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A novel paleo-bleaching proxy using boron isotopes and high-resolution laser ablation to reconstruct coral bleaching events

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Abstract

Coral reefs occupy only ~ 0.1 % of the oceans habitat, but are the most biologically diverse marine ecosystem. In recent decades, coral reefs have experienced significant global declines due to a variety of causes, one of the major being widespread coral bleaching events. During bleaching the coral expels its symbiotic algae losing its main source of nutrition generally obtained through photosynthesis. While recent coral bleaching events have been extensively investigated, there is no scientific data on historical coral bleaching prior to 1979. In this study, we employ high-resolution femtosecond Laser Ablation Multiple Collector Inductively Coupled Plasma Mass Spectrometry (LA-MC-ICP-MS) to demonstrate a distinct biologically-induced decline of boron (B) isotopic composition (δ^{11}B) as a result of coral bleaching. These findings and methodology offer a new use for a previously developed isotopic proxy to reconstruct paleo-coral bleaching events. Based on a literature review of published δ^{11}B data and our recorded "vital effect" of coral bleaching on the δ^{11}B signal, we also describe at least two possible coral bleaching events since the Last Glacial Maximum. The implementation of this bleaching proxy holds the potential of identifying occurrences of coral bleaching throughout the geological record. A deeper temporal view of coral bleaching will enable scientists to determine if it occurred in the past during times of environmental change and what outcome it may have had on coral population structure.

1 Introduction

1.1 Coral bleaching

Coral bleaching occurs when environmental stress, primarily increased water temperature and high irradiance, induces breakdown of the coral-algae symbiosis and the host initiates algae expulsion. As a result, corals either temporarily lose their pigmentation or die from lack of nourishment from the algae. Bleaching is, therefore, considered an acute risk to the health of coral reefs, although some studies suggest it is an adaptive response to environmental change (Fautin and Buddemeier, 2004).

Coral bleaching was first reported in the early 20th century (Yonge et al., 1931) and heavily documented since 1979, as widespread bleaching events have been recorded with increased frequency and severity (Hoegh-Guldberg, 1999). Isotopic dating of massive corals suggests that coral bleaching may have already caused mortality events by the end of the 19th century (Yu et al., 2006). While bleaching events have been proposed to have occurred throughout the geological record (suggested for symbiotic foraminifera during unstable sea surface temperature (SST) in the upper Eocene, Wade et al., 2008), there has been no experimentally established proxy to examine suspected paleo-coral bleaching.

1.2 Paleo bleaching proxy

Previous attempts at establishing a paleo-proxy for coral bleaching focused on carbon and oxygen isotopes (Heikoop et al., 2000; Suzuki et al., 2003) as well as skeletal ultraviolet fluorescence (Suzuki et al., 2003). However the balance between kinetic and metabolic processes, affected by factors such as coral growth rate and local light environment (i.e. shaded vs. unshaded side of a colony), complicates the use of these proxies (Suzuki et al., 2003). A correction method, suggested by Heikoop et al. (2000) to differentiate kinetic from metabolic effects, was recently refuted for the case of coral bleaching (Schoepf et al., 2014a). Boron isotopes, currently used for estimating $\mathrm{pH_{sw,}}$ may act as an effective paleo-bleaching proxy, as kinetic effects do not interfere with isotopic equilibrium during calcification (Zeebe et al., 2001).

Considerable research has been focused on paleo-techniques for estimating $\mathrm{pH_{sw}}$ and $p\mathrm{CO_{2\,atm}}$ as current atmospheric $\mathrm{CO_2}$ values of ~ 400 parts per million by volume (ppmv) are at the highest levels of the past million year timeframe (Caldeira and Wickett, 2003; Hoegh-Guldberg et al., 2007; Hönisch et al., 2012). At time scales shorter than one million years, paleo-$\mathrm{CO_2}$ analysis is derived mostly from air bubbles in ice cores (Monnin et al., 2001; Petit et al., 1999; Vinther et al., 2009) and boron isotopic composition (δ^{11}B) from carbonate skeletons of foraminifera (Foster, 2008; Hönisch and Hemming, 2005; Hönisch et al., 2009; Palmer et al., 2010; Palmer and Pearson, 2003; Sanyal et al., 1995) and corals (Douville et al., 2010; Gaillardet and Allegre, 1995; Liu et al., 2009; Pelejero et al., 2005; Wei et al., 2009). Skeletal δ^{11}B values are used for paleo pH reconstruction as they correlate with surrounding waters' pH levels. This correlation is based on the assumptions (1) that internal pH (i.e. where calcification takes place) is correlated with ambient pH, and (2) that in seawater only one B species, namely the isotopically lighter borate, is reacting with the aragonitic surface of corals rather than the isotopically heavier boric acid. The B species distribution and the δ^{11}B of the B species are pH dependent. If borate represents the only source of B in the skeletons of corals, than its δ^{11}B is equal to the δ^{11}B of the coral. Therefore, the δ^{11}B of corals is utilized as a proxy of ocean pH levels at the time of calcification.

