does not appear to have affected biocontrolled reef builders such as corals until the present day. This

suggests that bioinduced bacterial calcification is a sensitive indicator of early changes in ocean acidification that long predate anthropogenic influence.

Biocalcification

Many algae and invertebrates use aragonite and/or calcite (CaCO_3) to construct their skeletons, and bacteria can also promote precipitation of these minerals

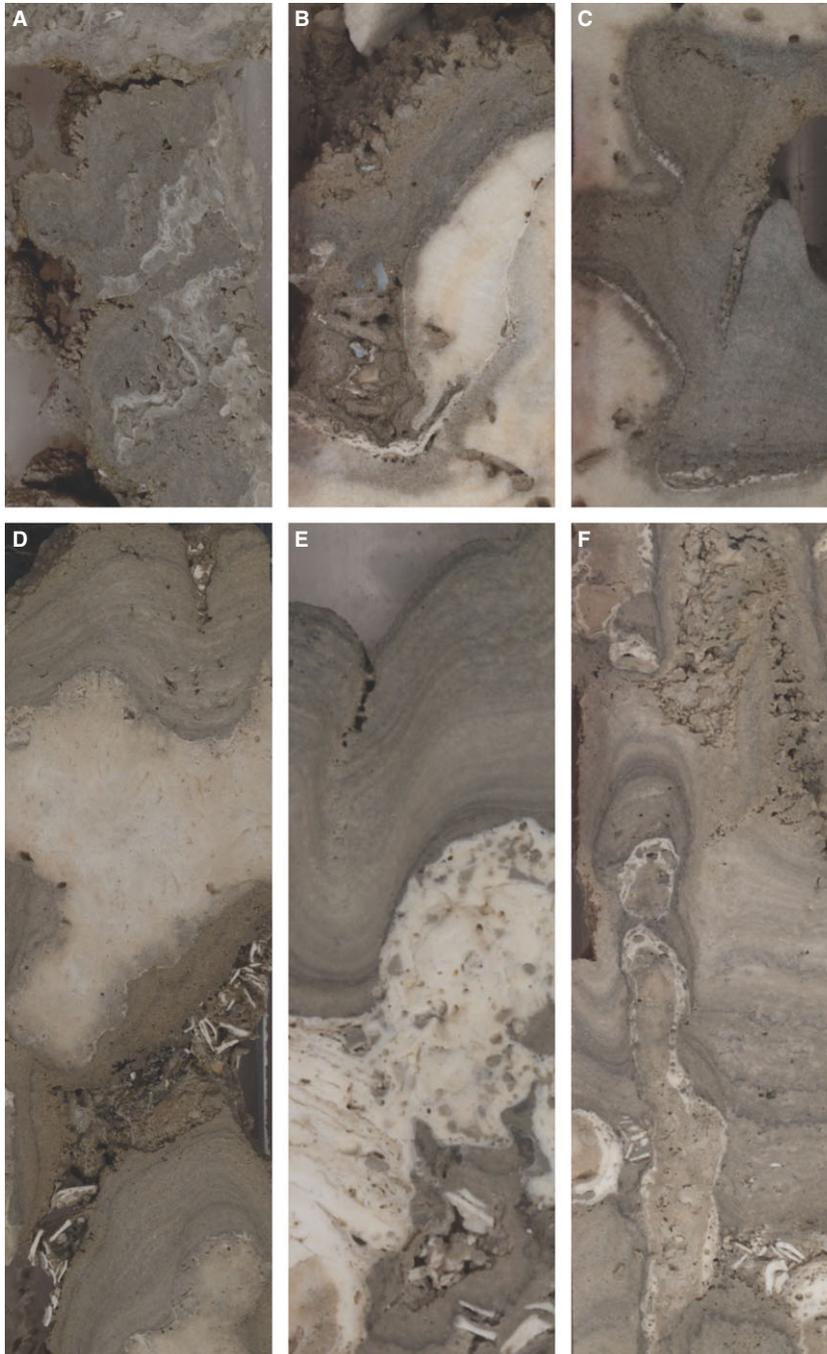


Fig. 1 Gray bacterial crusts on lighter colored coral and coralline algal reef framework and bioclastic debris in IODP Expedition 310 cores through latest Pleistocene–Early Holocene reef rock at Mara’a, SW Tahiti. Sample ages increase from A to F. (A) Irregularly layered locally dendritic crusts on finely branching and encrusting corals (paler gray) and coralline algae (white). IODP core image 310-M0007A-14R-01_21-30; age is slightly younger than 10 ka; width of view 4.5 cm. (B) Irregular crust, binding and encrusting debris (lower part) and *Porites*, and grading in the upper part from layered to dendritic fabric. IODP core image 310-M0007A-18R-01_61-70; age 10 ka; width of view 4.5 cm. (C) Crust filling cavity beside coral ranges from delicately layered (lower right) to dendritic and porous (upper right). 310-M0007B-21R-01_20-30; age 11.1 ka; width of view 6 cm. (D) Laminated crusts occluding framework cavity between *Acropora*; in the lower part, the crust rigidly binds bioclasts including white *Halimeda* segments. IODP core image 310-M0007A-29R-01_0-14; age ~12 ka, width of view 6 cm. (E) Smooth and delicately layered domical crust (top) veneering underlying coralline algae (white), and (bottom) binding *Halimeda* segments. 310-M0017A-18R-02_30-38; age 12.2 ka; width of view 2.5 cm. (F) Laminated crust, becoming dendritic near top, thickly veneering vertical coral branch (lower left) and coralline algae (white). IODP core image 310-M0005D-2R-01_47-63; age 12.4 ka; width of view 5 cm. Image numbers indicate expedition, hole, core, section, and interval. Original images available at <http://sedis.iodp.org/>. © IODP/ECORD.

(Leadbeater & Riding, 1986; Lowenstam & Weiner, 1989). The extent to which organisms control calcification ranges from poorly to closely regulated, and these end-members have been characterized as 'bioinduced' and 'biocontrolled' calcification, respectively (Lowenstam, 1981; Mann, 2001). These diverse processes are still being elucidated, and the terminology used in biocalcification and biomineralization studies continues to evolve. In addition to 'bioinduced' and 'biocontrolled', researchers examining how organic macromolecules and environmental conditions interact to influence mineralization have suggested 'organomineralization' (Trichet & Défarge, 1995) and 'organomineral' (Défarge & Trichet, 1995; Perry *et al.*, 2007), and 'biologically influenced mineralization' (Dupraz *et al.*, 2009; Perito & Mastromei, 2011); sometimes prompting spirited debate (Altermann *et al.*, 2009; Défarge *et al.*, 2009, 2010; Perry & Sephton, 2009). Reef-building coralline algae (Kamenos *et al.*, 2013) and invertebrates, including corals (Puvrel *et al.*, 2005; Allemand *et al.*, 2011; Moya *et al.*, 2012), display relatively controlled calcification (Orr *et al.*, 2005; Kleypas *et al.*, 2006). In contrast, bioinduced calcification is much less closely regulated, making it sensitive to changes in seawater carbonate chemistry (Kleypas *et al.*, 2006). The particular influence of ambient water chemistry on bacterial carbonates is reflected in their environmental distribution at the present day and by their secular abundance over geological time (Riding, 1982, 1992, 1993; Grotzinger, 1990; Grotzinger & Kasting, 1993; Webb, 2001; Konhauser & Riding, 2012).

Bacterial crusts

Bacterial carbonates (e.g., stromatolites) were important reef builders long before eukaryotes appeared (Hofmann, 2000). During the past 500 Ma, they are common in algal and invertebrate reefs (Pratt, 1982) and persist today in tropical reefs that have colonized shallow-water environments as sea level rose following the last glacial maximum 21 ka ago (Camoin *et al.*, 2012). Whereas the illuminated surfaces of these reefs are typically occupied by corals and algae, the bacterial carbonates form as late-stage veneers on the walls of cavities within the skeletal framework (Camoin *et al.*, 1999, 2006, 2012; Riding, 2011; Seard *et al.*, 2011). Initial studies drew attention to the importance of these rigid crusts for the synsedimentary lithification of Holocene reefs in the Caribbean (Macintyre *et al.*, 1968; Land & Goreau, 1970; Macintyre, 1977) and Great Barrier Reef (Marshall & Davies, 1981; Marshall, 1983). They played a similar sedimentological role in the late Miocene of the Mediterranean (Pedley, 1979; Riding *et al.*, 1991), during the Pleistocene–Holocene transition at Tahiti, French Polynesia (Montaggioni & Camoin, 1993), and in the Indian Ocean (Camoin *et al.*, 2004;

Gischler *et al.*, 2008). They also occur in submarine caves (Macintyre, 1984; Reitner, 1993; Zankl, 1993; Reitner *et al.*, 2000; Guido *et al.*, 2013) and on deep fore-reef slopes (Camoin *et al.*, 2006; Webster *et al.*, 2009).

These reefal bacterial crusts are typically millimetric to centimetric in thickness, exceptionally 20 cm (Camoin *et al.*, 1999), with smoothly domical to irregularly 'knobby', microcolumnar or complex dendritic external morphologies, and aphanitic to patchy or delicately laminated internal macrofabric (e.g., Land, 1971; Macintyre, 1977; Marshall, 1986; Sherman *et al.*, 1999; Webb *et al.*, 1999; Camoin *et al.*, 1999, 2006; Cabioch *et al.*, 2006, p. 304; Fig. 1). In thin section, they have a distinctive gray to brown clotted microfabric (Camoin *et al.*, 2007; Westphal *et al.*, 2010) with silt-size, apparently autochthonous, peloids distributed within a microsparitic, locally fenestral, microfabric that has an overall grainstone appearance (Riding & Tomás, 2006).

Reefal bacterial crusts in late Neogene reefs have variously been termed cements (Macintyre *et al.*, 1968; James *et al.*, 1976; Lighty *et al.*, 1985; Macintyre, 1985), stromatolites (Riding *et al.*, 1991), microbialites (Cabioch *et al.*, 1999b; Camoin *et al.*, 1999), and thrombolites (Brachert & Dullo, 1991; Camoin *et al.*, 2006). They appear to be invariably composed of magnesian calcite, typically in the range 12–18 mole % MgCO₃ (Macintyre *et al.*, 1968; Land & Goreau, 1970; Macintyre, 1977, 1984; Camoin *et al.*, 1999), and preferentially develop in cavities on high-energy reef margins (Macintyre, 1977; p. 513; Marshall & Davies, 1981; Marshall, 1983; Montaggioni & Camoin, 1993; Camoin & Montaggioni, 1994; Cabioch *et al.*, 1999a; Seard *et al.*, 2011) where they typically constitute a late, often the last, stage of reef growth. They contain abundant biomarkers with intermediate-to-high specificity for sulfate-reducing bacteria, whereas biomarkers indicative of cyanobacteria are absent (Heindel *et al.*, 2010, 2012), confirming earlier suggestions of sulfate reduction from Jamaica (Land & Goreau, 1970; Pigott & Land, 1986), the Caribbean and Australia (Reitner *et al.*, 2000), Bahamas (Malone *et al.*, 2001), and Tahiti (Camoin *et al.*, 1999). Drill cores through ~90 m of post-glacial (<~14 ka) reef deposits at Papeete in NW Tahiti have revealed that whereas bacterial crusts are abundant in the older part of the succession (~12 ka ago), they are scarce or absent after ~6 ka ago (Camoin *et al.*, 1999). Subsequent IODP Expedition 310 drilling at Mara'a and Tiarei (in SW and N Tahiti, respectively) has provided a millennial-scale record of bacterial crusts through the reefs since the latest Pleistocene (Camoin *et al.*, 2007).

Ocean acidification

Variation in ocean pH is a natural part of glacial cycles, with pH being higher during glacials and lower during

interglacials (Archer & Meier-Reimer, 1994; Sanyal *et al.*, 1995). These changes are linked to fluctuations in atmospheric CO₂ (Peacock *et al.*, 2006; Anderson *et al.*, 2009; Sigman *et al.*, 2010). Analyses of air bubbles preserved in Antarctic ice reveal significant fluctuations in global atmospheric CO₂ level over the past 800 ka, with lower levels during glacial periods and higher levels during interglacials (Lüthi *et al.*, 2008). In the course of the deglaciation of the past 21 ka, CO₂ increased from 184 to 265 ppmv between 21 and 9 ka ago in the Concordia Dome ice core (Monnin *et al.*, 2001) and from 265 to 283 ppmv between 11.1 ka and 390 years ago in the Taylor Dome ice core (Indermühle *et al.*, 1999). Subsequent rise to the current global CO₂ level of ~395 ppmv is attributed to fossil fuel burning (Quay *et al.*, 1992; Feely *et al.*, 2004). Progressive dissolution of this additional atmospheric CO₂ in seawater should increase acidity, lowering ocean pH and carbonate saturation state (Ω) (Broecker *et al.*, 1971, 1979; Takahashi, 1979). Evidence that deglacial increase in atmospheric carbon dioxide has caused millennial-scale ocean acidification (Caldeira & Wickett, 2003) is supported by boron isotopes in foraminifer shells that indicate repeated pH fluctuation during glacial–interglacial cycles of the past 2.1 million years (Ma), with higher glacial and lower interglacial values (Hönisch & Hemming, 2005; Hönisch *et al.*, 2009).

MATERIAL AND METHODS

Reef crust thickness measurement

We obtained bacterial crust thickness data for the past 16.1 ka from Tahiti and more limited Global published data for the past 11.5 ka for localities elsewhere in the Pacific and in the Indian Ocean and Caribbean (Fig. 2).

Tahiti sites

We measured maximum crust thicknesses (see Table S1) in photographs of offshore cores. These cores were drilled through submerged reef intervals by Integrated Ocean Drilling Program (IODP) Expedition 310 ‘Tahiti Sea Level’ at Tahiti in October–November 2005 (Camoin *et al.*, 2007). High-resolution core images can be accessed at the IODP archive <http://sedis.iodp.org/> (Scientific Earth Drilling Information Service—SEDIS). To locate the images for the cores from IODP Expedition 310, under ‘search’, follow ‘Project/Expedition/Site/Hole’ (IODP, 310). Image numbers indicate expedition, hole, core, section, and interval. For example, number 310-M0017A-18R-02_30-38 indicates 310 (expedition), M0017A (hole), 18R (core), 02 (section), 30–38 (interval in cm from top of section).

