AGU PUBLICATIONS

Paleoceanography

RESEARCH ARTICLE
10.1002/2016PA002968

Key Points:
- Spatially variable correlations between Li/Mg and Sr/Ca ratios and temperature in Siderastrea siderea
- Downcore coral skeletal Li/Mg and Sr/Ca ratios are well correlated with HadISST in the forereef
- Li/Mg is a useful addition to the SST proxy toolbox in some regions

Supporting Information:
- Supporting Information S1
- Table S1
- Table S2
- Table S3
- Table S4
- Table S5

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Citation:
Fowell, S. E., K. Sandford, J. A. Stewart, K. D. Castillo, J. B. Ries, and G. L. Foster (2016), Intrareef variations in Li/Mg and Sr/Ca sea surface temperature proxies in the Caribbean reef-building coral *Siderastrea siderea*, *Paleoceanography*, *31*, 1315–1329, doi:10.1002/2016PA002968.

Received 19 APR 2016
Accepted 15 SEP 2016
Accepted article online 19 SEP 2016
Published online 5 OCT 2016

Intrareef variations in Li/Mg and Sr/Ca sea surface temperature proxies in the Caribbean reef-building coral *Siderastrea siderea*

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Abstract Caribbean sea surface temperatures (SSTs) have increased at a rate of 0.2°C per decade since 1971, a rate double that of the mean global change. Recent investigations of the coral *Siderastrea siderea* on the Belize Mesoamerican Barrier Reef System (MBRS) have demonstrated that warming over the last 30 years has had a detrimental impact on calcification. Instrumental temperature records in this region are sparse, making it necessary to reconstruct longer SST records indirectly through geochemical temperature proxies. Here we investigate the skeletal Sr/Ca and Li/Mg ratios of *S. siderea* from two distinct reef zones (forereef and backreef) of the MBRS. Our field calibrations of *S. siderea* show that Li/Mg and Sr/Ca ratios are well correlated with temperature, although both ratios are 3 times more sensitive to temperature change in the forereef than in the backreef. These differences suggest that a secondary parameter also influences these SST proxies, highlighting the importance for site- and species-specific SST calibrations. Application of these paleothermometers to downcore samples reveals highly uncertain reconstructed temperatures in backreef coral, but well-matched reconstructed temperatures in forereef coral, both between Sr/Ca-SSTs and Li/Mg-SSTs, and in comparison to the Hadley Centre Sea Ice and Sea Surface Temperature record. Reconstructions generated from a combined Sr/Ca and Li/Mg multiproxy calibration improve the precision of these SST reconstructions. This result confirms that there are circumstances in which both Li/Mg and Sr/Ca are reliable as stand-alone and combined proxies of sea surface temperature. However, the results also highlight that high-precision, site-specific calibrations remain critical for reconstructing accurate SSTs from coral-based elemental proxies.

1. Introduction

Global mean sea surface temperatures (SSTs) have been rising since the Industrial Revolution, primarily as a result of the change in the radiative forcing imposed by increasing anthropogenic greenhouse gas emissions (e.g., atmospheric pCO_2 change from 280 to 400 ppm [*Cubasch et al.*, 2013]). The atmosphere carries only 2% of the heat content of the ocean-atmosphere system, and in tandem with an increase in atmospheric temperature, the global average warming in the upper 75 m of the oceans has been 0.11°C per decade (between 1971 and 2010). This global SST increase is not geographically uniform and is amplified in areas such as the Caribbean Sea, where it has increased at a rate of more than 0.2°C per decade, resulting in a total change of ~0.8°C over the last 40 years [*Rhein et al.*, 2013; *Glenn et al.*, 2015].

Valuable insight into the impacts of future SST changes on areas of ecological importance, such as coral reefs, can be obtained from the response of ecosystems to past environmental change. Yet historical records of SST prior to the period of modern instrumentation (1970s) are based on relatively sporadic measurements acquired by using a wide range of SST monitoring techniques including buckets, shipboard sensors, floating buoys, and satellites. These techniques have differing accuracies, precisions, and sampling depths, leading to relatively large uncertainties and anomalies within the historical records [*Smith et al.*, 2008; *Kennedy et al.*, 2011]. Geochemical proxy reconstructions of SSTs therefore provide an attractive alternative to the intermittent in situ monitoring data sets and a means to potentially extend SST records well beyond that of the instrumental monitoring period [*Tierney et al.*, 2015]. To this end, a number of biogenic substrates have been utilized for geochemical proxy SST reconstruction including organic material such as alkenones [*Brassell et al.*, 1986] and membrane lipids of marine Crenarchaeota [*Schouten et al.*, 2002], as well as the calcium

carbonate skeletons of marine organisms such as planktonic foraminifera [*Anand et al.*, 2003], sclerosponges [*Rosenheim et al.*, 2004], and tropical corals [*Beck et al.*, 1992; *de Villiers et al.*, 1994; *Alibert and McCulloch*, 1997; *Swart et al.*, 2002; *Reynaud et al.*, 2007; *Maupin et al.*, 2008; *Mitsuguchi et al.*, 2008; *DeLong et al.*, 2014]. Of these possible archives for SST estimates, only the skeletons of tropical corals offer the fine-scale temporal resolution and long growth histories necessary to resolve SST changes over the last ~300 years at an interannual resolution [*Anderson et al.*, 2013].

Corals are used as paleothermometers because the partition coefficients between seawater and coral aragonite ($K_D = (X/Ca)_{coral}/(X/Ca)_{sw}$) of various auxiliary cations such as Li^+ [*Marriott et al.*, 2004a], Mg^{2+} [*Mitsuguchi et al.*, 1996], and Sr^{2+} [*Beck et al.*, 1992] are understood to be temperature-dependent. These ions are transported from seawater to the semi-isolated extracellular calcifying fluid [*Sinclair and Risk*, 2006; *Gaetani et al.*, 2011; *Tambutté et al.*, 2011; *Gagnon et al.*, 2012] by direct diffusion [*Cohen et al.*, 2006; *Gaetani and Cohen*, 2006; *Gagnon et al.*, 2007, 2012] or by active transport [*Ip and Lim*, 1991; *Ferrier-Pagès et al.*, 2002]. Sr^{2+} ions are thought to replace Ca^{2+} ions in the aragonite lattice due to their similar ionic radii (1.31 Å and 1.18 Å, respectively [*Shannon*, 1976; *Watson*, 1996; *Allison et al.*, 2005]). However, it is argued that the ionic radii of Mg^{2+} and Li^+ (0.89 Å and 0.92 Å, respectively [*Shannon*, 1976]) are too small to directly substitute for Ca^{2+} [*Finch and Allison*, 2008; *Montagna et al.*, 2014]. Nonetheless, while the incorporation pathways remain debated, the similar ionic sizes and partition coefficients ($K_D \ll 1$) for both Mg^{2+} and Li^+, and the positive correlation between Mg/Ca and Li/Ca ratios in coral [*Montagna et al.*, 2014], provide evidence that similar processes govern their incorporation into coral aragonite [*Case et al.*, 2010; *Hathorne et al.*, 2013b; *Raddatz et al.*, 2013; *Montagna et al.*, 2014].

The Sr/Ca ratio is the most commonly used geochemical temperature proxy in coral archives [e.g., *Weber*, 1973; *Beck et al.*, 1992; *de Villiers et al.*, 1994; *McCulloch et al.*, 1994; *Alibert and McCulloch*, 1997; *Cohen et al.*, 2001, 2002; *Ferrier-Pagès et al.*, 2002; *Swart et al.*, 2002; *Fallon et al.*, 2003; *Gagnon et al.*, 2007; *Reynaud et al.*, 2007; *Maupin et al.*, 2008; *Mitsuguchi et al.*, 2008; *Caroselli et al.*, 2012; *Gagan et al.*, 2012; *Gagnon et al.*, 2013; *Raddatz et al.*, 2013; *DeLong et al.*, 2014]. However, the reliability of this proxy has been recently called into question. For instance, the sensitivity of Sr/Ca to temperature change differs among and between coral species, and relative to inorganically precipitated aragonite [e.g., *Cohen et al.*, 2006; *Corrège*, 2006], suggesting that species- and even colony-specific calibrations are needed [e.g., *Alpert et al.*, 2016].