Thermally bleached corals however show diminished symbiont photosynthesis (Glynn, 1996) causing a concomitant drop in pH measured at the corals diffusive boundary layer (DBL) (Al-Horani, 2005). While the interaction of coral biology with δ^{11}B (known as vital effects) has been previously quantified (McCulloch et al., 2012; Trotter et al., 2011), the change in physiology due to coral bleaching is hypothesized to go beyond the natural vital effect, decoupling internal and ambient pH, and by that, enabling the use of δ^{11}B as a proxy for paleo-bleaching. This approach was recently challenged by Schoepf et al. (2014b) who reported no difference in δ^{11}B signal imprinted in the skeletons of corals that experienced short term (ca. two weeks) bleaching event. We hypothesize however, that longer bleaching events, and higher resolution sampling techniques, may allow the detection of the boron-bleaching footprint in coral skeletons.

In this study, we examined the footprint of coral bleaching manifested in the δ^{11}B values of coral skeletons using experimentally and naturally bleached specimens. Through the use of laser ablation, high-resolution sampling of the coral skeleton deposited while in a bleached state, we quantify a "boron bleaching footprint". We applied this proxy to published coral δ^{11}B records to investigate the signature of coral bleaching since the Last Glacial Maximum.

2 Materials and methods

2.1 Experimentally induced *Porites* sp. bleaching

2.1.1 Experimental set-up

Two adjacent *Porites* sp. colonies were collected at 10 m depth in the Gulf of Aqaba, in the northern Red Sea (29°30′06″ N, 34°55′00″ E). The coral was cut into 2 cm × 2 cm "nubbins" and left to recover in controlled laboratory conditions (23 °C, pH of 8.17 and salinity of 40.7 psu) for three weeks prior to starting the experiment. Nubbins were maintained in open-system water tables with an input flow rate of ~ 2.0 L min^{-1} and constant light of an average of 150 µmol photons m^{-2} s^{-1}. Temperature fluctuations are outlined for both control and experimental treatments in the Supplement (Table S1). Nubbins were stained at the beginning of the experiment with Alizarin Red S.

Fv/Fm values were measured approximately every two days for the first three weeks of the experiment until bleaching was seen. Twelve dark-adapted samples were measured for each treatment using the single turnover flash of over 10 000 µE on a fast repetition rate fluorometer (FRRF, FIRe system, Satlantic, Halifax, Nova Scotia, Canada).

Oxygen and pH were measured with microelectrodes in the diffusive boundary layer (DBL) of a healthy and bleached coral during the bleached period (Fig. S1 in the Supplement). At the end of the experiment, the tissue of all coral was removed using a high pressure airbrush.

2.1.2 δ^{11}B analysis

A total of six coral nubbins were analyzed for δ^{11}B using UV femtosecond LA-MC-ICP-MS, two from the control treatment and four from the bleaching treatment. By using a femtosecond (fs) laser ablation system we avoided issues such as thermal fractionation and matrix effects that can occur using nanosecond lasers when using glass standards for carbonate samples (Fietzke et al., 2010; Horn and von Blanckenburg, 2007). Furthermore, the fs-laser ablation technique (ultra-short ~ 200 fs pulses) allows for fast and accurate determination of the isotopes in the coral skeleton with minimal melting of the material caused by heat transfer.