IODP Expedition 310 drilled between 2 and 13 holes in each of three offshore areas around Tahiti. The cores are 65 mm in diameter. The reef sediments of the Last Deglaciation were penetrated by 16 cores that range in depth from 45 to 122 m below present-day sea level and in age from ~5.9 to 16.1 ka ago. We measured bacterial crusts in the following cores from two of these areas for which there are numerous dates at various levels (Abbey *et al.*, 2011; Camoin *et al.*, 2012; Deschamps *et al.*, 2012):

Maraa: M0005A, M0005C, M0005D, M0007A, M0007B, M0015A, M0015B, M0016A, M0016B, M0017A, and M0018A

Tiarei: M0009B, M0009C, M0009D, M0021A, M0021B, M0023A, M0023B, M0024A, M0025B

Details of these boreholes, cores, and ages are given in Camoin *et al.* (2007, 2012), Westphal *et al.* (2010), Abbey *et al.* (2011, figs. 4, 5), and Deschamps *et al.* (2012, fig. S1).

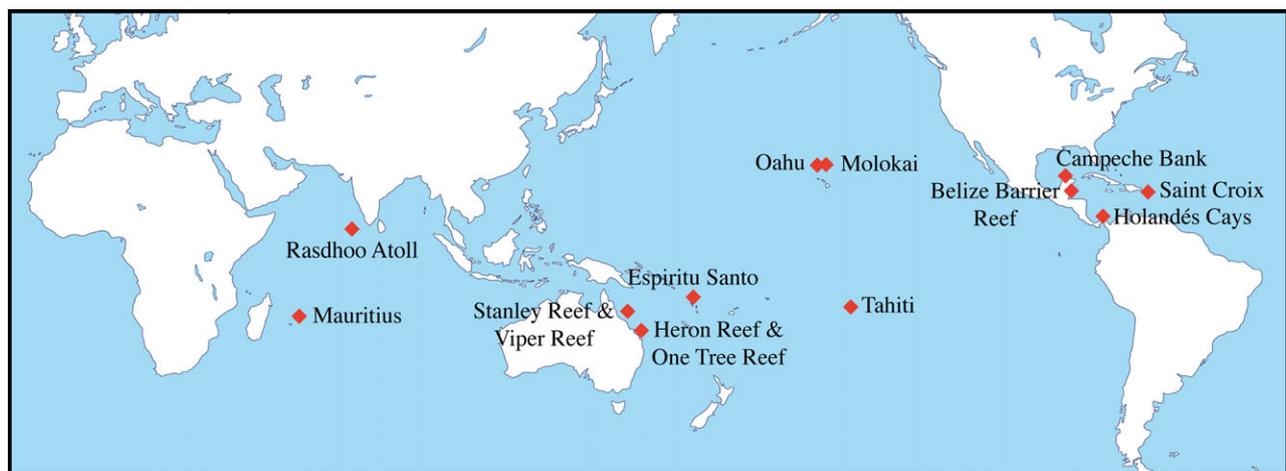


Fig. 2 Reef localities from which the crust thickness data in Fig. 3 were compiled (see Table S2).

We constrained crust ages in the data we collected (Table S1) by only measuring crusts in cores with dated horizons (see Abbey *et al.*, 2011; table 4, figs. 4 and 5; Camoin *et al.*, 2012; fig. 1a; Deschamps *et al.*, 2012; table S2). The ages provided by Abbey *et al.* (2011) were obtained by radiocarbon dating of corals and coralline algae, those provided by Camoin *et al.* (2012) by radiocarbon and U/Th radiometric dating of corals, and those of Deschamps *et al.* (2012) by U/Th radiometric dating of corals.

Global tropical sites

We compiled crust thicknesses from published descriptions of reefs in the Caribbean, Indian Ocean, and Pacific (other than Tahiti; Fig. 2; for data sources see Table S2).

Seawater chemistry

Calculations, past 21 ka

We calculated pH, dissolved inorganic carbon, and saturation states for calcite and aragonite for surface seawater at Tahiti over the past 21 ka using CO2SYS (version 2.1, 18 September 2012: CO2Sys_v2.1.xls), a computer code developed for CO₂ system calculations (Pierrot *et al.*, 2006). We based CO₂ partial pressure data (pCO₂) on atmospheric values indicated by ice core records (Indermühle *et al.*, 1999; Monnin *et al.*, 2001). We took Tahiti seawater surface salinity to be 36.2‰ at the present day (Gouriou & Delcroix, 2002) and 37.3‰ 21 ka ago, that is, 3‰ saltier than present day due to ice formation, as indicated by lower sea level (Sigman & Boyle, 2000). Average present-day sea-surface temperature at Tahiti is 27 °C (Ballantyne *et al.*, 2005), and estimates for the equatorial Pacific during the last glacial maximum (LGM) range from -1 to -3 °C (Lea *et al.*, 2000) of present-day values. Present-day average surface seawater has a total alkalinity of 2400 µmol kg⁻¹ corresponding to salinity of 35‰ (DOE, 1994). We projected this alkalinity to 2482 µmol kg⁻¹ for present-day salinity of 36.2‰ at Tahiti. We then allowed alkalinity to increase linearly to 3‰ higher at 21 ka ago, following the salinity trend. The carbonate system is well defined by the two given parameters of total alkalinity and pCO₂ out of the four system variables: total inorganic carbon, alkalinity, pH, and pCO₂ (Stumm & Morgan, 1996).

Under chemical equilibrium conditions, saturation state (Ω) for CaCO₃ minerals is determined by the activity products over the solubility constants (K_{CaCO_3}) of carbonate minerals: $\Omega = (Ca^{2+})(CO_3^{2-})/K_{CaCO_3}$, where K_{CaCO_3} differs for aragonite and calcite, and the data are from Mucci (1983) as implemented in CO2SYS. The concentration of calcium is calculated from the seawater composition (Table S3) and the corresponding salinity. Carbonate concentrations are calculated from the total CO₂, pH, and

the dissociation constants for carbonic acid. The values of Henry's law constant for CO₂ (K_H), equilibrium constants for carbonic acid (K_{a1} , K_{a2}), other constants for species, such as sulfate, phosphate, silicate, as well as calcium carbonate equilibrium constants ($K_{calcite}$ and $K_{aragonite}$) and their corresponding corrections for pressure and temperature, are incorporated in CO2SYS (Pierrot *et al.*, 2006). We selected the K_{a1} and K_{a2} values from K_{so4} (Millero, 2010), from Dickson (1990), and the total boron sources from Lee *et al.* (2010). The pH values reported here are based on the seawater scale. No pressure effects were considered, as calculations are for surface seawater. Previously (Riding *et al.*, 2011), we used PHREEQC code (Parkhurst & Appelo, 1999) to calculate carbonate speciation, pH, and saturation states of carbonate minerals. During the current study, we initially used both PHREEQC and CO2SYS (Pierrot *et al.*, 2006) and verified that, with the same input data, we produced the same outputs regardless of the code. Here, we present our results calculated using CO2SYS as this computer program can be easily implemented and the results compared with previously published work (Kleypas *et al.*, 2006).

Calculations, past 414 ka

In calculating the data shown in Fig. 6 (surface ocean fluctuations in pH and calcite saturation for the past 414 ka), we used CO2SYS (version 2.1, 18 September 2012: CO2Sys_v2.1.xls; Pierrot *et al.*, 2006) with CO₂ values from the Vostok ice core (Petit *et al.*, 1999; http://www.ncdc.noaa.gov/paleo/icecore/antarctica/vostok/vostok_co2.html), assuming average seawater surface salinity of 36.7‰, average sea-surface temperature of 25.5 °C, and average alkalinity of 2518 (µmol kg⁻¹ seawater) throughout. In this basic rendition of the concept, pH and calcite saturation have the same curve. The calculation shows a pH range of 8.18–8.31, a difference of 0.13, similar to the results of Hönisch & Hemming (2005).

RESULTS

Tahiti data

The core record commences ~16.1 ka ago and terminates ~3 ka ago (Camoin *et al.*, 1999; fig. 3). The sediments in these cores mainly comprise reef frameworks of corals encrusted by coralline algae, foraminifers, vermetids, bryozoans, and serpulids that formed at depositional depths of <10 to >20–30 m (Abbey *et al.*, 2011). The skeletal framework was subsequently commonly internally veneered by bacterial crust which partially or almost completely filled primary cavities. Locally, it constitutes the major volumetric component of the reef rock (Searid *et al.*, 2011).

Between 16.1 and 14.5 ka ago, the main reef builders at these locations were massive corals comprising two main

coral assemblages: (i) massive *Porites*, and (ii) robust *Pocillopora* and massive *Montipora* (Westphal *et al.*, 2010; Abbey *et al.*, 2011; Camoin *et al.*, 2012). Reef cavities around the massive corals were small. This reef structure limited crust development, and maximum crust thicknesses in this initial interval of reef growth are correspondingly relatively low, mostly <5 cm (Fig. 3A). In the reef deposits younger than ~14.6 ka, the dominance of branching colonies in the coral assemblages created cavernous structures in which crusts had more space to grow (Camoin *et al.*, 2012). These coral assemblages include (i) branching *Acropora*, (ii) branching *Porites* and *Pocillopora*, and (iii) branching *Porites* and encrusting *Porites* and *Montipora* (Camoin *et al.*, 2012). These frameworks persist today (Cabioch *et al.*, 1999a), although the reef framework at the top of most of the holes is built by encrusting corals (agariciids and faviids) together with thin coralline algal crusts. These are deepwater assemblages that reflect deepening at each site that preceded final ‘drowning’ that terminated reef growth as sea level rose (Westphal *et al.*, 2010; Camoin *et al.*, 2012). We therefore focus on the

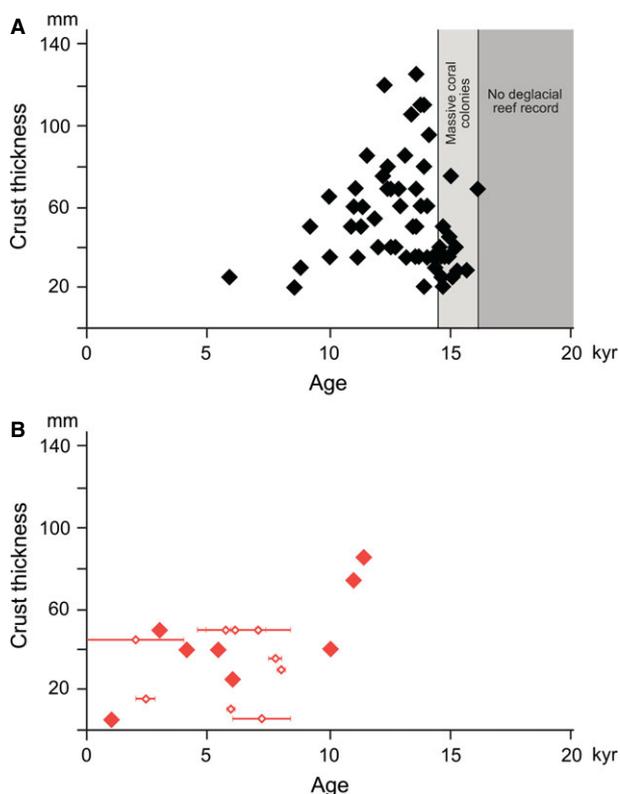


Fig. 3 Bacterial crust thicknesses. (A) Tahiti, measured from IODP Expedition 310 cores with known ages (Abbey *et al.*, 2011; Camoin *et al.*, 2012). Cavernous reef framework began to develop in these cores ~14.6 ka ago. (B) Other Pacific, Atlantic, and Indian Ocean reefs. Small open symbols with bars indicate samples whose age ranges are poorly constrained (see Supporting Information).

record of cavernous reef framework that commenced ~14.6 ka ago, about one-third of the way into the current deglaciation and that continues in the drill core until 3 ka ago. Our data show that maximum crust thickness was 12.5 cm 14 ka ago and 12 cm 12.5 ka ago, then declined steeply to 2 cm 8.5 ka ago, followed by slight increase to 2.5 cm 5.9 ka ago. After 5.9 ka, no bacterial reef crusts have been reported from the uppermost core-sections, which end ~3 ka ago (Searid *et al.*, 2011; Camoin *et al.*, 1999; fig. 3; Abbey *et al.*, 2011).

Global tropical data

The exceptional dataset provided by the continuous and well-dated Tahiti drill core described above is currently unmatched elsewhere. Deglacial reefs worldwide are mostly submerged due to continued sea level rise. As a result, apart from Tahiti, crust observations are scarce and, in addition, they commonly lack accurate thickness records and are commonly poorly dated. Nonetheless, the well-dated global crust thickness values that we have located show a distinct trend (Fig. 3B). These data show a maximum crust thickness of 8.7 cm 12 ka ago, steep decline to 3 cm 10 ka ago, slight increase to a plateau near ~5 cm from 7.5 to 3 ka ago, and then steep decline to 0.5 cm 1 ka ago.

Surface seawater calculated chemical values

We computed separate pH and saturation trends for LGM (21 ka) temperatures of 24 °C and of 26 °C, relative to the present day 27 °C at Tahiti. Changes in seawater composition were calculated based on salinity variation, that is, with total elemental composition corresponding to salinity change. The results are shown in Fig. 4b. In the Supplementary Information, they are also plotted without scale-breaks, to show pH variation (Fig. S1) and carbonate saturation states for calcite and aragonite (Fig. S2) over the last 21 ka.

Our calculations indicate pH decline from ~8.35 to 8.18, as p_{CO_2} increased from 21 ka to 390 years ago (Fig. 4B). During the corresponding period, Ω_{calcite} decreased from 9.35 to 7.44, and $\Omega_{\text{aragonite}}$ from 6.16 to 4.94. These calculated results are based on LGM temperatures of 24 °C 21 ka ago (Lea *et al.*, 2000). A temperature of 26 °C at the LGM (Ballantyne *et al.*, 2005) yielded slightly different starting values (pH 8.32, Ω_{calcite} 9.38, $\Omega_{\text{aragonite}}$ 6.22) but similar trends (Fig. 4B).