The lack of a robust universal Sr/Ca-SST calibration for a single species of coral, or even different individuals within the same colony, is well demonstrated [*Corrège*, 2006; *Saenger et al.*, 2008; *Gaetani et al.*, 2011]. Such intercolonial and intracolonial variations may arise from factors other than the temperature influence on the Sr/Ca ratio of coral skeletons. For example, some studies identify a mineralogical/microstructural control such as crystal shape and location within the skeletal microstructure [*Cohen et al.*, 2001; *Meibom et al.*, 2006; *Raddatz et al.*, 2013] and the influence of kinetic processes such as calcification rate [*Cohen et al.*, 2001; *Gaetani and Cohen*, 2006]. An additional complicating factor for Sr/Ca and all element to calcium ratios in biogenic carbonates is Rayleigh fractionation that occurs during the precipitation of ions from a semi-isolated batch of calcifying fluid, which is only periodically replenished by the diffusion of ions from seawater [*Gaetani and Cohen*, 2006]. The extent to which Rayleigh fractionation affects a particular elemental ratio depends on the partition coefficient (K_D) that is itself temperature-dependent [*Gaetani and Cohen*, 2006]. For example, as temperature increases from 5°C to 30°C, the $K_D^{Sr/Ca}$ for inorganic aragonite decreases by 14% [*Gaetani et al.*, 2011], resulting in fewer Sr ions becoming incorporated into the carbonate matrix. In aragonite, the K_D of Li/Ca and Mg/Ca also exhibits an inverse relationship with temperature [*Marriott et al.*, 2004b; *Gaetani et al.*, 2011]. Rayleigh fractionation influences the composition of an isolated fluid undergoing partial crystallization when the K_D of the participating elements is not equal to 1. As $CaCO_3$ is precipitated, the concentration of Ca in the calcifying fluid decreases, causing the concentration of other elements with a $K_D < 1$ to increase relative to Ca (and vice versa). The elemental composition of coral aragonite in terms of element-to-calcium ratio is therefore determined by the K_D of each element, its relationship with temperature, and the amount of Ca precipitated from each batch of calcifying fluid [*Cohen et al.*, 2006; *Gaetani and Cohen*, 2006; *Gagnon et al.*, 2007; *Montagna et al.*, 2014].

These complicating factors associated with coral Sr/Ca have prompted a search for alternative SST proxies, such as Li/Mg ratios [*Case et al.*, 2010; *Hathorne et al.*, 2013b; *Raddatz et al.*, 2013; *Montagna et al.*, 2014]. The potential of the Li/Mg-SST proxy lies in the opposing temperature controls on Li/Ca and Mg/Ca in the

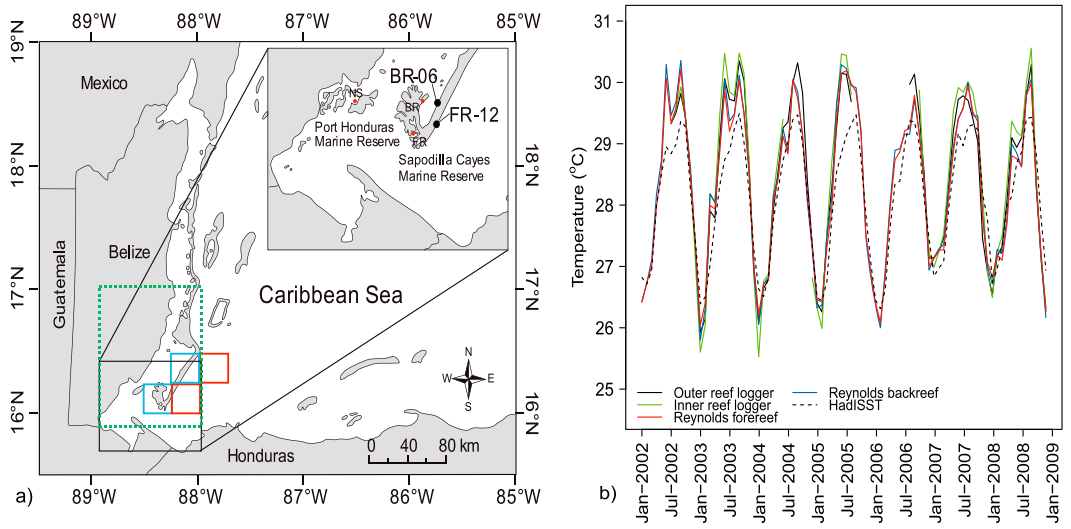

Figure 1. Coral core and temperature data locations in southern Belize. (a) The 0.25° × 0.25° grids represent the areas covered by the Reynolds forereef (red) and backreef (blue) temperature data. The red circles show the location of the temperature loggers, with the nearshore logger representing the inner reef, and the forereef and backreef representing the outer reef. The 1° × 1° green dashed box represents the area covered by the HadISST satellite temperature data. BR-06 and FR-12 are the sampling locations of the forereef FR-12 and backreef BR-06 cores, respectively, which were analyzed in the present study. (b) Monthly resolved temperature data from the outer reef in situ logger (black), inner reef in situ logger (green), Reynolds forereef composite (red), Reynolds backreef composite (blue), and HadISST data (dashed).

coral skeleton, thereby amplifying the effect of temperature on Li/Mg, and the similar responses of these ratios to Rayleigh fractionation, meaning that precipitation progress does not have a significant influence on the Li/Mg ratio of the calcifying fluid [*Montagna et al.*, 2014]. Li and Mg incorporation into aragonite is therefore, in theory at least, simply reliant on the temperature-dependent partition coefficients of Li and Mg, rather than on the extent of Rayleigh fractionation. Several recent studies have confirmed a strong temperature dependence for Li/Mg ratios in corals, which appears to be relatively insensitive to the species used [*Montagna et al.*, 2014, and references therein]. Use of the first multispecies Li/Mg-SST calibration permits reconstruction of SSTs with an uncertainty of ±1.8°C (at 95% confidence [*Montagna et al.*, 2014]), an improvement on the uncertainties associated with the *Porites*-only Li/Mg-SST calibrations [*Hathorne et al.*, 2013b].

Here we present new Li/Mg and Sr/Ca data from the previously unexamined coral species *Siderastrea siderea* sampled from the Caribbean Sea (Belize), which allow us to place this taxa in the broader context of other, tropical coral species utilized for SST reconstruction, such as *Porites* [*Hathorne et al.*, 2013b]. Additionally, we examine the use of multiproxy calibrations to test whether combining elemental ratios with strong temperature dependencies improves the reliability of SST reconstructions. These detailed calibrations of SST proxies in the coral *S. siderea* allow us to assess the robustness of these proxies in characterizing the extent of ocean warming in the ecologically vulnerable region of the southern Mesoamerican Barrier Reef System.

2. Methodology

2.1. Sample Collection

In February 2009, coral cores were collected from the forereef and backreef in the Sapodilla Cayes Marine Reserve (southern Belize; western Caribbean Sea). A full description of the core extraction and sectioning methods is available in *Castillo et al.* [2011]. The cores analyzed in this study were FR-12 (16.10004°N, 88.26669°W) and BR-06 (16.14045°N, 88.26015°W; Figure 1a).