For boron analysis, the coral skeletons were grinded to flatten the surface and then immersed in an ultra-sonicated Milli-Q water bath for 5 min to remove any particles. Sodium Hypochlorite (NaClO) was used to remove any organics and finally samples were washed with Milli-Q water and Acetone. δ^{11}B analysis was performed using a Thermo Finnigan-Neptune MC-ICP-MS, connected to a UV fs (10^{-15} s) laser for ablation (Horn and von Blanckenburg, 2007). For δ^{11}B readings, the center cup was set at ~ 10.5 u with the left cup set to read ^{10}B (~ 10 u) and the right cup to read ^{11}B (~ 11 u). All cups were calibrated to capture the peak of the isotope's signal while avoiding interference from other unwanted masses. NIST SRM 610 was used as the reference material for bracketing.

2.2 Natural occurring *Stylophora pistillata* bleaching

A *Stylophora pistillata* fragment was taken from the coral documented by Nir et al. (2014) to undergo bleaching during summer 2010. The coral skeleton was sliced, cleaned and measured for δ^{11}B using the same procedures described above. After LA-MC-ICP-MS measurements, coral slices were polished to a thickness of ~ 0.5 mm on a microscope slide and photographed through a light microscope. Density bands (annual growth bands) were analyzed as gray intensity of pixels along the measurements path using ImageJ software.

2.3 Previously published δ^{11}B records examination

Following our experimental results that showed a distinctive bleaching footprint in coral's δ^{11}B values, we examined previously published coral and foraminifera's δ^{11}B records for δ^{11}B drops resembling the "bleaching foot print" evidenced in our experiment. Our search was focused on the time frame of present day to the penultimate deglaciation (∼ 125 kyr BP), when global temperatures were comparable to present day values (Fig. 2). δ^{11}B and calculated pH values, as well as SST and atmospheric CO_2 data, were retrieved from relevant publications' tabulated data if available. Data of Gaillardet and Allegre (Gaillardet and Allegre, 1995), which were not available, were recovered from graphics using GETDATA graph digitizer (http://getdata-graph-digitizer.com/). SST data for the open sea as close as possible to Arlington Reef (Lat. 17° S, Lon. 148° E, GBR) was taken from NOAA ERSST-3b database (http://nomads.ncdc.noaa.gov/las/getUI.do) monthly reconstruction (Smith et al., 2008). Meta data for the reviewed coral records are presented in the Supplement (Table S2). Relative δ^{11}B drops ($\Delta\delta^{11}$B) in published δ^{11}B records were calculated as the difference between a specific δ^{11}B value and the average δ^{11}B of the whole data series in which it belongs. For the comparison of experimental results and previous records, the effect of sampling resolution was estimated and corrected by averaging δ^{11}B throughout the whole experimental time series (Fig. 1).

3 Results

3.1 Experimental bleaching

Oxygen and pH micro-sensor analysis in the DBL of a bleached massive *Porites* sp. revealed a decrease in pH down to 7.85 (0.32 pH units below ambient pH values) during light conditions with no increase in oxygen, as opposed to a healthy coral which exhibited an increase in oxygen production and a re-alkalization of the DBL under the same light conditions following a period of dark incubation (Fig. S1). These measurements serve as validation of an already quantified phenomenon of reduced pH in the DBL as a result of bleaching (Al-Horani, 2005). While corals are known to elevate the pH at the site of calcification relative to ambient seawater (Venn et al., 2011), reduced seawater pH resulting from the chemical dissolution of CO_2 has been shown to reduce the calcifying medium pH, overwhelming up-regulatory compensation (Venn et al., 2013). Theoretically, the same would hold true for biological reductions of pH in the DBL evident in micro-sensor measurements.

Corals' responses to the heat stress conditions in the experimentally induced bleaching experiment varied individually, where two nubbins showed no apparent bleaching while the other two were either partially or fully bleached. Fully and partially thermally-induced bleached corals displayed a δ^{11}B drop ($\Delta\delta^{11}$B) of 2.2–3.7 ‰ relative to their recovered outer rim values, descending to 21.5 ‰ (Fig. 1). Due to the high resolution of sampling (~ 45 µm equals about two-three weeks of skeletal deposition) we were able to record low δ^{11}B values at the time of bleaching. In order to demonstrate the effect of sampling resolution and to allow comparison of our results with some lower resolution studies, we calculated the average values for the whole experiment (~ 7 months) consisting of unbleached acclimation, heat stress driven bleaching and recovery. In this case, partially and fully bleached corals showed δ^{11}B drop of −1.55 and −2.34 ‰ (respectively, Fig. 1). Interestingly, heat stressed corals showed a δ^{11}B drop of −0.78 ‰ even though not apparently bleached. This finding contradicts previous reports of increased δ^{11}B in elevated temperatures (Dissard et al., 2012) implying a distinctive difference between the effect of "normal" high temperatures within the natural habitat's range increasing photosynthesis and calcification rates, and the effect of heat-stress-temperature conditions depressing coral physiology.

