

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.

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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

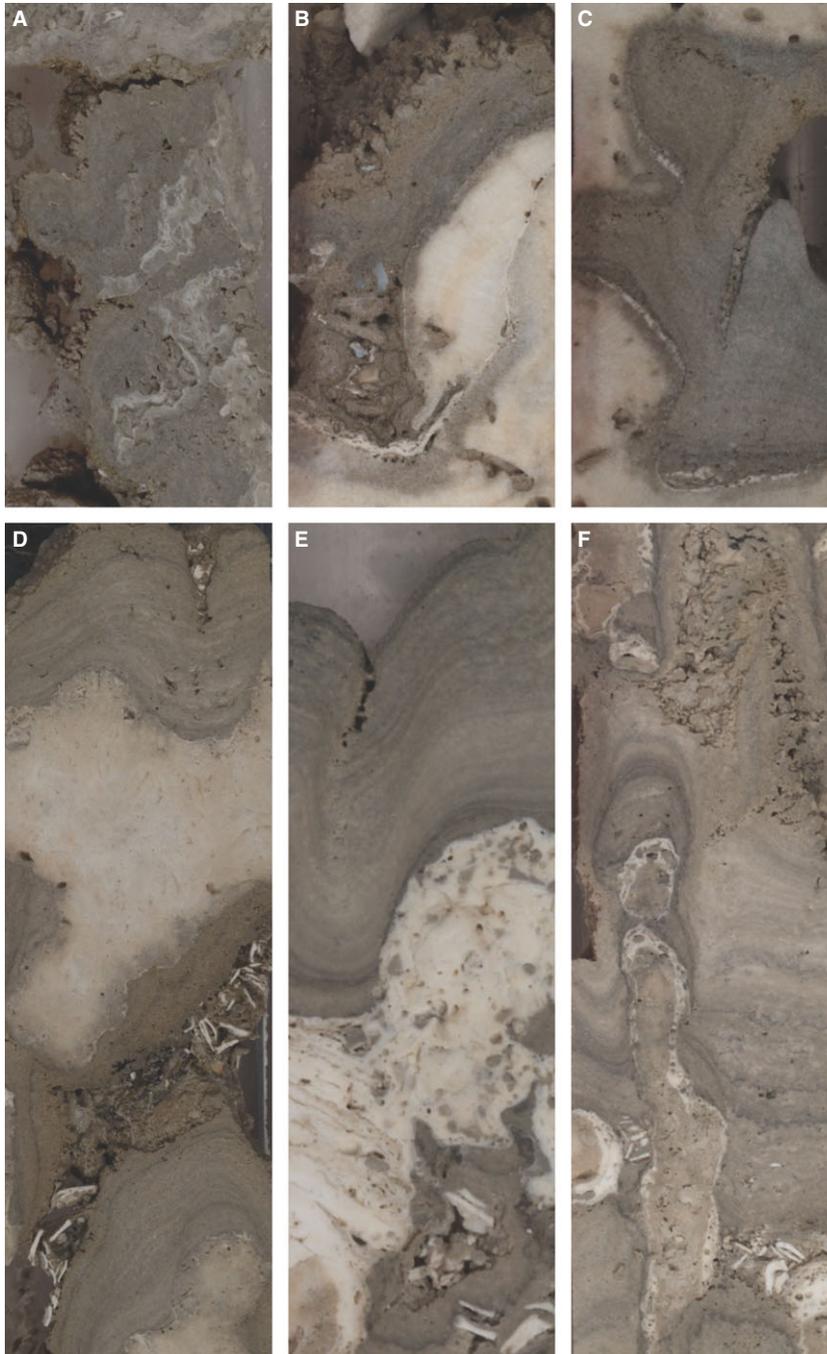


Fig. 1 Gray bacterial crusts on lighter colored coral and coralline algal reef framework and bioclastic debris in IODP Expedition 310 cores through latest Pleistocene–Early Holocene reef rock at Mara’a, SW Tahiti. Sample ages increase from A to F. (A) Irregularly layered locally dendritic crusts on finely 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).

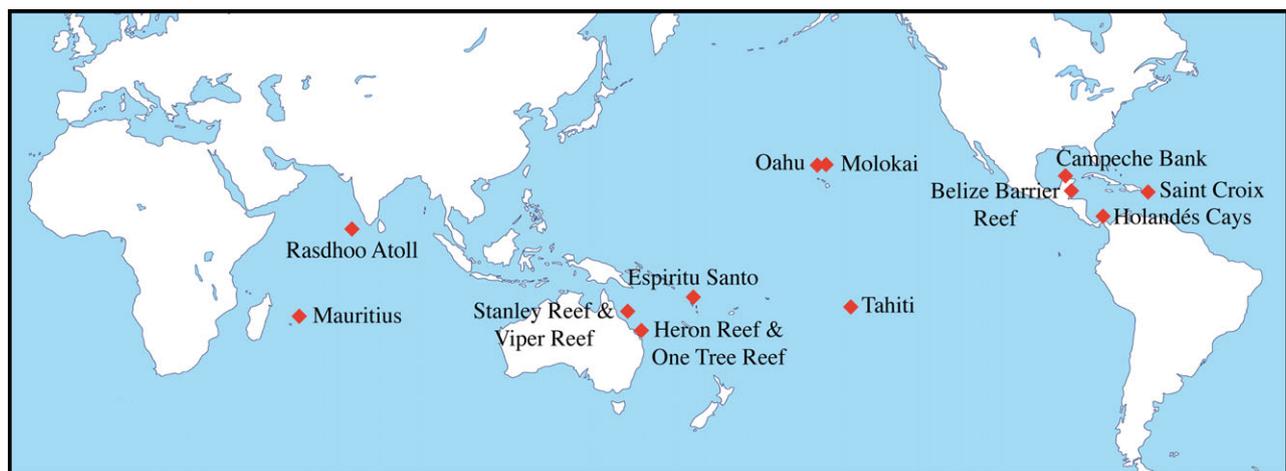


Fig. 2 Reef localities from which the crust thickness data in Fig. 3 were compiled (see Table S2).