2.2. Temperature Data

High temporal resolution in situ temperature measurements from the study site were acquired from 2002 to 2008 by using *Hobo* (Onset, Massachusetts) temperature loggers (Figure 1 and Table S1 in the supporting information) [*Castillo and Lima*, 2010]. These data were augmented by Reynolds SST data from paired 0.25° latitude/longitude sized grids (Figure 1 and Table S1; http://www.nhc.noaa.gov/sst/) to account for

incompleteness in the in situ logger records. Reynolds SSTs were found to be strongly correlated with the in situ SST measurements and are therefore representative of the temperature regimes experienced by the investigated corals [*Reynolds et al.*, 2007; *Castillo and Lima*, 2010; *Castillo et al.*, 2012]. No significant difference was found between the temperatures experienced in the two coral reef zones, either in the Reynolds data set ($p = 0.86$) or the temperature loggers ($p = 0.89$) of *Castillo and Lima* [2010].

The in situ temperature reconstructions were compared to the Hadley Centre Sea Ice and Sea Surface Temperature Version 1 (HadISST1) [*Rayner et al.*, 2003] historic temperature record for this location (16–17°N, 88–87°W). HadISST is a global SST product with 1° × 1° resolution grids and monthly temperature records from January 1870 to present (http://climexp.knmi.nl; Table S1). Grid points that are missing satellite data within the HadISST data set were statistically interpolated from adjacent grids [*Rayner et al.*, 2006]. Although the overall forereef and backreef Reynolds composites do not differ significantly from HadISST ($p = 0.26$ and $p = 0.20$, respectively), the summer temperatures are frequently lower in the HadISST record, with the Reynolds-derived summer temperatures being on average 0.41°C higher for the forereef and 0.44°C higher for the backreef (both with $p \ll 0.01$).

2.3. Sample Preparation and Analysis

2.3.1. Monthly Resolution Subsampling

Coral slabs (70 × 45 × 5 mm) were X-rayed by using a *Fuji Computed Radiography* radiography system at the University of North Carolina at Chapel Hill Campus Health Services Radiology Department, at 6 mA s^{-1} and 40 kV. These images were used to calculate an annual chronology by labeling the first high-density band (deposited the same winter as the collection) and counting each subsequent high-density band backward in time.

Slabs from FR-12 and BR-06 were sampled at monthly to bimonthly resolution from the top (September 2008 to January 2006 and September 2008 to February 2006, respectively) and bottom (November 1921 to December 1925 and November 1922 to January 1926, respectively) of each coral slab (Figure 2). A New Wave Research micromill with a 500 μm diameter diamond drill bit was used to drill ~1 mm wide trenches to a depth of 1 mm in the thecal wall (Figure 2), using a protocol similar to that of *DeLong et al.* [2011]. The widths of the thecal walls were identified under the microscope to minimize the chance of sampling the columella. Sample sizes ranged from 0.3 to 1.4 mg.

Final age models were built for the field calibrations following a standard approach [e.g., *Felis et al.*, 2004; *Maupin et al.*, 2008; *Felis et al.*, 2009]. A preliminary age range was estimated by counting annual high-density bands (Figures 2a and 2c). Then, this annually resolved age model, the coral age at collection, the skeletal location of the first monthly sample, and subsequent peaks and troughs in the Sr/Ca ratio were used to identify warm and cold intervals in the SST time series, assuming the inverse relationship between Sr/Ca and SST seen in other studies [*Maupin et al.*, 2008; *DeLong et al.*, 2011, 2014]. A polynomial curve was fit through 6 depth-age points allowing the age at each sample depth to be predicted. Instrumental SST was then interpolated on to this coral age scale to permit direct comparison of temperature records.

Downcore samples from FR-12 (1921–1925) and BR-06 (1922–1926) were dated by counting the annual density bands on the X-ray images (Figures 2b and 2d). To determine the exact months, a method similar to that of *Maupin et al.* [2008] was used whereby the summer and winter peaks from the reconstructed SSTs were tied to the monthly resolved Hadley Centre's HadISST gridded temperature data set for the corresponding year.

2.3.2. Cleaning Procedure

Residual organic matter removal protocols are derived from foraminiferal calcite oxidative cleaning techniques and following the standard protocol of *Henehan et al.* [2013], originally described by *Barker et al.* [2003]. Micromill extracted $CaCO_3$ powders were oxidatively cleaned in 250–500 μL of 1% H_2O_2 (buffered in 0.1 M NH_4OH_4) at 80°C for a total of 15 min with intermittent ultrasonication. The spent oxidative mixture was removed, and samples were thoroughly rinsed by using 18.2 MΩ Milli-Q water. Between each subsequent rinse step, the powdered samples were centrifuged for 2 min (13,000 rpm) to minimize sample loss. Samples were then transferred into acid-cleaned microcentrifuge tubes before a weak acid (0.0005 M HNO_3) leach was performed to remove any ions readsorbed onto the sample surface. Samples were then dissolved in the minimum volume of 0.5 M HNO_3. Dissolved sample solutions were finally centrifuged for 3 to 5 min (13,000 rpm) and transferred into clean vials to separate the supernatant from any remaining noncarbonate solids.