3.2 Natural bleaching

A mesophotic (60 m depth) *S. pistillata* coral documented to go through a seasonal summer bleaching (Nir et al., 2014) showed a δ^{11}B drop of $\Delta\delta^{11}\text{B} = -5.1$ ‰ during bleached period (Fig. 2). The "bleached" low δ^{11}B value falls on the value calculated with boron isotope equilibrium constant ($^{11-10}K_B$) of Klochko et al. (2006) (not accounted for vital effect) while the "healthy" high δ^{11}B value coincides with the normal value measured for this species at pH 8.2 (with symbionts) (Krief et al., 2010).

In contrast to our findings, recent explorations of boron isotopes in bleached corals found no effect of short-term bleaching on the skeletal boron signal (Schoepf et al., 2014b). Our study may have been able to capture the depletion in δ^{11}B due to (1) the use of high resolution sampling across the coral growth axis and (2) the relatively long bleached period, allowing a coral to precipitate "new" aragonite encompassing the Boron signal of bleaching. This allows for an intricate time series comparison within the same individuals enabling the detection of relative changes in the skeletal boron isotopes at multiple time points before, during and after a bleaching event sustained over approximately three months.

3.3 Establishment of the δ^{11}B bleaching proxy

Our experimental results showed decreased pH at the DBL accompanied by a sharp δ^{11}B drop for bleached coral held at constant ambient $\mathrm{pH_{sw}}$. A field "ground truth" for this boron bleaching foot print was found in a naturaly bleached mesophotic (60 m depth) *S. pistillata* coral. Further evidence that δ^{11}B drop can serve as a "bleaching footprint" can be gathered from a recent coral bleaching event on Australia's Great Barrier Reef (GBR) (Wei et al., 2009). Using a ca. 200 year-old Porites, Wei et al. reported low δ^{11}B values ($\delta^{11}B_{1998} = 21.06$ ‰, $\Delta\delta^{11}B_{1998} = -2.3$ ‰ and $\delta^{11}B_{2001} = 21.93$ ‰, $\Delta\delta^{11}B_{2001} = -1.4$ ‰, Fig. 2) during the 1998 and early 2002 bleaching events. These low values, measured at times of bleaching events, are similar to the low δ^{11}B values recorded in our experimentally bleached coral.

Based on our laboratory results as well as on natural records of *Porites* sp. bleaching, we define the "boron bleaching footprint" as δ^{11}B drop of at least 1.5 ‰. This value was chosen by estimating the average $\Delta\delta^{11}$B for ca. one year in the experimentally bleached corals, simulating the common paleo pH δ^{11}B records temporal resolution (Table S2). This value also falls outside the range of the natural variability measured in *Porites lobata* coral skeleton throughout two annual cycles (Hemming et al., 1998) (Fig. 3 – green boxes). In applying this proxy to identify paleo-bleaching events, we also inspected concomitant paleo-SST, air temperature and $p\text{CO}_{2\,\text{atm}}$ records to provide support for our conclusions (Fig. 3). In cases where a drastic drop in δ^{11}B is correlated with high SST or severe warming rather than $p\text{CO}_2$ increase, we propose that a thermal stress may have induced bleaching and resulted in the low δ^{11}B values, rather than a pH_{sw} drop.

It is important to note that most coral paleo-reconstruction studies focus on the analysis of a single core due to the difficulty in preparation and analysis of the samples. Coral bleaching however can be spatially heterogeneous with neighboring individuals exhibiting variable responses (Baker et al., 2008) making broad generalizations difficult. Thus if a depletion in δ^{11}B values is not found where bleaching is expected this does not necessarily mean that coral bleaching did not occur on that reef at some point in time. For example, in a recent analysis of a massive Porites core from Guam (Shinjo et al., 2013), no bleaching signal is found in the δ^{11}B signature from the period of 1940–2000. This does not rule out bleaching in the region. In fact, slight depressions in the δ^{11}B values ($-0.5 > \Delta\delta^{11}\text{B} > -1$ ‰) coincide with El-Niño years and may indicate physiological heat stress of the coral. Alternatively, when the boron bleaching footprint is evident in fossil coral core samples, as outlined in the coming examples, based on our experimental findings it may indicate that coral bleaching has occurred.