Overall, these pH and carbonate saturation trends exhibit steep decline from 17 to 11 ka ago, with a pause ~14 to 12 ka ago and slight recovery 11 to 7 ka ago, then gradual decline to pre-industrial levels 390 years ago. Subsequent pH and Ω values both show sharp decline to the present day (Fig. 4B).

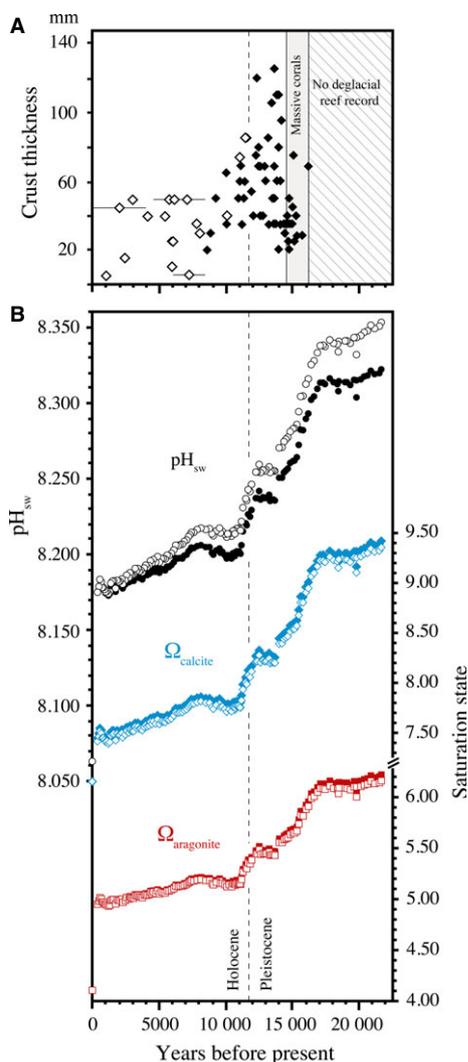


Fig. 4 A: Crust thicknesses at Tahiti (filled diamonds, from Fig. 3), and from Global localities (open diamonds). B: Calculated chemical parameters for surface seawater at Tahiti over the past 21 ka: pH (based on seawater scale; black symbols), carbonate saturation states of calcite (blue symbols), and aragonite (red symbols). These show decreasing trends in response to increase in atmospheric CO₂ since the last glacial maximum (Indermühle *et al.*, 1999; Monnin *et al.*, 2001). Calculations are based on Tahiti present-day seawater surface data (salinity 36.2‰, temperature 27 °C). At the LGM (21 ka ago), 3% higher salinity and 3 °C lower temperature values are assumed (Lea *et al.*, 2000) than at the present day, and data calculated with this LGM temperature (24 °C) are shown by open symbols. Data calculated with a temperature of 26 °C at the LGM (Ballantyne *et al.*, 2005) are shown by filled symbols. At time 0, note low present-day pH and saturation state values (left-hand margin). For details, see Methods and Results.

COMPARISON OF RESULTS

We compared calculated surface seawater calcite saturation (Ω) values (Fig. 4B) with the maximum crust thickness measured in cores with dated horizons from Tahiti, and also with the thicknesses from published descriptions of reefs in the Caribbean, Indian Ocean, and Pacific (other

than Tahiti; Fig. 4A). The best correlation is obtained using Ω values calculated with 26 °C starting temperatures. For the combined data from Tahiti and elsewhere, a two-tailed Pearson's correlation between maximum crust thickness and calculated omega calcite (based on LGM 26 °C) values shows a direct, significant relationship ($r = 0.621$, $P < 0.01$, $n = 44$).

Our calculated values for surface seawater pH and carbonate saturation show a declining trend from ~17 to 10 ka ago (Fig. 4B). We have no crust thickness data from cavernous reef framework until ~14.6 ka ago, and there is no decline in crust thickness until 11–12 ka ago, near the Pleistocene–Holocene boundary (11.7 ka ago; Fig. 4A). Our combined data (Fig. 4A,B) indicate three stages; (i) Decline in maximum crust thickness from 12 cm 12.5 ka ago to 5 cm 9 ka ago, with steepest decline from 12.5 to 11 ka ago, as Ω_{calcite} fell from 8.3 to 7.8 and pH decreased by 0.04 units. This decline commenced during the Younger Dryas and coincides with a period of increased rate of CO₂ rise that has been linked to strengthening of southern hemisphere westerly winds (Mayr *et al.*, 2013); (ii) relative stability, with moderate calcification (thicknesses near 5 cm) and Ω_{calcite} between 7.4 and 7.9, from 9 to 2 ka ago; (iii) either continued stability, or possibly further decline to the present day. Data are scarce, but at the present day, bacterial crusts in tropical reef cavities appear to be generally thin or absent, coincident with values of tropical surface seawater pH (8.06), Ω_{calcite} (6.17), and $\Omega_{\text{aragonite}}$ (4.10) that are the lowest of the past 21 ka.

These similarities between secular patterns of crust thickness and calculated carbonate saturation and pH for the past ~14 ka, together with evidence that these changes were widespread in the tropical realm, are consistent with the interpretation that deglacial decline in reefal microbial crusts reflects progressive ocean acidification (Riding *et al.*, 2011). Although crust thickness is significantly reduced near the Pleistocene–Holocene transition, no corresponding changes in coral calcification have been reported. The Tahiti post-glacial reef record since ~14.1 ka is commensurate with vigorous coral growth. The fauna includes abundant acroporids, regarded as typical of healthy reefs (Cabiocch *et al.*, 1999a; Abbey *et al.*, 2011; Camoin *et al.*, 2012). Evidence of significant decline in bacterial crust thickness during this interval, long before observed effects on biocontrolled calcification, therefore suggests bioinduced bacterial calcification as an early indicator of ocean acidification.

DISCUSSION

Seawater carbonate chemistry

Our calculated pre-industrial (390 years ago) saturation values of surface seawater at Tahiti are $\Omega_{\text{aragonite}}$ 4.94 and

Ω_{calcite} 7.44 (Fig. 4B). These are compatible with $\Omega_{\text{aragonite}} > 4.5$ estimated for the region in year 1765 (Feely *et al.*, 2009), equivalent to $\Omega_{\text{calcite}} > \sim 6.75$. Our calculated values of surface seawater pH at Tahiti are 8.18 (pre-industrial, 390 years ago) and 8.06 (present-day; Fig. 4B). The latter value is compatible with present-day surface seawater pH at Tahiti (Moorea) of ~ 8.1 (Douville *et al.*, 2010; based on Pelejero *et al.*, 2005). The calculated pH is sensitive to p_{CO_2} , and the measured pH values are also dependent on the localized chemical compositions of microenvironments.

So far as we are aware, our results are the first detailed calculated trends of seawater pH and saturation state of carbonate minerals for the past 21 ka. Previous calculations of pH and carbonate saturation values were for shorter intervals or for separate time points; for example, the LGM, 390 years ago, and the present day (Kleypas *et al.*, 2006). The absolute values of our calculated seawater carbonate chemistry differ from the estimates of Kleypas *et al.* (2006) because these authors used different input values, including lower salinity, temperature, and alkalinity, than we used in this study. Lower salinity corresponds to a lower ionic concentration, lower temperature favors carbonate dissolution, and lower alkalinity results in a lower carbonate concentration; all these would contribute to lower saturation values for carbonate minerals. The overall data trends are, however, similar to Kleypas *et al.* (2006), that is, our calculated value of Ω_{calcite} declined from 9.35 at 21 ka ago to 7.44 in pre-industrial time due to the increase in CO_2 . To compare our methodologies, using the input values of Kleypas *et al.* (2006), we obtained identical output values. Our calculated seawater pH of 8.33 (± 0.02) and 8.18, for the LGM and 390 years ago, respectively, is similar to those based on boron isotopes (Hönisch & Hemming, 2005). Additionally, the difference in pre-industrial pH between our results and those of Kleypas *et al.* (2006) is small, with our calculated pH of 8.18 being comparable to their value of 8.16. The slightly higher pH value that we obtained is consistent with the somewhat higher alkalinity and salinity of surface seawater at Tahiti.

Framework and crust development

Two quite different variables that can influence crust thickness are seawater carbonate saturation and the framework space available for cryptic crust growth. The latter complicates interpretation of the record of Tahiti crust thickness data prior to ~ 14.6 ka ago when the reefs were dominated by massive coral colonies (Fig. 3A). We attribute lower crust thicknesses at Tahiti ~ 16 –5 to 14.6 ka ago to the limited space available for their development in the relatively small cavities of this more massive initial reef (Searid *et al.*, 2011). This situation altered when the reef structure changed to branching framework ~ 14.6 ka ago as sea level

rise increased (Deschamps *et al.*, 2012). It might be expected that these open frameworks, with thick crusts generated by ‘catch-up’ reef growth, would return to denser framework with thinner crusts as sea level rise slowed. In this case, the observed pattern of crust increase and decline might simply reflect change in rate of sea level rise. However, following the ‘massive coral’ interval, the reef framework continued to be dominated by branching species (*Acropora robusta*, *A. danai*) until the end of the reef record 3 ka ago (Cabioch *et al.*, 1999a; Abbey *et al.*, 2011; Camoin *et al.*, 2012). Consequently, despite large variations in coral composition after 14.6 ka, there is no sustained recurrence of massive coral. Furthermore, the reef accretion rate of ~ 7.5 mm year⁻¹ between 7.67 and 5.65 ka ago (estimated from data in Cabioch *et al.*, 1999a; fig. 3) resembles that of the same reef 12–10 ka ago (Abbey *et al.*, 2011; Camoin *et al.*, 2012). We therefore infer that the Tahiti record of crust decline since ~ 14.6 ka ago reflects changes in factors that promote crust accretion rate (such as carbonate saturation) rather than available space within the framework. It also does not appear to reflect reduction in the time available for crust formation, because bacterial crusts can accrete at rates of 2.9 mm/100 years (Jell & Webb, 2012). We conclude that decline in maximum measured crust thickness at Tahiti since ~ 14.6 ka ago is unlikely to be an artifact of reef structure.

Peloids and crust formation

Peloids are granular micritic aggregates (McKee & Gutschick, 1969). In addition to forming cavity-veneering crusts, silt-size peloids commonly occur in reef interstices as geopetal and layered fills (James *et al.*, 1976; Lighty *et al.*, 1985; Macintyre, 1985; Reid *et al.*, 1990; Macintyre & Aronson, 2006; Noé *et al.*, 2006) that appear to be allochthonous (Land & Moore, 1980; Lighty *et al.*, 1985). These allochthonous (or quasi-autochthonous) peloids were interpreted as bacterial by Chafetz (1986). A possible mechanism for their fabric development is provided by studies of calcifying organic material influenced by bacterial decay of sponges in reef caves at Lizard Island and St Croix (Reitner, 1993; Reitner *et al.*, 2000). Nonetheless, such a mucus matrix mechanism does not rule out the possibility that peloids can form as precipitated flocs in suspension in water and subsequently settle out (Land & Moore, 1980; Lighty *et al.*, 1985). If peloids precipitated around bacterial cells, as Chafetz (1986) proposed, then saturation could have been increased by processes of the bacteria themselves, especially in isolated cavities. Organic remains preserved in peloid cores (Reitner *et al.*, 2000), support Chafetz’s (1986) report of bacterium-sized pores within peloid crystals. Reitner *et al.* (2000) also suggested that increased alkalinity in the sponges undergoing decay resulted from sulfate reduction.

An additional environment in which Late Pleistocene–Holocene peloidal crusts developed is on drowned reefs and fore-reef slopes that are now at depths of up to 500 m (Brachert & Dullo, 1991; Webster *et al.*, 2004, 2009; Camoin *et al.*, 2006) or more (Brachert, 1999). Whereas peloidal sediments in reef crusts and fills often exhibit grainstone fabrics (James *et al.*, 1976; Reid *et al.*, 1990; Riding & Tomás, 2006), crusts on these more open deeper water surfaces tend to be packstones (Webster *et al.*, 2009) and can be mixed with allochthonous carbonate and siliciclastic sediment. They commonly overlie deep-water assemblages of corallines and foraminifers, are partly contemporaneous with phosphate-FeMg crusts, and are themselves overlain by planktic carbonates (Camoin *et al.*, 2006; Webster *et al.*, 2009). Shallow-water peloidal crusts in poorly illuminated reef cavities or caves are also commonly associated with sciaphilous organisms. Garrett (1969) noted that, as light diminishes, surfaces of reef caves are successively occupied by coralline algae, bryozoans, foraminifers, and serpulids. Martindale (1992, fig. 7) suggested that the same sequence, superimposed on coral framework, indicates light reduction, either in cavities in the aggrading reef framework or as a result of deepening caused by relative sea level rise. Peloidal reef crusts typically occupy the final position in this succession (Marshall, 1983; Jones & Hunter, 1991; Montaggioni & Camoin, 1993; Camoin *et al.*, 1999, 2006; Reitner *et al.*, 2000; Cabioch *et al.*, 2006). In Lizard Island caves, peloidal crusts succeed crustose coralline algae when light levels are <5 lx (Reitner *et al.*, 2000, p. 151). Restriction of peloidal crusts to low-light habitats suggests inability to compete in more illuminated sites (Reitner *et al.*, 2000, p. 156). Relegation of microbial carbonates to low-light habitats due to competition for space with eukaryotes is consistent with competitive interactions that have long been linked to long-term geological decline in stromatolite abundance (Garrett, 1970; Awramik, 1971).