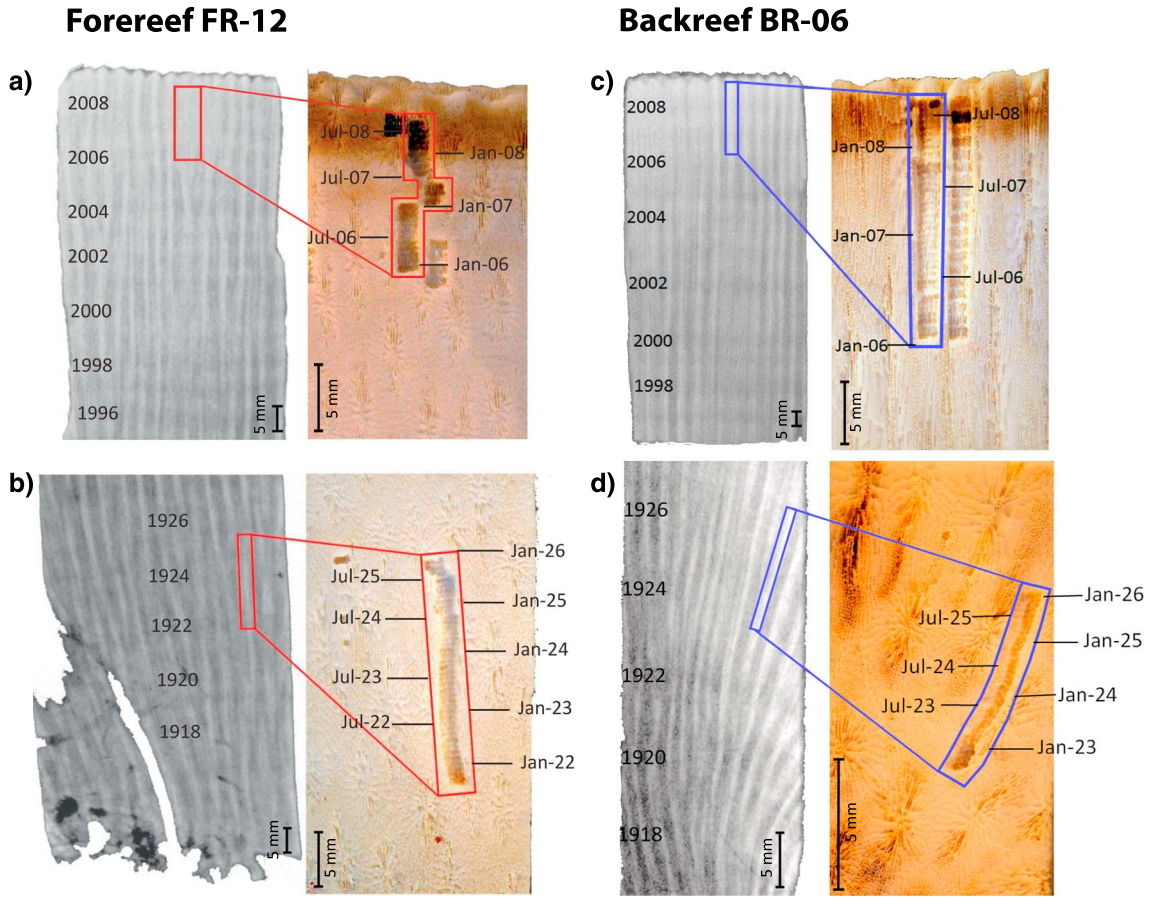

Figure 2. Coral slab X-rays with annual bands labeled. The rectangles indicate where the coral was subsampled along the high-density theca wall (bright vertical bands). Optical images after subsampling are labeled with the position of the January and July samples. Theca walls are identified by a smoother, less porous appearance. (a) Top of the forereef FR-12 coral. (b) Downcore FR-12. (c) Top of the backreef BR-06 coral. (d) Downcore BR-06.

2.3.3. Inductively Coupled Plasma–Mass Spectrometry Analysis

All analyses were carried out at the University of Southampton (UK). Calcium concentrations of the dissolved samples were first determined by using quadrupole inductively coupled plasma–mass spectrometry (ICP-MS; Thermo Scientific X-Series), giving an estimate of the major elemental composition of the dissolved samples in order to accurately matrix match for subsequent quantitative multielemental analysis. X-Series standards and samples were made by using 3% HNO_3 spiked with 5 ppb In, 5 ppb Re, and 20 ppb Be, which act as internal standards to monitor drift and correct for mass bias in the absence of bracketing standards. A multielement standard stock solution made by using high-concentration (10,000 ppm) single element (B, Mg, Al, Sr, and Ca) solutions was diluted to make four gravimetric standards with differing Ca concentrations (0.2 to 3 ppm Ca). To monitor the accuracy and precision of the measurements, consistency standards of 1 ppm, 3 ppm, and 7 ppm Ca CS2 and CS3 [*Ni*, 2006; *Ni et al.*, 2007] were analyzed at the beginning and end of each analytical session. Based on these analyses, the external precision at 1σ was estimated to be ±1.01% for 1 ppm Ca, ±4.91% for 3 ppm Ca, and ±4.94% for 7 ppm Ca.

An Element XR (Thermo Scientific) sector field ICP-MS was used to determine the element to Ca ratios of the coral dissolutions. A suite of element intensity ratios (including Li/Ca, B/Ca, Mg/Ca, and Sr/Ca) were measured to determine the skeletal elemental composition of the samples and also the efficacy of sample cleaning (e.g., Al/Ca < 100 μmol/mol indicative of minimal clay mineral contamination). Further information regarding the measurement of Li can be found in Text S1 and Figure S1 in the supporting information [*Al-Ammar et al.*, 2000; *Ni*, 2006]. Samples were analyzed in batches of equal Ca concentrations between 1 mM and 3 mM and blank corrected with a 0.5 M HNO_3 "blank" measured between every sample/standard [*Rosenthal et al.*, 1999]. Each block of three samples was bracketed against a matrix-matched (i.e., of equal Ca concentration

Table 1. Comparison of JCp-1 Elemental Ratios Measurements[a]

	This Study	Interlab Comparison	*Hathorne et al.* [2013b]	*Montagna et al.* [2014]
Sr/Ca mmol/mol average	8.66 ($n = 20$)	8.84 ($n = 179$)		
Standard deviation	0.10	0.04		
External precision (%)[b]	2.21	0.95[c]		
Li/Mg mmol/mol average	1.51 ($n = 16$)	1.48 ($n = 5$)	1.51 ($n = 25$)	1.43
Standard deviation	0.03	0.06	0.04	
External precision (%)[b]	4.45	7.43	5.30	3.20

[a]Long-term precision is determined by repeat JCp-1 measurements, which are compared with the recent Li/Mg studies of *Hathorne et al.* [2013b] and *Montagna et al.* [2014] in addition to the international laboratory comparison [*Hathorne et al.*, 2013a].
[b]External precision reported as 2 relative standard deviations.
[c]Median interlab external precision is 0.28%.

to the samples [*Rosenthal et al.*, 1999]), well-characterized, gravimetric standard solution (prepared by Cardiff University). Sample ratios were calculated by calibrating to the standard solution, which had values of 11.38 μmol/mol, 2.44 mmol/mol, and 1.43 mmol/mol for Li/Ca, Mg/Ca, and Sr/Ca respectively, allowing samples to be corrected for instrumental and matrix-induced mass bias.

Additionally, three consistency standards (SECS1, SECS2, and SECS3; University of Southampton) of matching [Ca] but different gravimetrically prepared and cross-calibrated elemental ratios (Table S2) were used as internal standards to monitor accuracy and thus efficiency of correcting for mass bias effects and instrumental drift. Using the bracketing standards method, precise values of repeat measurements were obtained for these standards. SECS3 is the most similar in composition to the coral samples and yielded average measured values (2σ) for Sr/Ca of 1.97 ± 0.04 mmol/mol and Li/Mg of 5.51 ± 0.09 mmol/mol compared to 2 mmol/mol and 5.73 mmol/mol, respectively, determined gravimetrically (Table S2).

Alongside each batch of ~15 coral samples, a JCp-1 standard (international coral reference material made from homogenized *Porites* [*Okai et al.*, 2002]) was analyzed in the same manner as the coral samples in this study (1 to 2 mg JCp-1). Replicates of JCp-1 passed through the entire sample cleaning and analytical protocol provide a rigorous assessment of true external precision. The average JCp-1 values and standard deviation during the course of this study are shown in Table 1. While Li/Mg measurements of JCp-1 for this study are comparable to those of other laboratories, our mean Sr/Ca value is at the low end of the range of values in the *Hathorne et al.* [2013a] interlaboratory study (Table 1). By comparing analyses of cleaned and uncleaned samples of JCp-1, we found that both Li/Ca and Mg/Ca ratios decreased by 25% as a result of the removal of organic matter (Figure S2), a similar result to that observed in foraminferal calcite Mg/Ca following oxidative cleaning [*Barker et al.*, 2003]. In contrast, both Sr/Ca and Li/Mg ratios are shown to be relatively unaffected by this sample cleaning procedure (Text S2 and Figure S2), the latter due to a precisely equal reduction in [Mg] and [Li]. Further details about the cleaning test can be found in the supporting information [*Ni*, 2006; *Ni et al.*, 2007].

2.4. Data Handling

2.4.1. Statistical Analysis

The statistical software package R Studio [*R Development Core Team*, 2013] was used for all data analysis and for constructing linear regression models on measured Li/Mg and Sr/Ca data. The uncertainty of the temperature estimates using the linear regression models was assessed by using 95% prediction intervals. Welch unequal variance two sample *t* tests (two-tailed) were also used to determine whether there were significant differences between mean summer or winter temperatures between reconstructed temperatures and the historic HadISST record.

2.4.2. Data Compilations

A "multispecies" Li/Mg-T calibration of cold-water, temperate, and tropical coral species was developed by using the data from this study and solution ICP-MS data from previous studies [*Case et al.*, 2010; *Hathorne et al.*, 2013b; *Raddatz et al.*, 2013; *Montagna et al.*, 2014]. Based on a consideration of the long-term average of JCp-1 at the University of Southampton, Li/Mg results from *Montagna et al.* [2014] were increased by 5% to make them comparable with the results of the present study (Table 1).