3.4 Coral bleaching events recorded since the Last Glacial Maximum

Over the past 800 000 years of glacial/interglacial cycles, atmospheric CO_2 oscillated between 180–280 ppmv, with an increase of less than 30 ppmv from the Holocene until the beginning of the industrial revolution (~ 1860). Ocean surface's pH paleo-records exhibit more acute and radical changes than atmospheric $p\text{CO}_2$ (Fig. 3). These shifts have been interpreted as major oceanographic events such as alterations of ocean circulation deriving from upwelling of cold, low pH waters to the surface (Douville et al., 2010; Liu et al., 2009). We inspected published paleo-pH records from coral skeletons through the Eemian interglacial stage (~ 130 kyr BP) and identified six suspected data points (Fig. 3 – red vertical lines) that meet our "boron bleaching footprint" definition of a depletion in δ^{11}B values greater than 1.5 ‰ relative to the average values measured in that series (Fig. 3 – dotted line). We make a case for these instances that represent potential bleaching events.

3.4.1 20th century, GBR

Pelejero et al. (2005) measured a 280 year δ^{11}B record of *Porites* sp. and reported the lowest δ^{11}B value for the last three centuries at Flinders Reef, GBR, ca. 1988 (using 5 year averages) (22.99 ‰, 7.91 pH units) with an overall trend of low pH values correlated with positive values of the Interdecadal Pacific Oscillation (IPO) index (El Niño like conditions), interpreted to result in low rates of water exchange at the Flinders Reef's lagoon. However, high-resolution inspection of 1987–1988 reveals that the lowest δ^{11}B value was recorded during the warmest month (February 1988, δ^{11}B = 22.26 ‰, stands 1.65 ‰ below the multi annual average) even though wind speed, normally correlated with a high lagoonal water exchange, was high that month. Since this low δ^{11}B value also coincides with warm SST and the 1988 worldwide mass bleaching (Williams and Bunkley-Williams, 1990), it is likely that the reported low δ^{11}B value is due to heat stress or coral bleaching. This value was preceded by a period of lower values that commenced at the transition from cooler to warmer SST during the austral summer of 1987 and could indicate a sustained bleaching period, such as was seen in the δ^{11}B values of our experimentally bleached coral skeletons.

Additional low δ^{11}B values (δ^{11}B < 21.65 ‰, stands 1.67 ‰ below the multi annual average) were recorded for Arlington reef at two sampling points during 1937–1940 (Wei et al., 2009) that coincide with a trend of rapidly warming SST (Smith et al., 2008; Fig. S2), suggested to indicate pronounced bleached periods within this time frame.

3.4.2 6 kyr BP, SCS

Liu et al. (2009) measured Porites sp. δ^{11}B from the South China Sea (SCS) and reported a δ^{11}B drop, at ~ 6 kyr BP ($\Delta\delta^{11}B = -1.82$ ‰) interpreted by the authors as low pH during the Holocene thermal optimum (~ 5–9 kyr BP). This period was suggested to be characterized by an intensified summer monsoon that resulted in strengthened upwelling and introduced low pH deep water to the surface of SCS. However, no sign of cold deep water upwelling is evidenced in the reported SST values (Yu et al., 2005). Furthermore, Mg/Ca derived SST records related to SCS upper waters (0–30 m) temperature show a peak in SST around 6 kyr BP (Steinke et al., 2008) ascending to 29 °C. Translating pH values to $p\text{CO}_2$ (using CO2sys software, Pierrot and Wallace, 2006) shows that although Holocene $p\text{CO}_{2\,\text{atm}}$ was relatively stable (260–290 ppmv, not including the 20th century), reported pH values are equivalent to much higher $p\text{CO}_2$ levels, up to 571 ppmv at 6 kyr BP. This drop of δ^{11}B (at 6 kyr BP) corresponds better with high SST, rather than a drastic increase in $p\text{CO}_2$ or upwelling introducing low pH water to the surface. Therefore, we propose that the low δ^{11}B values imprinted in SCS corals 6 kyr BP are the result of a bleaching event.