Bacterial dissimilatory sulfate reduction (DSR) (Postgate, 1959) is important in the anaerobic decomposition of present-day marine organic matter (Jørgensen & Fenchel, 1974; Jørgensen, 1982; Jørgensen & Kasten, 2006), and the ability of DSR to increase ambient carbonate alkalinity has long been recognized (Gallagher, 1933; Abd-El-Malek & Rizk, 1963; Kaplan *et al.*, 1963; Richards, 1965). Among the factors that influence this process are iron and electron donor availability (Ben-Yaakov, 1973; Visscher *et al.*, 1998; Visscher & Stolz, 2005; Gallagher *et al.*, 2012, 2014) and the fate of the CO₂ and HS⁻ produced (Walter & Burton, 1990; Walter *et al.*, 1993). In diffusion-limited biofilms, accumulation of CO₂ can decrease pH and CaCO₃ mineral saturation states, creating localized microenvironments that are unfavorable for CaCO₃ precipitation. Similarly, as ambient pH decreases in the ocean to <pK_a of H₂S, the formation of H₂S will consume alkalinity,

which also affects CaCO₃ precipitation. Nonetheless, the overall ability of DSR to increase alkalinity gives it a significant role in promoting sedimentary CaCO₃ precipitation (Nadson, 1903, 1928; Berner *et al.*, 1970; Deelman, 1975; Jørgensen & Cohen, 1977; Lyons *et al.*, 1984; Pigott & Land, 1986; Castanier *et al.*, 2000). Although DSR is important in anoxic environments, many sulfate-reducing bacteria have developed strategies to deal with oxygen (Jørgensen, 1977; Dolla *et al.*, 2006) especially near oxic/anoxic interfaces, as in cyanobacterial mats (Canfield & Des Marais, 1991; Visscher *et al.*, 1992; Teske *et al.*, 1998; Minz *et al.*, 1999) where they can also participate in calcification (Visscher *et al.*, 2000; Dupraz & Visscher, 2005; Visscher & Stolz, 2005). Nonetheless, reefal crusts at Tahiti contain microborings consistent with poorly illuminated conditions (Heindel *et al.*, 2009), and biomarker studies that demonstrate the presence of sulfate-reducing bacteria also reveal an absence of cyanobacteria (Heindel *et al.*, 2010, 2012). Reefal crust microbial communities therefore appear to be unlike photic microbial mats, commonly linked to stromatolites, in which photosynthetic primary producers such as cyanobacteria support complex communities (Van Gernerden, 1993; Des Marais, 2003). We envisage that peloidal cryptic reef crusts are calcified biofilms dominated by sulfate-reducing bacteria that promoted their own calcification in restricted poorly illuminated (Cabioch *et al.*, 1999b) and low-oxygen (Heindel *et al.*, 2010) framework interstices where they were able to obtain nutrients from reef-derived organic matter (see Nutrient sources, below).

Nutrient sources

Reitner (1993) linked microbialite calcification at Lizard Island to alkalinity influx from continental silicate weathering. Subsequently, Holocene reduction in bacterial crust development at Vanuatu (Cabioch *et al.*, 1999b) and Tahiti (Camoin *et al.*, 1999) was also related to changes in groundwater supply from these volcanic islands. It was proposed that seepage and runoff promoted crust formation by supplying alkalinity and nutrients to the fringing reefs and that this ceased as slower sea level rise allowed the development of back-reef lagoons that impeded groundwater flow (Camoin *et al.*, 1999). Camoin *et al.* (2006) also linked upwelling of nutrient-rich deep water to crust formation on deep fore-reef slopes at Tahiti and the Marquesas Islands, and upwelling during rapid sea level rise was again invoked to explain reef crust abundance 16–10 ka ago at Vanuatu in the SW Pacific (Cabioch *et al.*, 2006). Heindel *et al.* (2012) considered that volcanic hinterlands serve to boost (but not trigger) microbialite formation and suggested that this could explain why Tahiti and Vanuatu microbialites are thicker than those in Maldive and Belize reefs. However, they probably were not

comparing similar ages. It is correct that older crusts at both Tahiti (12 ka) and Vanuatu (~11 to ~11.5 ka) can be 7.5 to 10 cm thick, whereas Maldivian and Belize crusts are thinner (3.5–4 cm), but the latter examples are also younger (~7.7 to ~5.4 ka; see Supporting Information).

Our results do not preclude local effects on alkalinity and nutrients from either terrestrial weathering or deep-water upwelling, but two broad considerations are pertinent. First, evidence that deglacial reefal bacterial crust reduction was widespread, the correspondence between thickness and saturation trends shown here, and compatibility of these changes with established links between bioinduced bacterial calcification and carbonate saturation, all suggest the involvement of global as well as local factors (Riding *et al.*, 2011). Second, reefs, in common with deep-sea environments, are supplied by pelagic particulate (Lochte & Turley, 1988; Gast *et al.*, 1998) and dissolved organic carbon (Paerl, 1993). These sources can support benthic heterotrophic bacteria (Cole *et al.*, 1987; Alongi, 1990) and can be supplemented by upwelling and runoff, as well as by interaction of interstitial fluids with basement rocks (Steinmann & Déjardin, 2004). In addition, heterotrophic bacteria such as sulfate reducers can be supported by particulate and dissolved organic matter derived from the reef organisms with which they are closely associated (Richter *et al.*, 2001; Scheffers *et al.*, 2005; Heindel *et al.*, 2012). It has been shown that decomposition of organic matter in reef frameworks produces interstitial waters that are sufficiently nutrient-rich for reefs to be net exporters of nutrients (Tribble *et al.*, 1990; Ayukai, 1993; Rougerie & Wauthy, 1993; Rasheed *et al.*, 2002). It therefore seems reasonable to infer that reef-derived nutrients could sustain cryptic bacterial crust development, irrespective of conditions of local runoff or upwelling.

High-energy reef margins

Reefal peloidal crusts are well developed on high-energy margins of late Quaternary reefs (e.g., Land & Goreau, 1970; Macintyre, 1977; Camoin & Montaggioni, 1994; Seard *et al.*, 2011). This non-uniform distribution suggests effects by seawater flushing on both precipitation (e.g., James *et al.*, 1976) and nutrient circulation. Reef frameworks are permeable structures in which lateral and vertical water circulation is promoted by wave, swell, and tidal fluxes, particularly in marginal zones (Buddemeier & Oberdorfer, 1986). Seawater flushing favors precipitation by replenishing solutes (Morse & Mackenzie, 1990, p. 266) and in shallow zones promotes warming and degassing of water that locally raises saturation state (e.g., Whittle *et al.*, 1993, p. 239). Marshall (1986, p. 23) recognized that these effects are likely to vary during reef accretion. Preferential development of crusts on high-energy margins is therefore consistent with the dependence of bioinduced

bacterial calcification on increased carbonate saturation state.

Magnesian calcite

The mineralogy and composition of the CaCO₃ precipitated during biocalcification affects its response to dissolution. Aragonite is more soluble than calcite, and at high levels of magnesium incorporation, magnesian calcite solubility can exceed that of aragonite (Berner, 1975; Andersson *et al.*, 2003; Morse *et al.*, 2006). It is therefore significant that reefal bacterial crusts appear consistently to be high-magnesian calcite (Land & Goreau, 1970; Macintyre, 1977, 1984; Camoin *et al.*, 1999), although the reasons for this are not clear. A possible contributing factor is the location of these crusts in reef interstices, because selective aragonite precipitation by corals could locally increase seawater [Mg²⁺]:[Ca²⁺] ratio in poorly flushed microenvironments. In addition, Mg increases the stability of amorphous CaCO₃ (ACC), thereby inhibiting vaterite crystallization and favoring direct transformation of ACC to calcite. A neutral starting pH can also favor crystallization of ACC to calcite (Rodríguez-Blanco *et al.*, 2012). Although bacterial sulfate reduction can occur in acidic environments, it is most commonly observed at circumneutral pH (Widdel, 1988; Church *et al.*, 2007; Bayraktarov *et al.*, 2013). Whatever the factors influencing magnesian calcite formation, its increased solubility with respect to associated Ca-carbonates is likely to increase the sensitivity of reefal bacterial crusts (Andersson & Mackenzie, 2011) and can therefore be expected to have contributed to their early decline in response to progressive acidification.

Reef structure over glacial–interglacial cycles

Cryptic bacterial crusts enhance reef strength and volume by rigidly coating skeletons and fragments, especially in branched frameworks with extensive cavities (Fig. 1). Centimetric to decimetric crusts locally constitute 80% of reef framework in Tahiti reefs near Papeete (Camoin *et al.*, 1999), conferring strength that promotes reef accretion and relief (Camoin & Montaggioni, 1994; Camoin *et al.*, 1999; Seard *et al.*, 2011). Conversely, where crusts are thin or absent, branched coral frames are more prone to storm fragmentation (Hubbard *et al.*, 1990; fig. 5), as reflected by commonly poor core recovery in Holocene reefs (Engels *et al.*, 2004). Boron isotope values in foraminifer shells indicate repeated pH fluctuation, with higher glacial (~8.24–8.29) and lower interglacial (~8.14) values, as CO₂ has varied over the past 2.1 Ma (Hönisch & Hemming, 2005; Hönisch *et al.*, 2009). Glacial–interglacial cycles profoundly affect shallow reef environments, particularly changes in water depth and accommodation space. We propose that thicker crusts in glacial reefs, due to



Fig. 5 Last interglacial reef crest deposit (Little Bay, NE Barbados), showing framework fragmentation. Hammer is 30 cm long.

increased carbonate saturation (Fig. 6), should also have influenced reef development. Glacial reef frameworks could have been strengthened, and interglacial reefs may have been left more prone to bioerosion and physical damage that could result in lower overall accretion rate.

Most glacial reefs are now submerged by sea level rise (Thomas *et al.*, 2009). Nonetheless, deeper cores at Tahiti indicate the presence of thick microbial crusts in reefs that predate a corallal interval that yields ages of 133 to

138 ka (Thomas *et al.*, 2009; Iryu *et al.*, 2010). The corallal interval probably corresponds to the last interglacial (Marine Isotope Stage (MIS) 5e; Blanchon *et al.*, 2014). The underlying reefs with microbial crusts therefore probably formed during the penultimate deglaciation (Termination II). The reef record of the last interglacial (MIS-5e, ~125 ka ago) is more accessible because it formed during higher sea level. Raised reefs of this age in the Caribbean (Fig. 5) and Red Sea appear to lack crusts and are commonly heavily bored and fragmented, and reef crest corals other than massive colonies are commonly broken into rudstone (Chen *et al.*, 1991; Strasser *et al.*, 1992; Pandolfi *et al.*, 1999; Blanchon & Eisenhauer, 2001; Perry, 2001; Bruggemann *et al.*, 2004; Schellmann & Radtke, 2004; Blanchon, 2010). Although these data are limited, they support the view that crusts were thicker during glacial periods when carbonate saturation was increased and thinner during interglacial acidification (Fig. 6). Further studies, especially of well-dated cores such as those obtained at Tahiti, are needed to explore the relationships between reef structure, crust development, and fluctuations in seawater chemistry in Pleistocene reefs. We did not examine marine cementation in our samples, but there is evidence that precipitation of abiotic cements, which in Quaternary reefs are mainly aragonite and magnesian calcite (Perrin, 2011), has been slowed by recent acidification (Andersson *et al.*, 2003; Manzello *et al.*, 2008), also weakening the structure of Holocene reefs (Rasser & Riegl, 2002).

Tropical carbonates during glacial cycles

In addition to changes produced by higher glacial salinities due to storage of fresh water as polar snow and ice, marine alkalinity could have been affected as sea level fluctuations

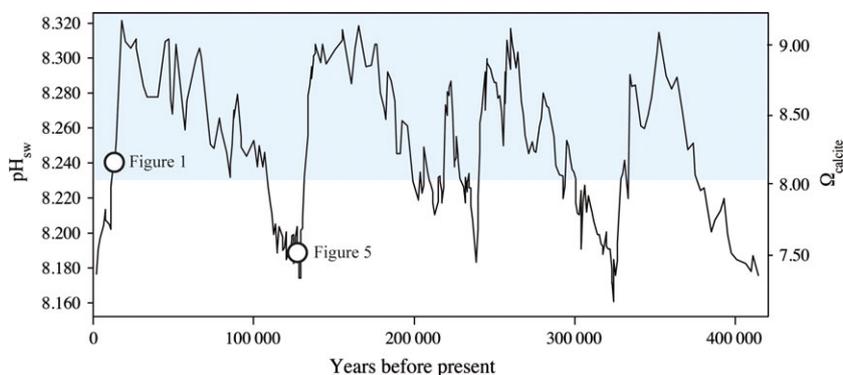


Fig. 6 Calculated surface ocean fluctuations in pH and calcite saturation state during the past four glacial cycles (414 ka). Calculation based on CO_2 values from the Vostok ice core (Petit *et al.*, 1999), assuming average seawater surface salinity of 36.7‰, average sea-surface temperature of 25.5 °C, and average alkalinity of 2518 ($\mu\text{mol kg}^{-1}$ seawater) throughout. Numbered circles show the relative positions of the reef deposits illustrated in Figs 1 and 5. We propose that increased carbonate saturation during glacial periods (blue shading) resulted in thicker crusts that strengthened reef frameworks, such as at Tahiti (Fig. 1), whereas thinner crusts formed under conditions of ocean acidification, leaving interglacial reefs more prone to biological and physical damage (Fig. 5).

expanded or reduced the shelf area available for shallow-water carbonate precipitation. Sea level rise since the LGM is estimated to have increased coral reef habitats by ~80% (Kleypas, 1997). Although we did not attempt to include this factor in our estimates of seawater chemistry, the opposite effect should have left surplus CaCO_3 in solution in glacial oceans. These fluctuations, between more alkaline glacial and more acidic interglacial surface seawater, may have affected not only reefs but shallow marine carbonate precipitation generally. Among the earliest processes likely to be affected are abiotic (cement, ooid) precipitation and bioinduced calcification by bacteria (and also by green algae such as *Halimeda*, *Penicillus*, and dasycladaleans). However, as with glacial reefs, scarcity of shallow-water glacial environments due to sea level rise during the latest interglacial limits the evidence currently available to examine this suggestion.

Pre-Quaternary acidification events

Evidence for similar acidification effects on calcification and reef structure might be preserved in much older glacial cycles in the geologic record, and also in non-glacial acidification events (Hönisch *et al.*, 2012), such as the Paleocene–Eocene thermal maximum (PETM) ~56 Ma ago (Zachos *et al.*, 2005) and also near the Permian–Triassic boundary (PTB) 252 Ma ago (Payne *et al.*, 2007, 2010; Montenegro *et al.*, 2011). The PETM has been suggested as an analog for present-day ocean acidification (Doney *et al.*, 2009, pp. 183–184). By that time, calcified cyanobacteria were already scarce in marine environments (Arp *et al.*, 2001), but peloidal microbial crusts occur and thickly encrusted late Thanetian reef corals that precede the PETM (Zamagni *et al.*, 2009). Subsequently, in the earliest Ypresian, corals such as *Goniopora* and *Actinacis* formed reef ‘knobs’ but coral frame-building capacity was otherwise reduced (Zamagni *et al.*, 2012), and thick microbialites have not been reported from this interval. The PETM also coincided with large decline in dasycladalean green algal diversity (Aguirre & Riding, 2005). Present-day well-calcified dasycladaleans are limited to warm and tropical seas with increased carbonate saturation. Their bioinduced, essentially aragonitic, calcification makes them prone to reduction in carbonate saturation state. More details are required of the secular pattern of decline of dasycladaleans at the PETM to evaluate whether they were responding to a geologically short-lived episode of marine acidification.