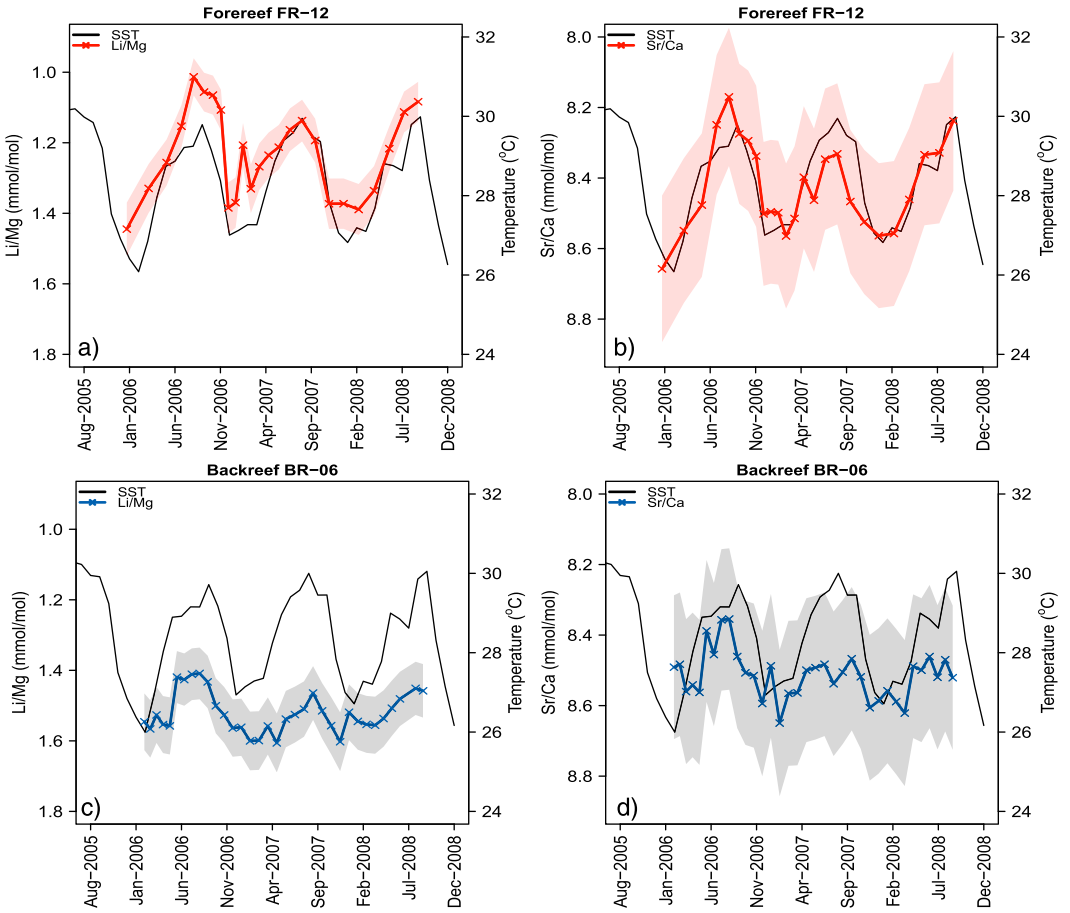

Figure 3. Monthly resolved Li/Mg and Sr/Ca ratios in forereef FR-12 (red) and backreef BR-06 (blue) samples. The crosses represent the ICP-MS measured data with 2σ external reproducibility shown as a shaded band. Reynolds composite temperature records are shown in black for comparison.

3. Results

3.1. Monthly Resolved Sr/Ca and Li/Mg Ratios

Geochemical coral data (Table S3) are compared to composite observational temperature data (Table S1) in Figure 3. Both the Li/Mg and Sr/Ca ratios in the forereef coral FR-12 (Figures 3a and 3b) demonstrate a strong seasonal cycle in step with observed intraannual temperature fluctuations. Similar, but smaller-amplitude cycles, are also present in the backreef coral BR-06 (Figures 3c and 3d). In both corals, these elemental ratios are higher during colder months, demonstrating that both Li/Mg and Sr/Ca ratios exhibit typical inverse relationships with temperature.

3.2. Calibrations

Simple linear regressions reveal that the Li/Mg ratio of the forereef coral FR-12 has the best defined correlation with more than 70% of variation explained by temperature ($r^2 = 0.71$, $p \ll 0.01$; Figure 4a), as opposed to only 40% explained by temperature in the backreef coral BR-06 ($r^2 = 0.40$, $p \ll 0.01$; Figure 4c). The Sr/Ca ratio is also better correlated with temperature in the forereef coral FR-12 ($r^2 = 0.69$, $p \ll 0.01$; Figure 4b) than in the backreef BR-06 coral ($r^2 = 0.26$, $p \ll 0.01$; Figure 4d). These relationships between elemental ratios and temperature are also summarized in Table 2.

Stronger correlations the forereef calibrations result in more precise SST reconstructions than for the backreef calibrations and, independent of elemental ratios, lower reconstruction uncertainties are associated with the forereef samples (Table 2).

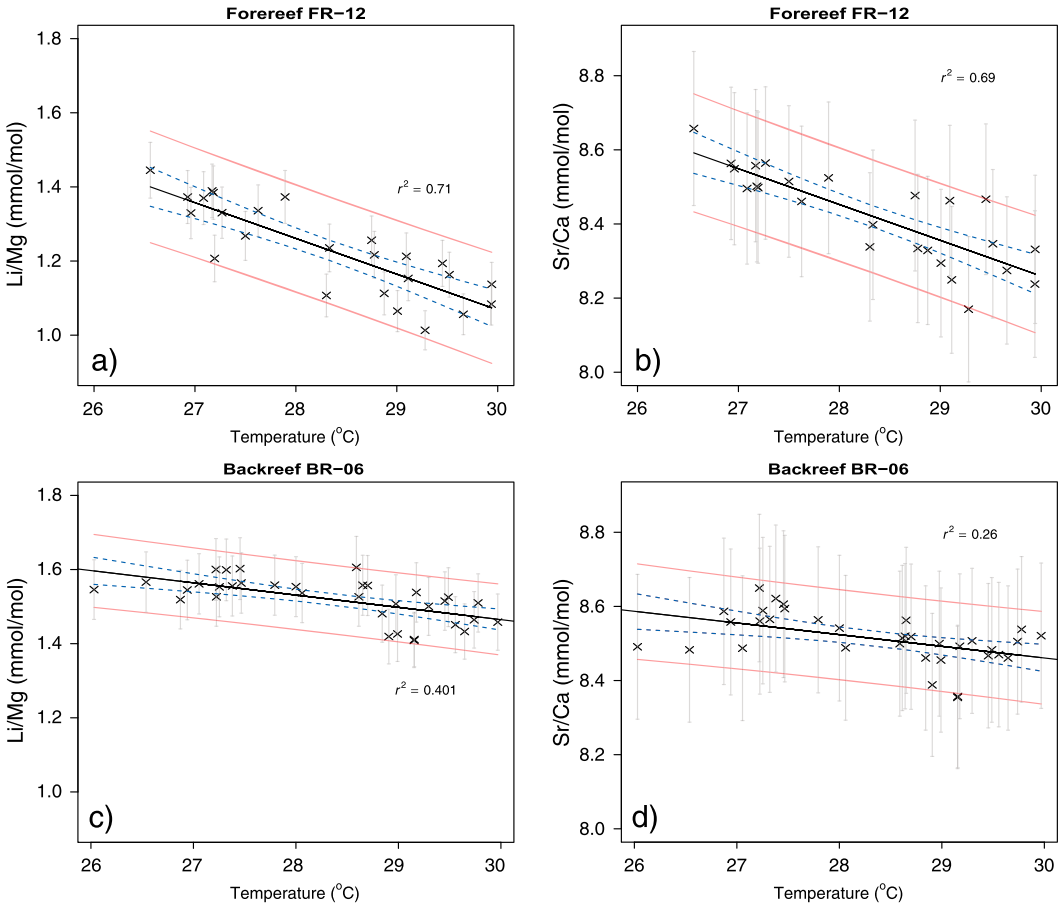

Figure 4. Forereef and backreef field-based calibrations of Sr/Ca and Li/Mg temperature proxies in *Siderastrea siderea*. The crosses indicate the individual samples with 2σ external reproducibility errors. The blue and red dashed lines show the 95% confidence and prediction intervals, respectively.