3.4.3 11.5 kyr BP, Central Pacific

Both Gaillardet and Allegre (1995) and Douville et al. (2010) reported a severe drop of δ^{11}B measured in central sub-equatorial pacific corals (*Acropora* sp. from Tahiti (Gaillardet and Allegre, 1995) and *Porites* sp. from Marquesas Is. (Douville et al., 2010)) at the end of the Younger Dryas period ~ 11.5 kyr BP ($\Delta\delta^{11}B = -2.18$ ‰). This drop deviated from the otherwise stable values measured before and after this time period by more than 1.4 ‰ (interpreted as pH drop ~ 0.2, Douville et al., 2010) (Fig. 2,). The authors attributed this dip to sustained La-Niña like conditions which introduced lower pH cold waters in the central sub-equatorial Pacific (Douville et al., 2010). The equatorial Pacific SST gradient (ΔSST), which coincides with the strength of westward low pH water advection (Koutavas et al., 2002), was intensified at the end of Younger Dryas, potentially extending the low pH "cold tongue" westward closer to the Tahiti Islands. Nevertheless, ΔSST was only as high as modern times remaining constant throughout the Holocene, while δ^{11}B returned to background values (Fig. 3) (Kienast et al., 2001; Koutavas et al., 2002). The dominance of La-Niña patterns at this period is further challenged by alternative suggestions of El-Niño conditions prevailing during the Bolling interstadial and the end of Younger Dryas (Koutavas and Sachs, 2008). Furthermore, following the cold Younger Dryas period was a period of rapid warming (Asami et al., 2009; Schmidt et al., 2006), which likely increased seasonal maximum temperatures (Fig. 3). The yearly increases in temperature, the major cause of coral bleaching in the modern era (Baker et al., 2008), could have resulted in a coral bleaching event 11.5 kyr BP in the central sub-equatorial Pacific. This offers an alternative explanation for the low δ^{11}B values obtained for corals, rather than sustained La-Niña like conditions.

4 Conclusions

Coral bleaching exerts a considerable footprint on δ^{11}B measurements taken from the scleractinian corals *S. pistilata* and massive *Porites* sp. ($\Delta\delta^{11}$B = 1.5–5.1 ‰). Employing high-resolution femtosecond LA-MC-ICP-MS, we provide evidence that δ^{11}B is sensitive, and highly influenced by the physiological interactions of the photosymbiont and the calcifying organism (i.e., a drop in photosynthetic activity of photosymbionts during bleaching events). When supported with concurrent $p\mathrm{CO}_{2\,\mathrm{atm}}$, foraminifera pH and SST records, this proxy opens the door to investigations that utilize δ^{11}B as a paleo-bleaching marker. Our findings provide evidence that coral bleaching may not be an exclusively modern phenomenon and we have identified at least two instances since the LGM (~ 20 kyr BP) prior to the industrial revolution where coral bleaching likely occurred. If short-term bleaching is indeed untraceable with δ^{11}B measurements (Schoepf et al., 2014b),then the suspected paleo-bleaching events may be a result of longer sustained bleaching episodes.

Overall, our experimental results, along with previously published data, highlight the challenges of utilizing δ^{11}B as a straight forward proxy for paleo-pH$_{sw}$. To gain an accurate interpretation of δ^{11}B values, the bleaching state of the organism from which the data is derived must be considered.

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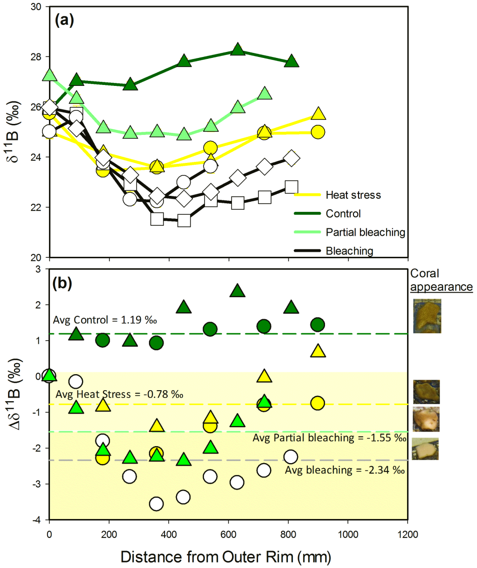