At the PTB, attention has focused on microbialites that are locally abundant near the boundary (Schubert & Bottjer, 1992; Baud *et al.*, 1997, 2007; Kershaw *et al.*, 2011). It has been suggested that these deposits were immediately preceded by a submarine dissolution event that was followed by immediate subsequent increase in CaCO_3 precipitation (Payne *et al.*, 2007). It is also possible to

consider the subsequent history of microbialite decline at the end of the *Hindeodus parvus* conodont zone (Ezaki *et al.*, 2008; Kershaw *et al.*, 2011), within <100 ka of the PTB (Shen *et al.*, 2011). Whereas dasycladaleans declined abruptly at the PETM, in the Early Triassic they are entirely lacking throughout the Induan, only reappearing in the late Olenekian, nearly 5 Ma after the PTB (Aguirre & Riding, 2005; Ioan Bucur, *pers. comm.*). Calcified cyanobacteria similarly disappear during this interval (Arp *et al.*, 2001). However, if the scale and duration of these reductions in calcified bacteria and algae following the PTB are confirmed, then they raise questions, as recovery of ocean buffering from even intense acidification is not expected to be so prolonged (Archer *et al.*, 1997; Berner, 2002; Caldeira & Wickett, 2003).

SUMMARY AND CONCLUSIONS

Over geologically short timescales, atmospheric CO_2 increase can cause ocean acidification. Quaternary seawater was more alkaline during glacial periods and more acidic during interglacials. Whether these changes affected biocontrolled calcification, as in corals, for example, remains uncertain. Here, we present evidence that bacterially bioinduced calcification in reefs has responded to recent millennial-scale changes in ocean acidification. Bacterial calcification is sensitive to changes in carbonate saturation state and pH. It declined significantly in reefs ~12 ka ago, near the Pleistocene–Holocene transition, and has diminished further since then. This is indicated by changes in the thickness of centimetric lithified bacterial crusts that veneer cavities in tropical reefs. Well-dated IODP cores through reefs at Tahiti show that these crusts declined in thickness from 12 cm 12.5 ka ago to ~2 cm 6 ka ago. Global data are more limited, because most Holocene reefs are now at or below sea level and few have been cored, but tropical reefs worldwide show signs of similar progressive reduction in crust thickness over the past 12 ka. This trend matches decline in calculated tropical surface ocean pH and carbonate saturation for the same interval.

Bacterial crusts are most abundant in cavernous reef frameworks in exposed high-energy locations where seawater flushing is intense, and they locally constitute 80% of the solid reef. They can substantially strengthen reef structure by rigidly bonding and stabilizing skeletal frameworks. We infer that bacterial reef crusts would have been thicker during glacial periods, when seawater carbonate saturation was increased, thereby strengthening reef frameworks, and thinner in response to interglacial acidification, leaving reefs weaker. Evidence for similar acidification effects on calcification, reef structure, and possibly marine carbonate sediments in general could be preserved in earlier glacial cycles. However, reliable reef crust thickness and age data are scarce, underscoring a need for more detailed studies,

such as that carried out by IODP at Tahiti, to further elucidate glacial reef history, including fluctuations in crust development.

Previous studies attributed Holocene thinning of bacterial crusts to reduction in the supply of nutrients and alkalinity as slowing sea level rise caused decline in terrestrial runoff and/or deepwater upwelling. We do not rule out these local effects. However, the apparent global extent of tropical crust decline, its correspondence with calculated ocean acidification rate, and its compatibility with the dependence of bioinduced bacterial calcification on degree of carbonate saturation all implicate a progressive global factor, such as deglacial ocean acidification, as a more likely proximal cause.

Our results suggest that deglacial ocean acidification has been causing decline in bioinduced bacterial calcification in tropical reefs for at least 12 ka, long before any observed effects on biocontrolled calcifiers. As anthropogenic carbon dioxide release exacerbates this millennial-scale 'natural' trend, it could start to affect reef organisms such as corals and coralline algae that, until now, appear to have been able to maintain close control over their calcification. The sensitivity of bacterial reef crusts, and other bioinduced calcifiers such as green algae, to changes in seawater carbonate chemistry, together with their long geological history, could assist identification of ocean acidification events much deeper in Earth history.

ACKNOWLEDGMENTS

This research used samples provided by the Integrated Ocean Drilling Program (IODP). IODP is supported by NSF; Japan's Ministry of Education, Culture, Sports, Science and Technology; the European Consortium for Ocean Drilling Research; and the People's Republic of China, Ministry of Science and Technology. LL acknowledges scientific support by the U.S. Department of Energy (DOE), Office of Science, Office of Biological and Environmental Research to Oak Ridge National Laboratory (ORNL). ORNL is managed by UT Battelle, LLC, for the U.S. Department of Energy under contract DE-AC05-00OR22725. We thank anonymous reviewers, including four for Geobiology, whose very helpful suggestions improved this work. We are grateful to María del Mar Rueda for statistical help, Fabio Tosti for assistance with figure drafting, and Kurt Konhauser for editorial guidance.

REFERENCES

- Abbey E, Webster JM, Braga JC, Sugihara K, Wallace CC, Iryu Y, Potts DC, Done TJ, Camoin G, Seard C (2011) Variation in deglacial coralgal assemblages and their paleoenvironmental significance: IODP Expedition 310, "Tahiti Sea Level". *Global and Planetary Change* **76**, 1–15.
- Abd-El-Malek Y, Rizk SG (1963) Bacterial sulphate reduction and the development of alkalinity. III. Experiments under natural conditions in the Wadi Natrun. *Journal of Applied Bacteriology* **26**, 20–26.
- Aguirre J, Riding R (2005) Dasycladalean algal biodiversity compared with global variations in temperature and sea level over the past 350 Myr. *Palaeos* **20**, 581–588.
- Allemand D, Tambutté E, Zoccola D, Tambutté S (2011) Coral calcification, cells to reefs. In *Coral Reefs: An Ecosystem in Transition* (eds Dubinsky Z, Stambler N). Springer, Dordrecht, pp. 119–150.
- Alongi DM (1990) Bacterial growth rates, production and estimates of detrital carbon utilization in deep-sea sediments of the Solomon and Coral Seas. *Deep Sea Research* **37**, 731–746.
- Altermann W, Böhmer C, Gitter F, Heimann F, Heller I, Lächli B, Putz C (2009) Defining biominerals and organominerals: direct and indirect indicators of life. Perry *et al.*, *Sedimentary Geology* **201**, 157–179. *Sedimentary Geology* **213**, 150–151.
- Anderson RF, Ali S, Bradtmiller LL, Nielsen SHH, Fleisher MQ, Anderson BE, Burckle LH (2009) Wind-driven upwelling in the Southern Ocean and the deglacial rise in atmospheric CO₂. *Science* **323**, 1443–1448.
- Andersson AJ, Gledhill D (2013) Ocean Acidification and coral reefs: effects on breakdown, dissolution, and net ecosystem calcification. *Annual Review of Marine Science* **5**, 321–348.
- Andersson AJ, Mackenzie FT (2011) Ocean acidification: setting the record straight. *Biogeochemistry Discussion* **8**, 6161–6190.
- Andersson AJ, Mackenzie FT, Ver LM (2003) Solution of shallow-water carbonates: an insignificant buffer against rising atmospheric CO₂. *Geology* **31**, 513–516.
- Andersson AJ, Mackenzie FT, Gattuso J-P (2011) Effects of ocean acidification on benthic processes, organisms, and ecosystems. In *Ocean Acidification* (eds Gattuso J-P, Hansson L). Oxford University Press, New York, pp. 122–153.
- Anthony KRN, Kline DI, Diaz-Pulido G, Dove S, Hoegh-Guldberg O (2008) Ocean acidification causes bleaching and productivity loss in coral reef builders. *Proceedings of the National Academy of Sciences of the USA* **105**, no. 45, 17442–17446.
- Archer D, Meier-Reimer E (1994) Effect of deep-sea sedimentary calcite preservation on atmospheric CO₂ concentration. *Nature* **367**, 260–263.
- Archer D, Kheshgi H, Maier-Reimer E (1997) Multiple timescales for neutralization of fossil fuel CO₂. *Geophysical Research Letters* **24**, 405–408.
- Arp G, Reimer A, Reitner J (2001) Photosynthesis-induced biofilm calcification and calcium concentrations in Phanerozoic oceans. *Science* **292**, 1701–1704.
- Awramik SM (1971) Precambrian columnar stromatolite diversity: reflection of metazoan appearance. *Science* **174**, 825–827.
- Ayukai T (1993) Temporal variability of the nutrient environment on Davies Reef in the Central Great Barrier Reef, Australia. *Pacific Science* **47**, 171–179.
- Ballantyne AP, Lavine M, Crowley TJ, Liu J, Baker PB (2005) Meta-analysis of tropical surface temperatures during the Last Glacial Maximum. *Geophysical Research Letters* **32**, L05712.
- Baud A, Cirilli S, Marcoux J (1997) Biotic response to mass extinction: the Lowermost Triassic microbialites. *Facies* **36**, 238–242.
- Baud A, Richoz S, Pruss S (2007) The lower Triassic anachronistic carbonate facies in space and time. *Global and Planetary Change* **55**, 81–89.
- Bayraktarov E, Price RE, Ferdelman TG, Finster K (2013) The pH and pCO₂ dependence of sulphate reduction in shallow-sea hydrothermal CO₂-venting sediments (Milos Island, Greece). *Frontiers in Microbiology* **4**, 1–10.

- Ben-Yaakov S (1973) pH buffering of pore water of recent anoxic marine sediments. *Limnology and Oceanography* **18**, 86–94.
- Berner RA (1975) The role of magnesium in the crystal growth of calcite and aragonite from sea water. *Geochimica et Cosmochimica Acta* **39**, 489–604.
- Berner RA (2002) Examination of hypotheses for the Permo-Triassic boundary extinction by carbon cycle modelling. *Proceedings of the National Academy of Sciences of the USA* **99**, 4172–4177.
- Berner RA, Scott MR, Thomlinson C (1970) Carbonate alkalinity in the pore waters of anoxic marine sediments. *Limnology and Oceanography* **15**, 544–549.
- Blanchon P (2010) Reef demise and back-stepping during the last interglacial, northeast Yucatan. *Coral Reefs* **29**, 481–498.
- Blanchon P, Eisenhauer A (2001) Multi-stage reef development on Barbados during the Last Interglaciation. *Quaternary Science Reviews* **20**, 1093–1112.
- Blanchon P, Granados-Corea M, Abbey E, Braga JC, Braithwaite C, Kennedy DM, Spencer T, Webster JM, Woodroffe CD (2014) Postglacial Fringing-Reef to Barrier-Reef conversion on Tahiti links Darwin's reef types. *Scientific Reports* **4**, 4997.
- Boyd PW, Doney SC (2002) Modelling regional responses by marine pelagic ecosystems to global climate change. *Geophysical Research Letters* **29**, 1806.
- Brachert TC (1999) Non-skeletal carbonate production and stromatolite growth within a Pleistocene deep ocean (Last Glacial Maximum, Red Sea). *Facies* **40**, 211–228.
- Brachert TC, Dullo WC (1991) Laminar micrite crusts and associated foreslope processes, Red Sea. *Journal of Sedimentary Research* **61**, 354–363.
- Broecker WS, Li Y-H, Peng T-H (1971) Carbon dioxide – Man's unseen artefact. In *Impingement of Man on the Oceans* (ed. Hood DW). Wiley Interscience, New York, pp. 287–324.
- Broecker WS, Takahashi T, Simpson HJ, Peng T-H (1979) Fate of fossil fuel carbon dioxide and the global carbon budget. *Science* **206**, 409–418.
- Bruggemann JH, Buffler RT, Guillaume MMM, Walter RC, von Cosel R, Ghebretensae BN, Berhe SM (2004) Stratigraphy, palaeoenvironments and model for the deposition of the Abdur Reef Limestone: context for an important archaeological site from the last interglacial on the Red Sea coast of Eritrea. *Palaeogeography, Palaeoclimatology, Palaeoecology* **203**, 179–206.
- Buddemeier RW, Oberdorfer JA (1986) Internal hydrology and geochemistry of coral reefs and atoll islands: key to diagenetic variations. In *Reef Diagenesis* (eds Schroeder JH, Purser BH). Springer-Verlag, Berlin, pp. 91–111.
- Cabioch G, Camoin GF, Montaggioni LF (1999a) Postglacial growth history of a French Polynesian barrier reef tract, Tahiti, central Pacific. *Sedimentology* **46**, 985–1000.
- Cabioch G, Taylor FW, Corrège T, Récy J, Edwards LR, Burr GS, Le Cornec F, Banks KA (1999b) Occurrence and significance of microbialites in the uplifted Tasmaloum reef (SW Espiritu Santo, SW Pacific). *Sedimentary Geology* **126**, 305–316.
- Cabioch G, Camoin G, Webb GE, Le Cornec F, Molina MG, Pierre C, Joachimski MM (2006) Contribution of microbialites to the development of coral reefs during the last deglacial period: case study from Vanuatu (South-West Pacific). *Sedimentary Geology* **185**, 297–318.
- Caldeira K, Wickett ME (2003) Anthropogenic carbon and ocean pH. *Nature* **425**, 365.
- Camoin GF, Montaggioni LF (1994) High energy corallgal-stromatolite frameworks from Holocene reefs (Tahiti, French Polynesia). *Sedimentology* **41**, 655–676.
- Camoin GF, Gautret P, Montaggioni LF, Cabioch G (1999) Nature and environmental significance of microbialites in Quaternary reefs: the Tahiti paradox. *Sedimentary Geology* **126**, 271–304.
- Camoin GF, Montaggioni LF, Braithwaite CJR (2004) Late glacial to post glacial sea levels in the Western Indian Ocean. *Marine Geology* **206**, 119–146.
- Camoin G, Cabioch G, Eisenhauer A, Braga J-C, Hamelin B, Lericolais G (2006) Environmental significance of microbialites in reef environments during the last deglaciation. *Sedimentary Geology* **185**, 277–295.
- Camoin G, Iryu Y, McInroy D, Expedition 310 Scientists (2007) Expedition 310. *Proc. IODP 310 Expedition Reports* <http://dx.doi.org/10.2204/iodp.proc.310.2007>.
- Camoin GF, Seard C, Deschamps P, Webster JM, Abbey E, Braga JC, Iryu Y, Durand N, Bard E, Hamelin B, Yokoyama Y, Thomas AL, Henderson GM, Dussouillez P (2012) Reef response to sea-level and environmental changes during the last deglaciation. Integrated Ocean Drilling Program Expedition 310, Tahiti Sea Level. *Geology* **40**, 643–646.
- Canfield DE, Des Marais DJ (1991) Aerobic sulfate reduction in microbial mats. *Science* **251**, 1471–1473.
- Castanier S, Le Métayer-Level G, Perthuisot J-P (2000) Bacterial roles in the precipitation of carbonate minerals. In *Microbial Sediments* (eds Riding R, Awramik SM). Springer, Berlin, pp. 32–39.
- Chafetz HS (1986) Marine peloids: a product of bacterially induced precipitation of calcite. *Journal of Sedimentary Petrology* **56**, 812–817.
- Chen JH, Curran HA, White B, Wasserburg GJ (1991) Precise chronology of the last interglacial period: 234U-230Th data from fossil coral reefs in the Bahamas. *Geological Society of America Bulletin* **103**, 82–97.
- Church CD, Wilkin RT, Alpers CN, Rye RO, McCleskey R (2007) Microbial sulfate reduction and metal attenuation in pH 4 acid mine water. *Geochemical Transactions* **8**, 10.
- Cole JJ, Honjo S, Erez J (1987) Benthic decomposition of organic matter at a deep-water site in the Panama Basin. *Nature* **327**, 703–704.
- De'ath G, Lough JM, Fabricius KE (2009) Declining coral calcification on the Great Barrier Reef. *Science* **323**, 116–119.
- Deelman JC (1975) Dolomite synthesis and crystal growth. *Geology* **3**, 471–472.
- Défarce C, Trichet J (1995) From biominerals to 'organominerals': the example of the modern lacustrine calcareous stromatolites from Polynesian atolls. In *Proceedings of the 7th International Symposium on Biomineralization* (eds Allemand D, Cuif JP). *Bulletin de l'Institut Océanographique de Monaco*, n° spéc. 14, **2**, pp. 265–271.
- Défarce C, Gautret P, Reitner J, Trichet J (2009) Defining organominerals: Comment on 'Defining biominerals and organominerals: Direct and indirect indicators of life' by Perry *et al.* (2007, *Sedimentary Geology*, 201, 157–179). *Sedimentary Geology* **213**, 152–155.
- Défarce C, Gautret P, Reitner J, Trichet J (2010) Reply to "Reply to comments on defining biominerals and organominerals: Direct and indirect indicators of life [Perry *et al.*, *Sedimentary Geology*, 201, 157–179]" by R.S. Perry and M.A. Sephton [Sedimentary Geology 213 (2009) 156]. *Sedimentary Geology* **223**, 390–391.
- Delille B, Harlay J, Zondervan I, Jacquet S, Chou L, Wollast R, Bellerby RGJ, Frankignoulle M, Borges AV, Riebesell U, Gattuso J-P (2005) Response of primary production and acidification to changes of pCO₂ during experimental blooms of