Two multiple linear regressions were also performed on the corals to generate multiproxy SST calibrations. The first multiple linear regression combined the Li/Mg and Sr/Ca ratios (hereafter referred to as "MLR1"). The second multiple linear regression combined Li/Ca, Sr/Ca, and Mg/Ca ratios (hereafter referred to as "MLR2"). The regression coefficients for these multiproxy calibrations are shown in Table 3.

The Li/Mg-SST calibrations were added to the existing combined-species calibration described in section 2.4.2 (Figure 5) to generate what will be referred to henceforth as the "multispecies calibration." The *S. siderea* samples broadly fit the trend of the multispecies calibration of *Montagna et al.* [2014] and extend the upper end of the temperature range by ~2°C. The backreef data are slightly offset from the curve fitted through the combined data (Figure 5). The resulting exponential equation of the multispecies calibration ($r^2 = 0.95$, $p \ll 0.001$) is

$$\mathrm{Li/Mg} = 5.405\exp^{(-0.05(\pm 0.001)\ \times\ T)} \quad (1)$$

Table 2. Regression Statistics for the Forereef and Backreef Calibrations[a]

Calibration	c	±2 SE	m	±2 SE	r^2	p	95% Precision at 28°C (°C)
Forereef Li/Mg	3.962	±0.730	−0.097	±0.013	0.71	<<0.01	1.5
Backreef Li/Mg	2.458	±0.406	−0.033	±0.007	0.40	<<0.01	2.7
Forereef Sr/Ca	11.158	±0.772	−0.097	±0.014	0.69	<<0.01	1.6
Backreef Sr/Ca	9.406	±0.536	−0.031	±0.009	0.26	<0.01	4.0

[a]Calibrations in this study were fitted with a linear regression in the form Li/Mg = $m \times$ SST(°C) + c. Temperature precision estimates were derived from the prediction intervals.

Table 3. Multiple Linear Regression Statistics for the Multielemental Forereef and Backreef Calibrations[a]

Calibration	c	x_1	x_2	x_3	x_4	r^2	95% Precision at 28°C (°C)
Forereef MLR1	59.854	4.484	3.090	–	–	0.70	1.3
Forereef MLR2	33.177	–	1.205	0.657	2.066	0.75	1.2
Backreef MLR1	54.624	11.115	1.104	–	–	0.36	1.8
Backreef MLR2	38.153	–	0.490	3.466	3.722	0.38	1.8

[a]MLR1 calibrations are in the form $SST(°C) = c - (x_1 \times Li/Mg) - (x_2 \times Sr/Ca)$. MLR2 calibrations are in the form $SST(°C) = c - (x_3 \times Li/Ca) - (x_2 \times Sr/Ca) + (x_4 \times Mg/Ca)$. Temperature precision estimates were derived from the prediction intervals.

3.3. Downcore Samples and Temperature Reconstructions

Strong seasonal cycles in Li/Mg and Sr/Ca are evident in the forereef and backreef downcore samples (Figure 6 and Table S4). The mean Li/Mg of the forereef coral (1.33 mmol/mol) is significantly lower than that of the backreef coral (1.50 mmol/mol; $p \ll 0.01$). The mean Sr/Ca ratios, however, are not significantly different between reef zones (8.50 mmol/mol and 8.53 mmol/mol in the forereef and backreef, respectively; $p = 0.27$).

Forereef and backreef field-based *S. siderea* calibrations (Table 2) were applied to their respective downcore time series to reconstruct monthly resolved SSTs between 1921 and 1926 (Table S4). In both reef zones the temperature reconstructions using single regressions of Li/Mg and Sr/Ca are within uncertainty (2σ) of each other, although this is largely a consequence of the propagation of the uncertainty in the backreef calibrations, which are up to ±12°C in some instances (Figure 7). Table 4 shows a comparison between the individual SST reconstructions and the HadISST data set. In the forereef, the overall means of both the Li/Mg-SSTs and Sr/Ca-SSTs are within 0.3°C of HadISST, and within 0.7°C and 0.1°C in the summer and winter, respectively, all within calibration uncertainties (±1.5°C; Table 2). In the backreef, the overall means of the Li/Mg- and Sr/Ca-SSTs are both within 1.4°C of HadISST; however, summer Li/Mg-SSTs are 3.3°C greater than HadISST and

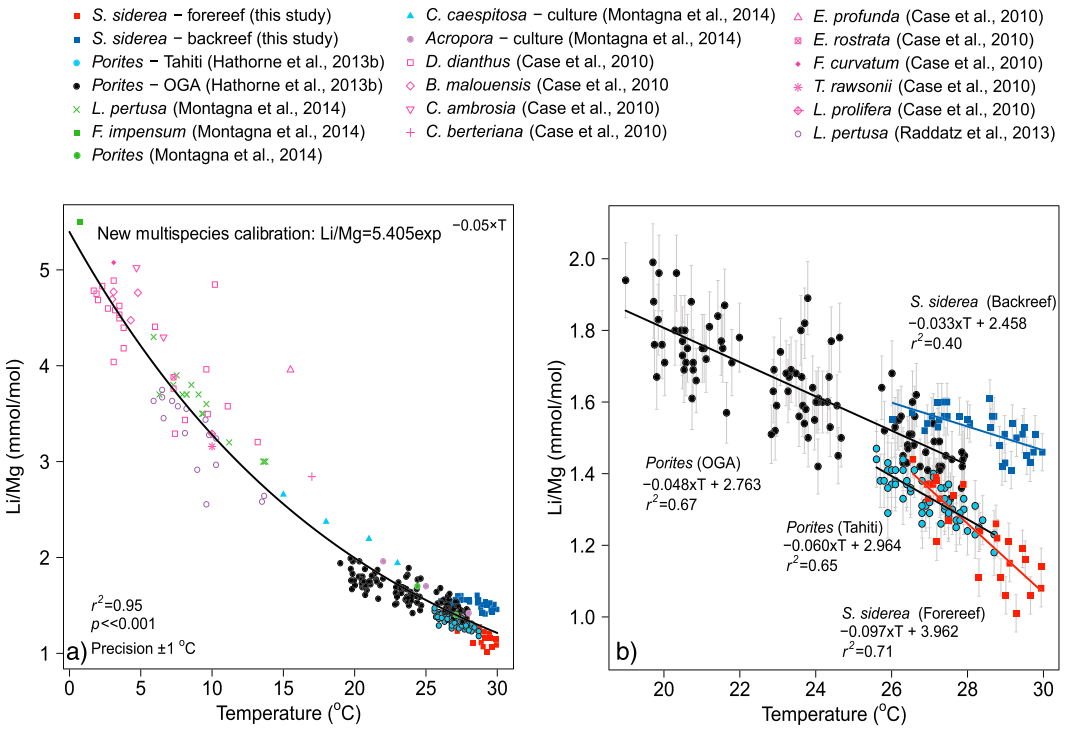

Figure 5. (a) Combined Li/Mg-T calibration for a range of coral species at seawater temperatures between 0°C and 30°C. An exponential regression is used to form the new multispecies calibration. The forereef and backreef calibrations of *S. siderea* from this study are shown by the solid red and blue squares, respectively. (b) Comparison of the linear relationships of the Li/Mg ratios of the tropical species *Porites* (closed circles) and forereef and backreef *S. siderea* (closed squares). The 2σ external precision error bars are shown.