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

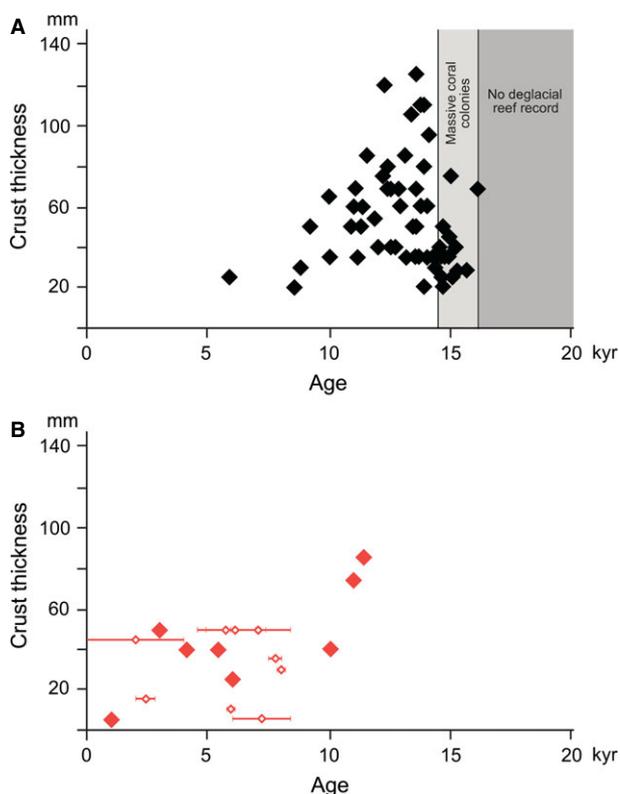


Fig. 3 Bacterial crust thicknesses. (A) Tahiti, measured from IODP Expedition 310 cores with known ages (Abbey *et al.*, 2011; Camoin *et al.*, 2012). Cavernous reef framework began to develop in these cores ~14.6 ka ago. (B) Other Pacific, Atlantic, and Indian Ocean reefs. Small open symbols with bars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

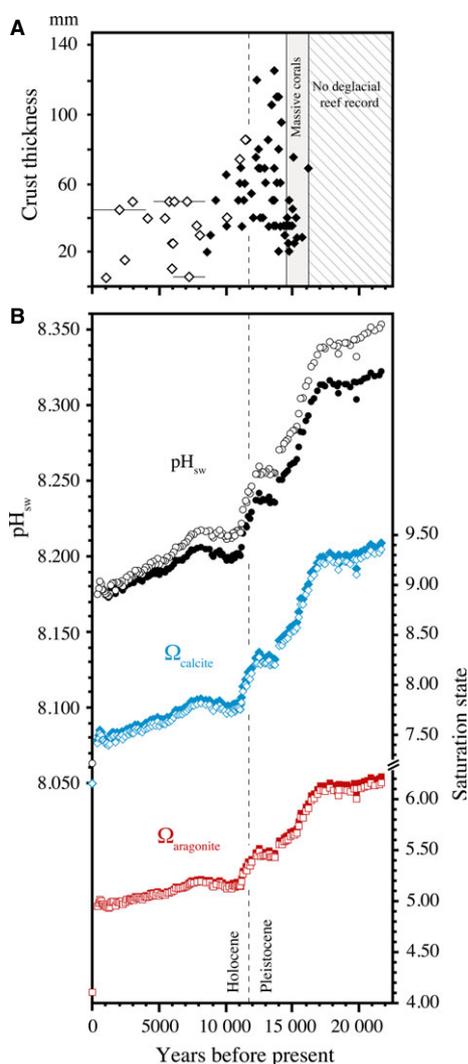


Fig. 4 A: Crust thicknesses at Tahiti (filled diamonds, from Fig. 3), and from Global localities (open diamonds). B: Calculated chemical parameters for surface seawater at Tahiti over the past 21 ka: pH (based on seawater scale; black symbols), carbonate saturation states of calcite (blue symbols), and 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 Maldive 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

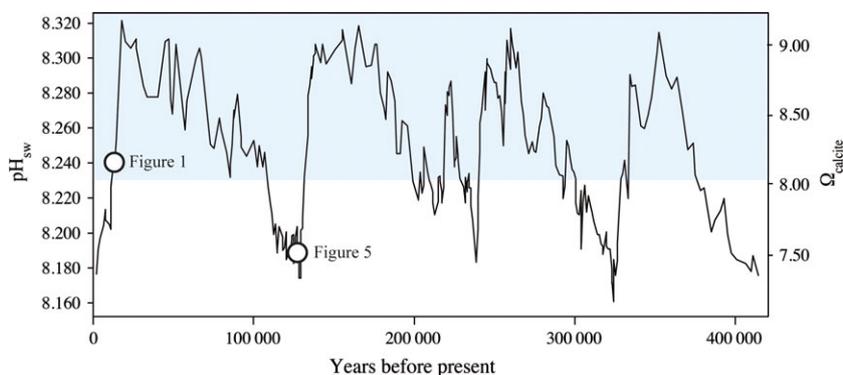


Fig. 6 Calculated surface ocean fluctuations in pH and calcite saturation state during the past four glacial cycles (414 ka). Calculation based on CO_2 values from the Vostok ice core (Petit *et al.*, 1999), assuming average seawater surface salinity of 36.7‰, average sea-surface temperature of 25.5 °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.

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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).