- the coccolithophorid *Emiliania huxleyi*. *Global Biogeochemical Cycles* **19**. doi: 10.1029/2004GB002318
- Des Marais DJ (2003) Biogeochemistry of hypersaline microbial mats illustrates the dynamics of modern microbial ecosystems and the early evolution of the biosphere. *Biological Bulletin* **204**, 160–167.
- Deschamps P, Durand N, Bard E, Hamelin B, Camoin G, Thomas AL, Henderson GM, Okuno J, Yakoyama Y (2012) Ice-sheet collapse and sea-level rise at the Bolling warming 14,600 years ago. *Nature* **483**, 559–564.
- Dickson AG (1990) Standard potential of the reaction: $\text{AgCl(s)} + \frac{1}{2}\text{H}_2\text{(g)} = \text{Ag(s)} + \text{HCl(aq)}$, and the standard acidity constant of the ion HSO_4^- in synthetic sea water from 273.15 to 318.15 K. *Journal of Chemical Thermodynamics* **22**, 113–127.
- DOE (1994) 'Handbook of Methods for the Analysis of the Various Parameters of the Carbon Dioxide System in Sea Water; Version 2', in A.G. Dickson, C. Goyet (eds), ORNL/CDIAC-74, Oak Ridge, TN: US Dept. of Energy.
- Dolla A, Fournier M, Dermoun Z (2006) Oxygen defense in sulfate-reducing bacteria. *Journal of Biotechnology* **126**, 87–100.
- Doney SC, Fabry VJ, Feely RA, Kleypas JA (2009) Ocean acidification: the other CO₂ problem. *Annual Review of Marine Science* **1**, 169–192.
- Douville E, Paterne M, Cabioch G, Louvat P, Gaillardet J, Juillet-Leclerc A, Ayliff L (2010) Abrupt sea surface pH change at the end of the Younger Dryas in the central sub-equatorial Pacific inferred from boron isotope abundance in corals (Porites). *Biogeosciences* **7**, 2445–2459.
- Dupraz C, Visscher PT (2005) Microbial lithification in marine stromatolites and hypersaline mats. *Trends in Microbiology* **13**, 329–438.
- Dupraz C, Reid PR, Braissant O, Decho AW, Norman RS, Visscher PT (2009) Processes of carbonate precipitation in modern microbial mats. *Earth-Science Reviews* **96**, 141–162.
- Engels MS, Fletcher CH III, Field ME, Storlazzi CD, Grossman EE, Rooney JJB, Conger CL, Glenn C (2004) Holocene reef accretion: southwest Molokai, Hawaii, USA. *Journal of Sedimentary Research* **74**, 255–269.
- Erez J, Reynaud S, Silverman J, Schneider K, Allemand D (2011) Coral calcification under ocean acidification and global change. In *Coral Reefs: An Ecosystem in Transition* (eds Dubinsky Z, Stambler N). Springer, Dordrecht, pp. 151–176.
- Ezaki Y, Liu J, Nagano T, Adachi N (2008) Geobiological aspects of the earliest Triassic microbialites along the southern periphery of the tropical Yangtze Platform: initiation and cessation of a microbial regime. *Palaaios* **23**, 356–369.
- Feely RA, Sabine CL, Lee K, Berelson W, Kleypas J, Fabry VJ, Milero FJ (2004) Impact of anthropogenic CO₂ on the CaCO₃ system in the oceans. *Science* **305**, 362–366.
- Feely RA, Doney SC, Cooley SR (2009) Ocean acidification: present conditions and future changes in a high-CO₂ world. *Oceanography* **22**, 36–47.
- Gallagher KL, Kading T, Braissant O, Dupraz C, Visscher PT (2012) Inside the alkalinity engine: the role of electron donors in the organomineralization potential of sulfate-reducing bacteria. *Geobiology* **10**, 518–530.
- Gallagher KL, Dupraz C, Visscher PT (2014) Two opposing effects of sulfate reduction on carbonate precipitation in normal marine, hypersaline, and alkaline environments. *Comment. Geology* **42**, e313–e314.
- Gallier EW (1933) The sulfur cycle in sediments. *Journal of Sedimentary Petrology* **3**, 51–63.
- Garrett P (1969) The geology and biology of large cavities in Bermuda reefs. In *Reports of research 1968 seminar on organism-sediment relationships* (eds Ginsburg RN, Garrett P). Bermuda Biological Field Station Research Special Publication 6: 77–88.
- Garrett P (1970) Phanerozoic stromatolites: noncompetitive ecologic restriction by grazing and burrowing animals. *Science* **169**, 171–173.
- Gast GJ, Wiegman S, Wieringa E, van Duyl FC, Bak RPM (1998) Bacteria in coral reef water types: removal of cells, stimulation of growth and mineralization. *Marine Ecology Progress Series* **167**, 37–45.
- Gattuso J-P, Pichon M, Frankignoulle M (1995) Biological control of air-sea CO₂ fluxes: effect of photosynthetic and calcifying marine organisms and ecosystems. *Marine Ecology Progress Series* **129**, 307–312.
- Gischler E, Hudson JH, Pisera A (2008) Late Quaternary reef growth and sea level in the Maldives (Indian Ocean). *Marine Geology* **250**, 104–113.
- Gouriou Y, Delcroix T (2002) Seasonal and ENSO variations of sea surface salinity and temperature in the South Pacific Convergence Zone during 1976–2000. *Journal of Geophysical Research* **107**, 8011. doi:10.1029/2001JC000830
- Grotzinger JP (1990) Geochemical model for Proterozoic stromatolite decline. *American Journal of Science* **290A**, 80–103.
- Grotzinger JP, Kasting JF (1993) New constraints on Precambrian ocean composition. *Journal of Geology* **101**, 235–243.
- Guido A, Heindel K, Birgel D, Rosso A, Mastandrea A, Sanfilippo R, Russo F, Peckmann J (2013) Pendant bioconstructions cemented by microbial carbonate in submerged marine caves (Holocene, SE Sicily). *Palaogeography, Palaeoclimatology, Palaeoecology* **388**, 166–180.
- Heindel K, Wisshak M, Westphal H (2009) Microbioerosion in Tahitian reefs: a record of environmental change during the last deglacial sea-level rise (IODP 310). *Lethaia* **42**, 322–340.
- Heindel K, Birgel D, Peckmann J, Kuhnert H, Westphal H (2010) Formation of deglacial microbialites in coral reefs off Tahiti (IODP 310) involving sulfate-reducing bacteria. *Palaaios* **25**, 618–635.
- Heindel K, Birgel D, Brunner B, Thiel V, Westphal H, Gischler E, Ziegenbalg SB, Cabioch G, Sjövall P, Peckmann J (2012) Post-glacial microbialite formation in coral reefs of the Pacific, Atlantic, and Indian Oceans. *Chemical Geology* **304–305**, 117–130.
- Hoegh-Guldberg O, Mumby PJ, Hooten AJ, Steneck RS, Greenfield P, Gomez E, Harvell CD, Sale PF, Edwards AJ, Caldeira K, Knowlton N, Eakin CM, Iglesias-Prieto R, Muthiga N, Bradbury RH, Dubi A, Hatzioiols ME (2007) Coral reefs under rapid climate change and ocean acidification. *Science* **318**, 1737–1742.
- Hofmann HJ (2000) Archean stromatolites as microbial archives. In *Microbial Sediments* (eds Riding R, Awramik SM). Springer, Berlin, pp. 315–327.
- Hönisch B, Hemming NG (2005) Surface ocean pH response to variations in pCO₂ through two full glacial cycles. *Earth and Planetary Science Letters* **236**, 305–314.
- Hönisch B, Hemming NG, Archer D, Siddall M, McManus JF (2009) Atmospheric carbon dioxide concentration across the mid-Pleistocene transition. *Science* **324**, 1551–1554.
- Hönisch B, Ridgwell A, Schmidt DN, Thomas E, Gibbs SJ, Sluijs A, Zeebe R, Kump L, Martindale RC, Greene SE, Kiessling W, Ries J, Zachos JC, Royer DL, Barker S, Marchitto TM, Jr., Moyer R, Pelejero C, Ziveri P, Poster GL, Williams B (2012) The geological record of ocean acidification. *Science* **335**, 1058–1063.
- Hubbard DK, Miller AI, Scaturro D (1990) Production and cycling of calcium carbonate in a shelf-edge reef system (St. Croix, U.S. Virgin Islands): applications to the nature of reef