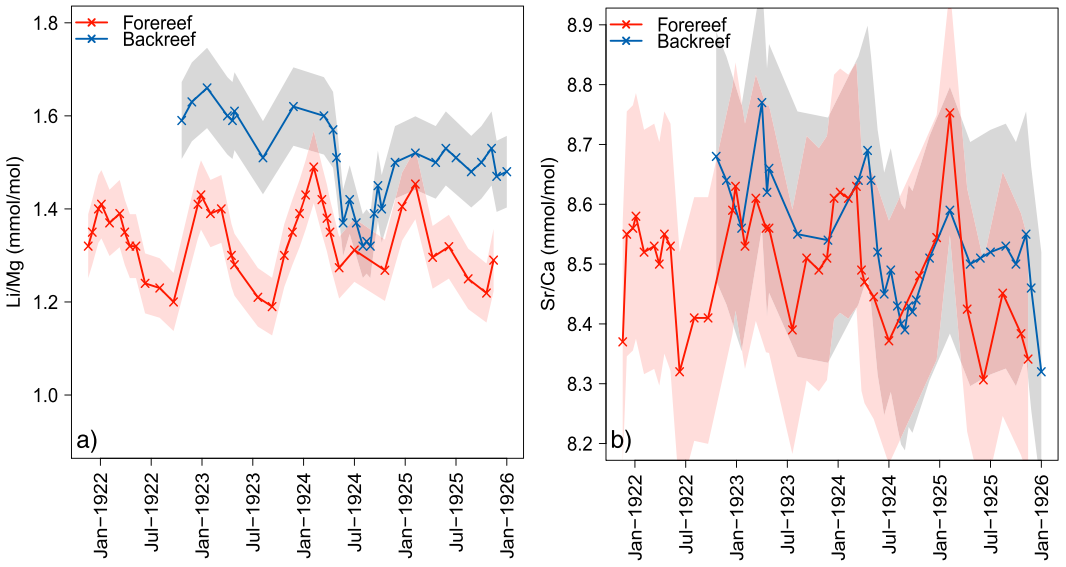

Figure 6. Downcore (a) Li/Mg ratios and (b) Sr/Ca ratios of FR-12 forereef (red) and BR-06 backreef (blue) *S. siderea* samples from years 1921 to 1926. The error envelopes (pink and grey) represent the 2σ external precision. HadISST data are shown in black for comparison (black line).

winter Sr/Ca-SSTs are 1.9°C greater than HadISST (Table 4). In both of the reef zones, however, the root-mean-square error (RMSE) is within the uncertainties of the single proxy calibrations (Tables 2 and 4).

The multiproxy calibrations yield temperature records similar to those predicted by the single-proxy calibrations (Table 4). However, the multiproxy calibrations have lower reconstruction uncertainties (Table 3), and therefore predict temperatures that match more closely between reef zones and between reconstructed SSTs and HadISST (Table 4), particularly with respect to the backreef reconstruction, albeit with a tendency to reconstruct lower amplitude seasonal variations (Figures 7b and 7d). The multiproxy SSTs in the backreef reduce the differences from HadISST to $\leq$1.6°C (Table 4). As with the single proxy reconstructions, the RMSE of the multiproxy-based means are within the uncertainty of the calibration when comparing to the HadISST data set.

4. Discussion

4.1. Li/Mg-SST, Sr/Ca-SST, and Multiproxy SST Models in *S. siderea*

Both Sr/Ca and Li/Mg ratios exhibit a well-correlated inverse relationship with temperature in both reef zones (Figures 3 and 4). Within the same reef zone, the slopes of both calibrations are within error of each other, suggesting that both proxies have similar temperature sensitivities. Both Li/Mg and Sr/Ca are also more strongly correlated with temperature in the forereef coral (Table 2). These differences arise even though both reef zones experienced similar temperature histories according to the available observational data (Figure 1b), suggesting that at least one other factor must be influencing both SST proxies.

Geographic differences in Sr/Ca-SST calibrations have been reported before. Several studies have ascribed such variability to the influence of other variables such as seawater pH [*Tanaka et al.*, 2015], seawater Sr/Ca composition [*de Villiers et al.*, 1994], extension rate [*de Villiers et al.*, 1994], and calcification rate [*Ferrier-Pagès et al.*, 2002; *Kuffner et al.*, 2012], which individually, or in combination, influence variation in the extent of Rayleigh fractionation and elemental incorporation in coral aragonite at a particular site. We confirm here that Li/Mg also exhibits a geographically dependent SST calibration, and because the K_D for Li/Mg is close to unity, we cannot ascribe this variation to Rayleigh fractionation. The influence of a non-SST driver on Li, Mg, and Sr uptake in the backreef coral may also be indicated by (i) the generally poor agreement between Li/Mg-SST, Sr/Ca-SST, and HadISST for the backreef in the years 1922–1926 (Figure 7c), which contrasts the good agreement found for the forereef reconstruction (Figure 7a), and (ii) a lack of evidence for coral bleaching or mortality that would be expected to occur if SSTs were in excess of 32°C as suggested by backreef SST reconstructions (Figure 7). Potential differences between seawater pH of the backreef and forereef may partly explain the spatial variability in SST