Figure 1. δ^{11}B measurements of coral skeletons following different bleaching situations. **(a)** Dark green symbols represent control coral measurements, yellow symbols represent heat stressed corals, while bright green and white symbols represent partially and fully bleached corals respectively. Values of $\delta^{11}\mathrm{B} = [^{11}\mathrm{B}/^{10}\mathrm{B}]_{\mathrm{sample}}/[^{11}\mathrm{B}/^{10}\mathrm{B}]_{\mathrm{NIST\ 610\ standard}} - 1 \times 1000$. Values are given in parts per mil (‰). Error bars represent standard error (≤ 0.30 ‰, 2σ). Dark and bright green triangles, white diamonds and yellow triangles data series were subtracted with −2 ‰ to compensate for a change in instrumental setup (detailed in SOM). **(b)** Relative change from outer rim value for each sample ($\Delta\delta^{11}$B). All rim values (at 0 µm) were equaled to zero and the change in δ^{11}B values was plotted for each transect along the growth axis. Positive values equal an enrichment in values while negative values are depleted relative to the rim value. Dashed lines and above written values represent the average $\Delta\delta^{11}$B for a coral bleaching state. Coral's appearance during the heated stage of the experiment is illustrated by the nubbins pictures on the right side.

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A novel paleo-bleaching proxy using boron isotopes

G. Dishon et al.

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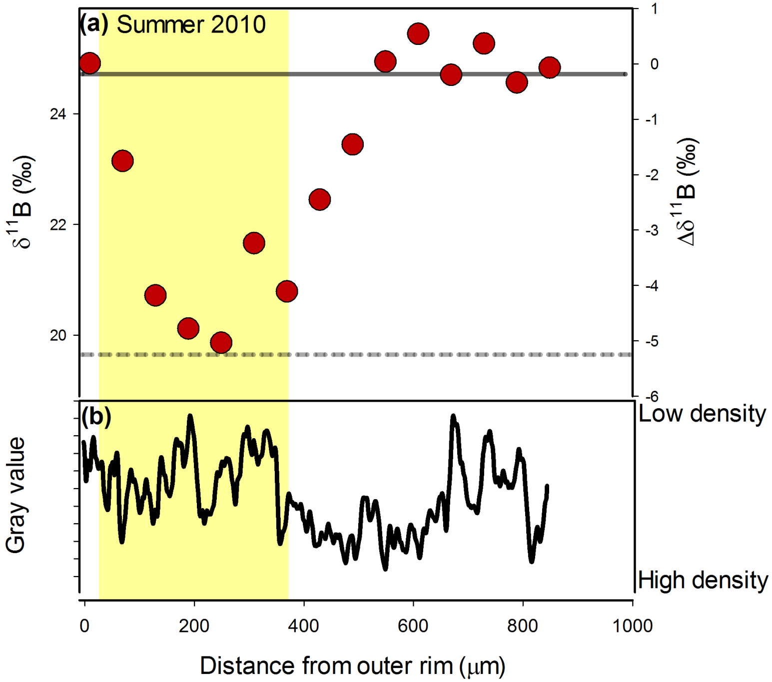

Figure 2. (a) δ^{11}B measurements of mesophotic (60 m) *Stylophora pistillata* coral documented to undergo bleaching during summer 2010 (Nir et al., 2014). **(b)** Skeleton density, reported as the gray value of pixels along the ablation transect. Yellow shaded area represents the low density skeleton band deposited in summer 2010. Solid and dashed gray lines represent the expected δ^{11}B value for $\text{pH}_{\text{sw}} = 8.2$ calculated with boron isotope equilibrium constant ($^{11-10}K_B$) of Klochko et al. (2006) (not accounted for vital effect) and an empirical coefficient specific to this species (with symbionts) by Krief et al. (2010) respectively.