- systems in the fossil record. *Journal of Sedimentary Petrology* **60**, 335–360.
- Indermühle A, Stocker TF, Joos F, Fischer H, Smith HJ, Wahlen M, Deck B, Mastroianni D, Tschumi J, Blunier T, Meyer R, Stauffer B (1999) Holocene carbon-cycle dynamics based on CO₂ trapped in ice at Taylor Dome, Antarctica. *Nature* **398**, 121–126.
- Iryu Y, Takahashi Y, Fujita K, Camoin G, Cabioch G, Matsuda H, Sato T, Sugihara K, Webster JM, Westphal H (2010) Sealevel history recorded in the Pleistocene carbonate sequence in IODP Hole 310-M0005D, off Tahiti. *Island Arc* **19**, 690–706.
- James NP, Ginsburg RN, Marszalek DS, Choquette PW (1976) Facies and fabric specificity of early subsea cements in shallow Belize (British Honduras) reefs. *Journal of Sedimentary Research* **46**, 523–544.
- Jell JS, Webb GE (2012) Geology of Heron Island and adjacent reefs, Great Barrier Reef, Australia. *Episodes* **35**, 110–119.
- Jones B, Hunter IG (1991) Corals to rhodolites to microbialites — a community replacement sequence indicative of regressive conditions. *Palaios* **6**, 54–56.
- Jørgensen BB (1977) Bacterial sulfate reduction within reduced microniches of oxidized marine sediments. *Marine Biology* **41**, 7–17.
- Jørgensen BB (1982) Mineralization of organic matter in the sea bed—the role of sulphate reduction. *Nature* **296**, 643–645.
- Jørgensen BB, Cohen Y (1977) Solar Lake (Sinai) 5. The sulfur cycle of the benthic cyanobacterial mats. *Limnology and Oceanography* **22**, 657–666.
- Jørgensen BB, Fenchel T (1974) The sulfur cycle of a marine sediment model system. *Marine Biology* **24**, 189–201.
- Jørgensen BB, Kasten S (2006) Sulfur cycling and methane oxidation. In *Marine Geochemistry*, 2nd edn (eds Schulz HD, Zabel M). Springer, Berlin, pp. 271–309.
- Kamenos NA, Burdett HL, Aloisio E, Findlay HS, Martin S, Longbone C, Dunn J, Widdicombe S, Calosi P (2013) Coralline algal structure is more sensitive to rate, rather than the magnitude, of ocean acidification. *Global Change Biology* **19**, 3621–3628.
- Kaplan IR, Emery KO, Rittenberg SC (1963) The distribution and isotopic abundance of sulphur in recent marine sediments off southern California. *Geochimica et Cosmochimica Acta* **27**, 297–331.
- Kershaw S, Crasquin S, Li Y, Collin P-Y, Forel M-B, Mu X, Baud A, Wang Y, Xie S, Maurer F, Guo L (2011) Microbialites and global environmental change across the Permian-Triassic boundary: a synthesis. *Geobiology* **10**, 25–47.
- Kleypas JA (1997) Modeled estimates of global reef habitat and carbonate production since the last glacial maximum. *Paleoceanography* **12**, 533–545.
- Kleypas JA, Buddemeier RW, Archer D, Gattuso J-P, Langdon C, Opdyke BN (1999) Geochemical consequences of increased atmospheric carbon dioxide on coral reefs. *Science* **284**, 118–120.
- Kleypas JA, Feely RA, Fabry VJ, Langdon C, Sabine CL, Robbins LL (2006) Impacts of ocean acidification on coral reefs and other marine calcifiers: a guide for future research. Report of a workshop held 18–20 April 2005, St. Petersburg, Florida, sponsored by NSF, NOAA, and the U.S. Geological Survey, 88 pp.
- Konhauser K, Riding R (2012) Bacterial biomineralization. In *Fundamentals of Geobiology* (eds Knoll AH, Canfield DE, Konhauser KO). John Wiley and Sons, Chichester, UK, pp. 105–130.
- Land LS (1971) Submarine lithification of Jamaican reefs. In *Carbonate Cements* (ed. Bricker OP). Johns Hopkins University Studies in Geology **19**, Baltimore, MD, pp. 59–62.
- Land LS, Goreau TF (1970) Submarine lithification of Jamaican reefs. *Journal of Sedimentary Research* **40**, 457–460.
- Land LS, Moore CH (1980) Lithification, micritization and syndepositional diagenesis of biolithites on the Jamaican Island slope. *Journal of Sedimentary Petrology* **50**, 357–370.
- Langdon C, Takahashi T, Sweeney C, Chipman D, Goddard J, Marubini F, Aceves H, Barnett H, Atkinson MJ (2000) Effect of calcium carbonate saturation state on the calcification rate of an experimental coral reef. *Global Biogeochemical Cycles* **14**, 639–654.
- Langer G, Geisen M, Baumann K, Kläs J, Riebesell U, Thoms S, Young JR (2006) Species-specific responses of calcifying algae to changing seawater carbonate chemistry. *Geochemistry, Geophysics, Geosystems* **7**, Q09006.
- Lea DW, Pak DK, Spero HJ (2000) Climate impact of Late Quaternary equatorial Pacific sea surface temperature variations. *Science* **289**, 1719–1724.
- Leadbeater BSC, Riding R (eds) (1986) *Biomimneralization in Lower Plants and Animals*. Systematics Association Special Volume 30. Clarendon Press, Oxford, 401 pp.
- Lee K, Kim T-W, Byrne RH, Millero FJ, Feely RA, Liu M-M (2010) The universal ratio of boron to chlorinity for the North Pacific and North Atlantic oceans. *Geochimica et Cosmochimica Acta* **74**, 1801–1811.
- Lighty RG (1985) Preservation of internal porosity and diagenetic sealing of submerged early Holocene barrier reef, southeast Florida shelf. In *Carbonate Cements* (eds Schneidermann N, Harris PM). Society of Economic Paleontologists and Mineralogists Special Publication 36, Tulsa, OK, 123–151.
- Lochte K, Turley CM (1988) Bacteria and cyanobacteria associated with phytodetritus in the deep-sea. *Nature* **333**, 67–69.
- Lowenstam HA (1981) Minerals formed by organisms. *Science* **211**, 1126–1131.
- Lowenstam HA, Weiner S (1989) *On Biomineralization*. Oxford University Press, New York, 336 pp.
- Lüthi D, Le Floch M, Bereiter B, Blunier T, Barnola J-M, Siegenthaler U, Raynaud D, Jouzel J, Fischer H, Kawamura K, Stocker TF (2008) High-resolution carbon dioxide concentration record 650,000–800,000 years before present. *Nature* **453**, 379–382.
- Lyons WB, Long DT, Hines ME, Gaudette HE, Armstrong PB (1984) Calcification of cyanobacterial mats in Solar Lake, Sinai. *Geology* **12**, 623–626.
- Macintyre IG (1977) Distribution of submarine cements in a modern Caribbean Fringing Reef, Galeta Point, Panama. *Journal of Sedimentary Petrology* **47**, 503–516.
- Macintyre IG (1984) Extensive submarine lithification in a cave in the Belize barrier reef platform. *Journal of Sedimentary Petrology* **54**, 221–235.
- Macintyre IG (1985) Submarine cements - the peloidal question. In *Carbonate Cements* (eds Schneidermann N, Harris PM). Society of Economic Paleontologists and Mineralogists Special Publication 36, Tulsa, OK, pp. 109–116.
- Macintyre IG, Aronson RB (2006) Lithified and unlithified Mg-calcite precipitates in tropical reef environments. *Journal of Sedimentary Research* **76**, 81–90.
- Macintyre IG, Mountjoy EW, d'Anglejan BF (1968) An occurrence of submarine cementation of carbonate sediments off the west coast of Barbados, W.I. *Journal of Sedimentary Research* **38**, 660–664.
- Malone MJ, Slowey NC, Henderson GM (2001) Early diagenesis of shallow-water periplatform carbonate sediments, leeward margin, Great Bahama Bank (Ocean Drilling Program Leg 166). *Geological Society of America Bulletin* **113**, 881–894.

- Mann S (2001) *Biomineralization: Principles and Concepts in Bioinorganic Materials Chemistry*. Oxford University Press, New York, 198 p.
- Manzello DP, Kleypas JA, Budd DA, Eakin CM, Glynn PW, Langdon C (2008) Poorly cemented coral reefs of the eastern tropical Pacific: possible insights into reef development in a high-CO₂ world. *Proceedings of the National Academy of Sciences of the USA* **105**, 10450–10455.
- Marshall JF (1983) Submarine cementation in a high-energy platform reef: One Tree Reef, southern Great Barrier Reef. *Journal of Sedimentary Research* **53**, 1133–1149.
- Marshall JF (1986) Regional distribution of submarine cements within an epicontinental reef system: Central Great Barrier Reef, Australia. In *Reef Diagenesis*. (eds Schroeder JH, Purser BH). Springer, Berlin, pp. 8–26.
- Marshall JF, Davies PJ (1981) Submarine lithification on windward reef slopes: Capricorn-Bunker Group, southern Great Barrier Reef. *Journal of Sedimentary Research* **51**, 953–960.
- Martindale W (1992) Calcified epibionts as palaeoecological tools: examples from the Recent and Pleistocene reefs of Barbados. *Coral Reefs* **11**, 167–177.
- Mayr C, Lücke A, Wagner S, Wissel H, Ohlendorf C, Haberzettl T, Oehlerich M, Schäbitz F, Wille M, Zhu J, Zolitschka B (2013) Intensified southern hemisphere westerlies regulated atmospheric CO₂ during the last deglaciation. *Geology* **41**, 831–834.
- McCulloch M, Falter J, Trotter J, Montagna P (2012) Coral resilience to ocean acidification and global warming through pH up-regulation. *Nature Climate Change* **2**, 623–627.
- McKee ED, Gutschick RC (1969) Analysis of lithology. In *History of the Redwall Limestone of Northern Arizona* (eds McKee ED, Gutschick RC). *Geological Society of America Memoir* **114**, 97–124.
- Millero FJ (2010) Carbonate constants for estuarine waters. *Marine and Freshwater Research* **61**, 139–142.
- Minz D, Flax JL, Green SJ, Muyzer G, Cohen Y, Wagner M, Rittmann BE, Stahl DA (1999) Diversity of sulfate-reducing bacteria in oxic and anoxic regions of a microbial mat characterized by comparative analysis of dissimilatory sulfite reductase genes. *Applied and Environmental Microbiology* **65**, 4666–4671.
- Monnin E, Indermühle A, Dällenbach A, Flückiger J, Stauffer B, Stocker TF, Raynaud D, Barnola JM (2001) Atmospheric CO₂ concentrations over the Last Glacial Termination. *Science* **291**, 112–114.
- Montaggioni LF, Camoin GF (1993) Stromatolites associated with coralgall communities in Holocene high energy reefs. *Geology* **21**, 149–152.
- Montenegro A, Spence P, Meissner KJ, Eby M, Melchin MJ, Johnston ST (2011) Climate simulations of the Permian-Triassic boundary: ocean acidification and the extinction event. *Paleoceanography* **26**, PA3207.
- Morse JW, Mackenzie FT (1990) *Geochemistry of Sedimentary Carbonates*. Elsevier, Amsterdam, 707 pp.
- Morse JW, Andersson AJ, Mackenzie FT (2006) Initial responses of carbonate-rich shelf sediments to rising atmospheric pCO₂ and ‘ocean acidification’: role of high Mg-calcites. *Geochimica et Cosmochimica Acta* **70**, 5814–5830.
- Moya A, Huisman L, Ball EE, Hayward DC, Grasso LC, Chua CM, Woo HN, Gattuso J-P, Foret S, Miller DJ (2012) Whole transcriptome analysis of the coral *Acropora millepora* reveals complex responses to CO₂-driven acidification during the initiation of calcification. *Molecular Ecology* **21**, 2440–2454.
- Mucci A (1983) The solubility of calcite and aragonite in seawater at various salinities, temperatures, and one atmosphere total pressure. *American Journal of Science* **283**, 780–799.
- Nadson GA (1903) *Microorganismi kak geoligitsbeskie diciatieli*. I. Tr. Komissii Isslect. Min. Vodg. Slavjanska, St. Petersburg, pp. 1–98.
- Nadson GA (1928) Beitrag zur Kenntnis der bakteriogenen Kalkablagerungen. *Archiv für Hydrobiologie* **19**, 154–164.
- Noé S, Titschack J, Freiwald A, Dullo W-C (2006) From sediment to rock: diagenetic processes of hardground formation in deep-water carbonate mounds of the NE Atlantic. *Facies* **52**, 183–208.
- Orr JC, Fabry VJ, Aumont O, Bopp L, Doney SC, Feely RA, Gnanadesikan A, Gruber N, Ishida A, Joos F, Key RM, Lindsay K, Maier-Reimer E, Matear R, Monfray P, Najjar RG, Plattner GK, Rodgers KB, Sabine CL, Sarmiento JL, Schlitzer R, Slater RD, Totterdell IJ, Weirig MF, Yamanaka Y, Yool A (2005) Anthropogenic ocean acidification over the twenty-first century and its impact on calcifying organisms. *Nature* **437**, 681–686.
- Paerl HW (1993) Interaction of nitrogen and carbon cycles in the marine environment. In *Aquatic Microbiology: An Ecological Approach* (ed. Ford T). Blackwell, Oxford, pp. 343–381.
- Pandolfi JM, Llewellyn G, Jackson JBC (1999) Pleistocene reef environments, constituent grains, and coral community structure: Curaçao, Netherlands Antilles. *Coral Reefs* **18**, 107–122.
- Pandolfi JM, Connolly SR, Marshall DJ, Cohen AL (2011) Projecting coral reef futures under global warming and ocean acidification. *Science* **333**, 418–422.
- Parkhurst DL, Appelo CAJ (1999) User’s guide to PHREEQC (version 2) - A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. *Water-Resources Investigations Report 99-4259*, US Geological Survey, Denver, Colorado, 326 pp.
- Payne JL, Lehrmann DJ, Follett D, Seibel M, Kump LR, Riccardi A, Altiner D, Sano H, Wei J (2007) Erosional truncation of uppermost Permian shallow-marine carbonates and implications for Permian-Triassic boundary events. *Geological Society of America Bulletin* **119**, 771–784.
- Payne JL, Turchyn AV, Paytan A, DePaolo DJ, Lehrmann DJ, Yu M, Wei J (2010) Calcium isotope constraints on the end-Permian mass extinction. *Proceedings of the National Academy of Sciences of the USA* **107**, 8543–8548.
- Peacock S, Lane E, Restrepo JM (2006) A possible sequence of events for the generalized glacial-interglacial cycle. *Global Biogeochemical Cycles* **20**, GB2010.
- Pedley HM (1979) Miocene bioherms and associated structures in the Upper Coralline limestone of the Maltese Islands: their lithification and palaeoenvironment. *Sedimentology* **26**, 577–591.
- Pelejero C, Calvo E, McCulloch MT, Marshall JF, Gagan MK, Lough JM, Opdyke BN (2005) Preindustrial to modern interdecadal variability in coral reef pH. *Science* **309**, 2204–2207.
- Perito B, Mastromei G (2011) Molecular basis of bacterial calcium carbonate precipitation. In *Molecular biomineralization: aquatic organisms forming extraordinary materials* (ed. Müller WEG). *Progress in Molecular and Subcellular Biology*, **52**. Springer, pp. 113–139.
- Perrin C (2011) Diagenesis. In *Encyclopedia of Modern Coral Reefs: Structure, Form and Process* (ed. Hopley D). Springer, Dordrecht, pp. 309–321.
- Perry CT (2001) Storm-induced coral rubble deposition: Pleistocene records of natural reef disturbance and community response. *Coral Reefs* **20**, 171–183.

- Perry RS, Sephton MA (2009) Reply to comments on defining biominerals and organominerals: direct and indirect indicators of life [Perry *et al.*, *Sedimentary Geology*, 201, 157–179]. *Sedimentary Geology* **213**, 156.
- Perry RS, Mcloughlin N, Lynne BY, Sephton MA, Oliver JD, Perry CC, Campbell K, Engel MH, Farmer JD, Brasier MD, Staley JT (2007) Defining biominerals and organominerals: direct and indirect indicators of life. *Sedimentary Geology* **201**, 157–179.
- Petit JR, Jouzel J, Raynaud D, Barkov NI, Barnola J-M, Basile I, Bender M, Chappellaz J, Davis M, Delaygue G, Delmotte M, Kotlyakov VM, Legrand M, Lipenkov VY, Lorius C, Pepin L, Ritz C, Saltzman E, Stievenard M (1999) Climate and atmospheric history of the past 420,000 years from the Vostok ice core, Antarctica. *Nature* **399**, 429–436.
- Pierrot DE, Lewis E, Wallace DWR (2006) *MS Excel Program Developed for CO₂ System Calculations*. ORNL/CDIAC-105a. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge, TN.
- Pigott JD, Land LS (1986) Interstitial water chemistry of Jamaican reef sediment: sulfate reduction and submarine cementation. *Marine Chemistry* **19**, 355–378.
- Postgate J (1959) Sulphate reduction by bacteria. *Annual Review of Microbiology* **13**, 505–520.
- Pratt BR (1982) Stromatolite decline, a reconsideration. *Geology* **10**, 512–515.
- Puverel S, Tambutté E, Zoccola D, Domart-Coulon I, Bouchot A, Lotto S, Allemand D, Tambutté S (2005) Antibodies against the organic matrix in scleractinians: a new tool to study coral biomineralization. *Coral Reefs* **24**, 149–156.
- Quay PD, Tilbrook B, Wong CS (1992) Oceanic uptake of fossil fuel CO₂: carbon-13 evidence. *Science* **256**, 74–79.
- Rasheed M, Badran MI, Richter C, Huettel M (2002) Effect of reef framework and bottom sediment on nutrient enrichment in a coral reef of the Gulf of Aqaba, Red Sea. *Marine Ecology Progress Series* **239**, 277–285.
- Rasser MW, Riegl B (2002) Holocene coral reef rubble and its binding agents. *Coral Reefs* **21**, 57–72.
- Raven J, Caldeira K, Elderfield H, Hoegh-Guldberg O, Liss PS, Riebesell U, Shepard J, Turley C, Watson AJ (2005) *Ocean Acidification due to Increasing Atmospheric Carbon Dioxide*. Policy Document 12/05, The Royal Society, London, 57 pp.
- Reid RP, Macintyre IG, James NP (1990) Internal precipitation of microcrystalline carbonate: a fundamental problem for sedimentologists. *Sedimentary Geology* **68**, 163–170.
- Reitner J (1993) Modern cryptic microbialite/metazoan facies from Lizard Island (Great Barrier Reef, Australia) formation and concepts. *Facies* **29**, 3–40.
- Reitner J, Thiel V, Zankl H, Michaelis W, Worheide G, Gautret P (2000) Organic and biogeochemical patterns in cryptic microbialites. In *Microbial Sediments* (eds Riding R, Awramik SM). Springer, Berlin, pp. 149–160.
- Richards FA (1965) Anoxic basins and fjords. In *Chemical Oceanography*, Vol. 1 (eds Riley JP, Skirrow G). Academic Press, London, pp. 611–645.
- Richter C, Wunsch M, Rasheed M, Körtter I, Badran MI (2001) Endoscopic exploration of Red Sea coral reefs reveals dense populations of cavity-dwelling sponges. *Nature* **413**, 726–730.
- Riding R (1982) Cyanophyte calcification and changes in ocean chemistry. *Nature* **299**, 814–815.
- Riding R (1992) Temporal variation in calcification in marine cyanobacteria. *Journal of the Geological Society of London* **149**, 979–989.
- Riding R (1993) Phanerozoic patterns of marine CaCO₃ precipitation. *Naturwissenschaften* **80**, 513–516.
- Riding R (2011) Reefal microbial crusts. In *Encyclopedia of Modern Coral Reefs* (ed. Hopley D). Encyclopedia of Earth Science Series, Springer, Heidelberg, pp. 911–915.
- Riding R, Tomás S (2006) Stromatolite reef crusts, Early Cretaceous, Spain: bacterial origin of *in situ* precipitated peloid microspar? *Sedimentology* **53**, 23–34.
- Riding R, Martín JM, Braga JC (1991) Coral stromatolite reef framework, Upper Miocene, Almería, Spain. *Sedimentology* **38**, 799–818.
- Riding R, Liang L, Braga JC (2011) Post-glacial ocean acidification and the decline of reefal microbial crusts. *American Geophysical Union*, Fall Meeting 2011, abstract # OS41C-02.
- Ries JB, Cohen AL, McCorkle DC (2009) Marine calcifiers exhibit mixed responses to CO₂-induced ocean acidification. *Geology* **37**, 1131–1134.
- Rodriguez-Blanco JD, Shaw S, Bots P, Roncal-Herrero T, Benning LG (2012) The role of pH and Mg on the stability and crystallization of amorphous calcium carbonate. *Journal of Alloys and Compounds* **536S**, S477–S479.
- Rougerie F, Wauthy B (1993) The endo-upwelling concept: from geothermal convection to reef construction. *Coral Reefs* **12**, 19–30.
- Sanyal A, Hemming NG, Hanson GN, Broecker WS (1995) Evidence for a higher pH in the glacial ocean from boron isotopes in foraminifera. *Nature* **373**, 234–236.
- Scheffers SR, Bak RPM, van Duyl FC (2005) Why is bacterioplankton growth in coral reef framework cavities enhanced? *Marine Ecology Progress Series* **299**, 89–99.
- Schellmann G, Radtke U (2004) A revised morpho- and chronostratigraphy of the Late and Middle Pleistocene coral reef terraces on Southern Barbados (West Indies). *Earth-Science Reviews* **64**, 157–187.
- Schubert JK, Bottjer DJ (1992) Early Triassic stromatolites as post-mass extinction disaster forms. *Geology* **20**, 883–886.
- Searl C, Camoin G, Yokoyama Y, Matsuzaki H, Durand N, Bard E, Sepulcre S, Deschamps P (2011) Microbialite development patterns in the last deglacial reefs from Tahiti (French Polynesia; IODP Expedition #310): implications on reef framework architecture. *Marine Geology* **279**, 63–86.
- Shen S, Crowley JL, Wang Y, Bowring SA, Erwin DH, Sadler PM, Cao C, Rothman DH, Henderson CM, Ramezani J, Zhang H, Shen YN, Wang XD, Wang W, Mu L, Li WZ, Tang YG, Liu XL, Liu LJ, Zeng Y, Jiang YF, Jin YG (2011) Calibrating the end-Permian mass extinction. *Science* **334**, 1367–1372.
- Sherman CE, Fletcher CH, Rubin KH (1999) Marine and meteoric diagenesis of Pleistocene carbonates from a nearshore submarine terrace, Oahu, Hawaii. *Journal of Sedimentary Research* **69**, 1083–1097.
- Sigman DM, Boyle EA (2000) Glacial/interglacial variations in atmospheric carbon dioxide. *Nature* **407**, 859–869.
- Sigman DM, Hain MP, Haug GH (2010) The polar ocean and glacial cycles in atmospheric CO₂ concentration. *Nature* **466**, 47–55.
- Steinmann M, Déjardin P (2004) The temporal evolution of fluid flow through the Tahiti barrier reef traced by Sr isotopes and pore water chemistry. *Chemical Geology* **203**, 51–73.
- Strasser A, Strohmenger C, Davaud E, Bach A (1992) Sequential evolution and diagenesis of Pleistocene coral reefs (south Sinai, Egypt). *Sedimentary Geology* **78**, 59–79.
- Stumm W, Morgan JJ (1996) *Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters*, 3rd edn. Wiley, New York, 1022 pp.

- Takahashi T (1979) Carbon dioxide chemistry in ocean water. In *Carbon dioxide, effects, research and assessment program. Workshop on the global effects of carbon dioxide from fossil fuels* (eds Elliott WP, Machta L). United States Department of Energy, Miami Beach, FL, March 7–11, 1977, CONF-770385, pp. 63–71.
- Teske A, Ramsin NB, Habicht K, Fukui M, Küver J, Jørgensen BB, Cohen Y (1998) Sulfate-reducing bacteria and their activities in cyanobacterial mats of Solar Lake (Sinai, Egypt). *Applied and Environmental Microbiology* **64**, 2943–2951.
- Thomas AL, Henderson GM, Deschamps P, Yokoyama Y, Mason AJ, Bard E, Hamelin B, Durand N, Camoin G (2009) Penultimate deglacial sea-level timing from uranium/thorium dating of Tahitian corals. *Science* **324**, 1186–1189.
- Tribble GW, Sansone FJ, Smith SV (1990) Stoichiometric modeling of carbon diagenesis within a coral reef framework. *Geochimica et Cosmochimica Acta* **54**, 2439–2449.
- Trichet J, Défarge C (1995) Non-biologically supported organomineralization. In *Proceedings of the 7th International Symposium on Biomineralization* (eds Allemand D, Cuif JP). *Bulletin de l'Institut Océanographique de Monaco*, n° spéc. 14, 2, pp. 203–236.
- Van Gernerden H (1993) Microbial mats: a joint venture. *Marine Geology* **113**, 3–25.
- Venn AA, Tambutté A, Holcomb M, Laurent J, Allemand D, Tambutté S (2013) Impact of seawater acidification on pH at the tissue–skeleton interface and calcification in reef corals. *Proceedings of the National Academy of Sciences of the USA* **110**, 1634–1639.
- Visscher PT, Stolz JF (2005) Microbial mats as bioreactors: populations, processes, and products. *Palaeogeography, Palaeoclimatology, Palaeoecology* **219**, 87–100.
- Visscher PT, Prins RA, van Gernerden H (1992) Rates of sulfate reduction and thiosulfate consumption in a marine microbial mat. *FEMS Microbiology Ecology* **86**, 283–294.
- Visscher PT, Reid RP, Bebout BM, Hoefft SE, Macintyre IG, Thompson JA (1998) Formation of lithified micritic laminae in modern marine stromatolites (Bahamas): the role of sulfur cycling. *American Mineralogist* **83**, 1482–1493.
- Visscher PT, Reid RP, Bebout BM (2000) Microscale observations of sulfate reduction: correlation of microbial activity with lithified micritic laminae in modern marine stromatolites. *Geology* **28**, 919–922.
- Walter LM, Burton EA (1990) Dissolution of Recent platform carbonate sediments in marine pore fluids. *American Journal of Science* **290**, 601–643.
- Walter LM, Bischof SA, Patterson WP, Lyons TW (1993) Dissolution and recrystallization in modern shelf carbonates: evidence from pore water and solid phase chemistry. *Philosophical Transactions of the Royal Society London A* **344**, 27–36.
- Webb GE (2001) Biologically induced carbonate precipitation in reefs through time. In *The History and Sedimentology of Ancient Reef Systems* (ed. Stanley G). Topics in Geobiology, 17, Kluwer Academic/Plenum, New York, pp. 159–203.
- Webb GE, Jell JS, Baker JC (1999) Cryptic intertidal microbialites in beachrock, Heron Island, Great Barrier Reef: implications for the origin of microcrystalline beachrock cement. *Sedimentary Geology* **126**, 317–334.
- Webster JM, Wallace L, Silver E, Potts D, Braga JC, Renema W, Riker-Coleman K, Gallup C (2004) Coralgal composition of drowned carbonate platforms in the Huon Gulf, Papua New Guinea; implications for lowstand reef development and drowning. *Marine Geology* **204**, 59–89.
- Webster JM, Braga JC, Clague DA, Gallup C, Hein JR, Potts DC, Renema W, Riding R, Riker-Coleman K, Silver E, Wallace LM (2009) Coral reef evolution on rapidly subsiding margins. *Global and Planetary Change* **66**, 129–148.
- Westphal H, Heindel K, Brandano M, Peckmann J (2010) Genesis of microbialites as contemporaneous framework components of deglacial coral reefs, Tahiti (IODP 310). *Facies* **56**, 337–352.
- Whittle GL, Kendall C, Dill RF, Rouch L (1993) Carbonate cement fabrics displayed: a traverse across the margin of the Bahama Platform near Lee Stocking Island in the Exuma Cays. *Marine Geology* **110**, 213–243.
- Widdel F (1988) Microbiology and ecology of sulfate- and sulfur-reducing bacteria. In *Biology of Anaerobic Microorganisms* (ed. Zehnder A). Wiley, New York, pp. 469–585.
- Zachos JC, Rohl U, Schellenberg SA, Sluijs A, Hodell DA, Kelly DC, Thomas E, Nicolo M, Raffi I, Lourens LJ, McCarren H, Kroon D (2005) Rapid acidification of the ocean during the Paleocene-Eocene thermal maximum. *Science* **308**, 1611–1615.
- Zamagni J, Košir A, Mutti M (2009) The first microbialite – coral mounds in the Cenozoic (Uppermost Paleocene) from the Northern Tethys (Slovenia): environmentally-triggered phase shifts preceding the PETM? *Palaeogeography, Palaeoclimatology, Palaeoecology* **274**, 1–17.
- Zamagni J, Mutti M, Košir A (2012) The evolution of mid Paleocene-early Eocene coral communities: how to survive during rapid global warming. *Palaeogeography, Palaeoclimatology, Palaeoecology* **317–318**, 48–65.
- Zankl H (1993) The origin of high-Mg-calcite microbialites in cryptic habitats of Caribbean coral reefs - their dependence on light and turbulence. *Facies* **29**, 55–60.

SUPPORTING INFORMATION

Additional Supporting Information may be found in the online version of this article:

Supplementary Tables (S1–S3) of crust thickness data and seawater major ion composition; Supplementary Figures (S1, S2) showing calculated seawater pH values and carbonate saturation state at Tahiti as a function of increased CO₂ partial pressure from 21 ka ago to the present day; Supplementary References.

Fig. S1 Calculated seawater pH values at Tahiti as a function of increased CO₂ partial pressure from 21 ka ago to the present day.

Fig. S2 Carbonate saturation state at Tahiti as a function of increased CO₂ partial pressure from 21 ka ago to the present day.

Table S1 Tahiti crust thickness data.

Table S2 Global crust thickness data.

Table S3 Major ion composition of seawater at a salinity of 35‰, and chlorinity of 19.374 (for source and references see DOE, 1994, table 6.1).