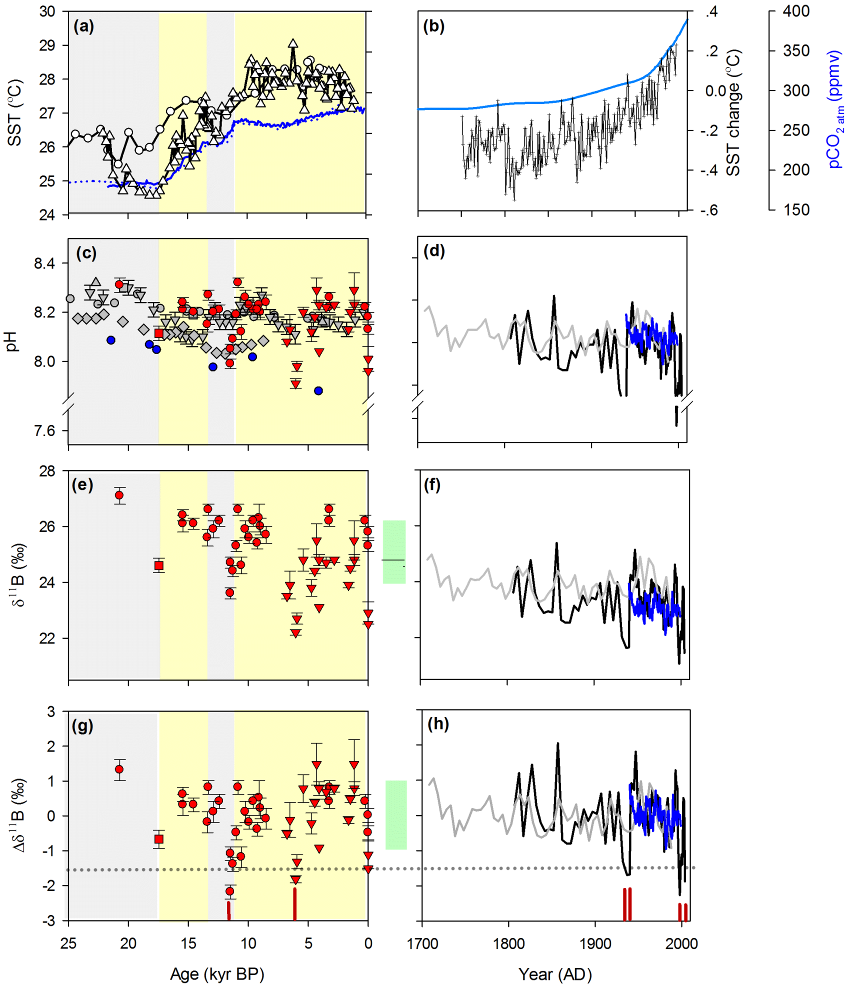
(a)
SST (°C)
30
29
28
27
26
25
24
(b)
SST change (°C)
.4
.2
0.0
-.2
-.4
-.6
$pCO_{2\,atm}$ (ppmv)
400
350
300
250
200
150
(c)
pH
8.4
8.2
8.0
7.6
(d)
(e)
$\delta^{11}B$ (‰)
28
26
24
22
(f)
(g)
$\Delta\delta^{11}B$ (‰)
3
2
1
0
-1
-2
-3
(h)
25
20
15
10
5
0
Age (kyr BP)
1700
1800
1900
2000
Year (AD)

Figure 3. 25 000 year records of paleo-ocean climate and pH **(a–d)** and boron isotopic compositions in coral skeletons **(e–h)**. Blue lines represent atmospheric $p\mathrm{CO}_2$ measured at ice cores trapped gas (Monnin et al., 2001, 2004; Petit et al., 1999; Robertson et al., 2001) and direct measurements (Tans, 2012), open symbols represent SST records (triangles – South China Sea (Steinke et al., 2008), circles – Western Caribbean sea (Schmidt et al., 2006) and crosses – modern tropics (Indian and Pacific oceans) (Wilson et al., 2006)). δ^{11}B derived pH from foraminifera (ocean surface in gray symbols–circles (Foster, 2008), inverted triangles (Palmer and Pearson, 2003), rectangles (Hönisch et al., 2009), diamonds (Palmer et al., 2010) and triangles (Hönisch and Hemming, 2005); Deep waters pH in blue symbols (Yu et al., 2010)) and coral (red symbols – circles (Douville et al., 2010), inverted triangles (Liu et al., 2009) and rectangles (Gaillardet and Allegre, 1995); grey (Pelejero et al., 2005) blue (Shinjo et al., 2013) and black (Wei et al., 2009) lines) is shown in **(c, d)**. The boron isotopic compositions, on which coral pH is based, are presented in **(e, f)**. The difference of δ^{11}B from the average value in record ($\Delta\delta^{11}$B) is shown in **(g, h)** together with a dotted line under which data points are suggested to represent coral bleaching. Green bars and line within represent δ^{11}B annual range and average measured at unbleached coral (Hemming et al., 1998). Red vertical lines mark the timing of suspected bleaching events. Grey and yellow shaded bars represent cold and warm periods respectively.