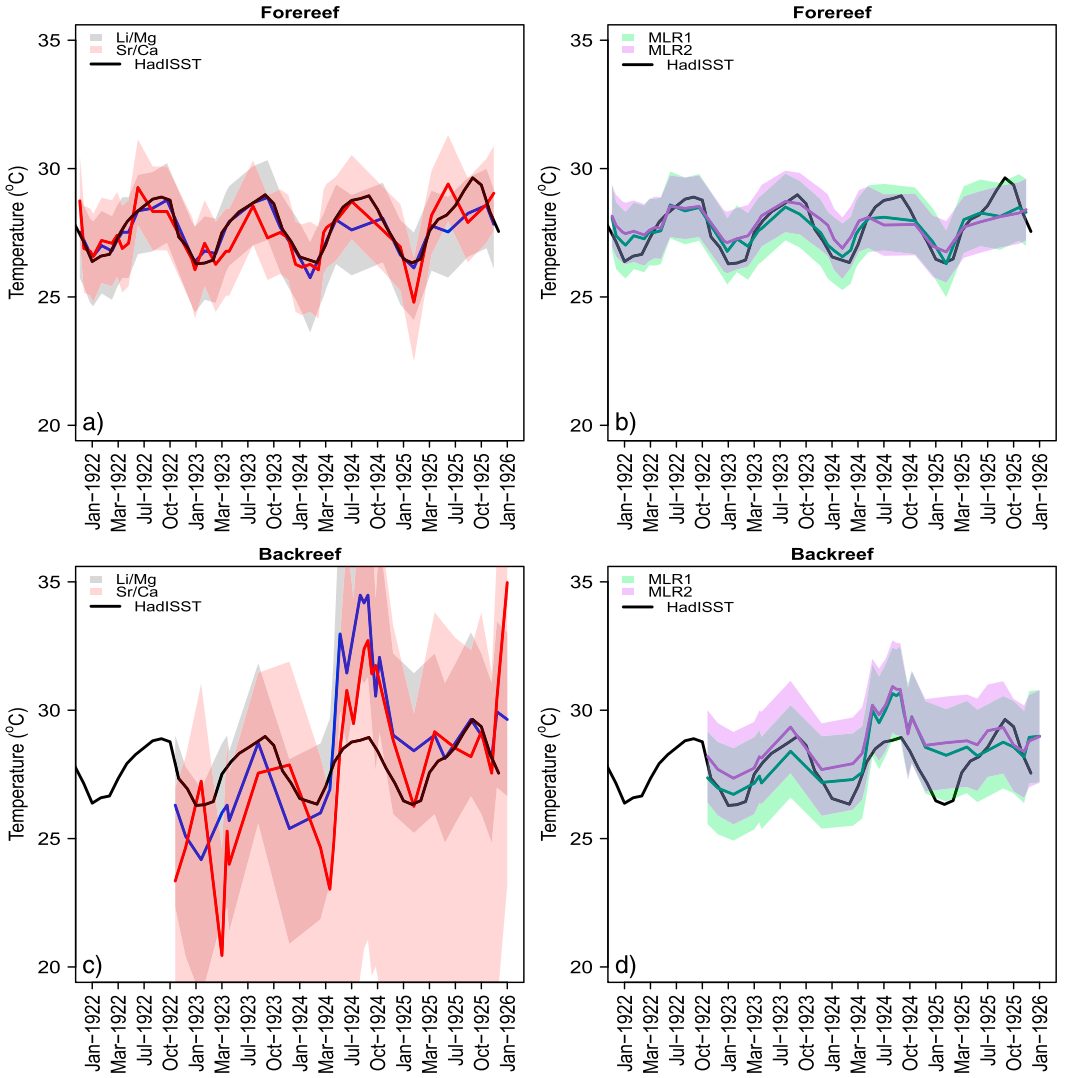

Figure 7. Sea surface temperature (SST) reconstructions from 1921 to 1926 using the site-specific *S. siderea* Li/Mg and Sr/Ca-SST proxies and multiproxy calibrations. The blue line shows the Li/Mg-SST, the red line shows the Sr/Ca-SST, the green line shows the combined Li/Mg-Sr/Ca-SST, and the purple line shows the combined Li/Ca-Sr/Ca-Mg/Ca-SST. The shaded regions show the precision estimates derived from the 95% prediction intervals of the linear regressions. HadISST data are also shown for comparison (black line).

Table 4. Mean Summer, Winter, and Overall Sea Surface Temperatures Based on the Li/Mg, Sr/Ca, and Multiproxy Reconstructions for Both the Forereef and Backreef[a]

Method	Mean SST (°C)	RMSE HadISST	Summer Mean (°C)	RMSE HadISST	Winter Mean (°C)	RMSE HadISST
HadISST	27.7 (±0.3)		28.9 (±0.2)		26.7 (±0.2)	
FR Li/Mg	27.4 (±0.3)	1.08	28.4 (±0.6)	0.76	26.8 (±0.3)	0.46
FR Sr/Ca	27.4 (±0.3)	1.27	28.2 (±0.6)	0.90	26.7 (±0.6)	0.96
FR MLR1	27.6 (±0.2)	0.97	28.3 (±0.2)	0.68	27.1 (±0.3)	0.68
FR MLR2	27.8 (±0.2)	0.96	28.4 (±0.4)	0.69	27.4 (±0.3)	0.86
BR Li/Mg	29.2 (±1.0)	3.03	32.2 (±2.3)	4.14	27.4 (±1.8)	2.40
BR Sr/Ca	28.1 (±1.2)	3.41	30.7 (±1.7)	2.76	28.6 (±2.5)	3.89
BR MLR1	28.6 (±0.4)	1.62	29.8 (±0.9)	1.44	27.9 (±0.7)	1.69
BR MLR2	29.0 (±0.4)	1.76	30.2 (±0.6)	1.52	28.2 (±0.5)	1.84

[a]Errors are reported as 2 standard errors. The RMSE of the reconstructed mean against the mean HadISST is also shown.

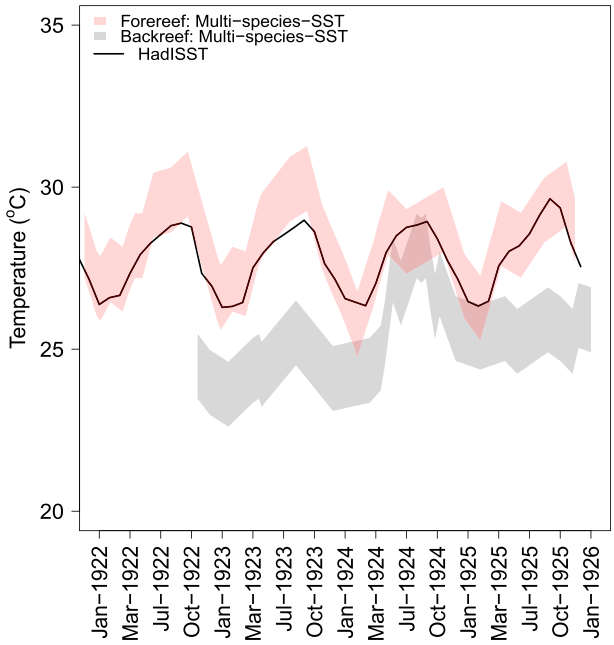

Figure 8. Sea surface temperature (SST) reconstructions from 1921 to 1926 using the updated multispecies Li/Mg-SST proxy. The error envelopes show the absolute SST precision estimates derived from the 2 standard error of the exponential calibration slope. Forereef SST reconstructions (red) and backreef SST reconstructions (grey) are compared against the HadISST data (solid black line).

calibrations [*Tanaka et al.*, 2015]. Furthermore, calibrating the SST proxies when extension rates of backreef corals were higher than forereef corals (since the 1990s [*Castillo et al.*, 2011]) and applying them to samples from a time when the extension rates of forereef and backreef corals were more similar may also be at least partially responsible for the breakdown of the Li/Mg- and Sr/Ca-SST proxies. Our assessment of the importance of parameters such as these on Li/Mg and Sr/Ca ratios is the focus of a future study. Nonetheless, part of the degraded performance of both proxies in the backreef coral is also likely due to the size of the analytical uncertainty (Table 1) and the shallower relationship between the measured ratio and observed temperature (Table 2). Indeed, the RMSE between Li/Mg-SST and Sr/Ca-SST with HadISST in the backreef is similar to the calibration uncertainty suggesting that the predictive capabilities of these proxies would improve if the analytical uncertainties were reduced (Tables 2 and 4).

Applying the multiproxy calibrations to the downcore data improved the precision of the reconstructions and reduced the extreme values recorded by the Li/Mg- and Sr/Ca-based SSTs in the backreef (Figure 7d). This improvement is likely, at least in part, a consequence of the increased precision resulting from using multiple variables (Table 3). Despite this advantage, the multiproxy models still fail to predict the expected wintertime temperatures in the backreef that are expected based upon the forereef reconstructions or the HadISST data (Table 4). This result suggests that although the multiproxy calibrations offer some improvement over the single-proxy models in the backreef (Table 4), combining the proxies does not completely eliminate the errors evident in the single-proxy models (Figure 7d and section 3.3).

4.2. Assessment of Tropical Coral Li/Mg-SST Calibrations

Previous studies have highlighted that Li/Mg ratios exhibit a similar inverse relationship with temperature across multiple coral species and over a temperature range of 0°C to 30°C (see references in Figure 5a). Although the forereef and backreef coral data generally agree with this overall trend (Figure 5a), detailed inspection reveals that both of the new Li/Mg-SST calibrations are slightly offset from the multispecies calibration, further highlighting the influence of a non-SST-based parameter(s) in driving Li/Mg variability (Figure 5b). Similar, but more subtle variations are also evident in *Porites* [*Hathorne et al.*, 2013b]. The slope of the backreef *S. siderea* (−0.033) is almost half that of both the Tahiti and OGA *Porites* data (−0.060 and −0.048, respectively [*Hathorne et al.*, 2013b]), which are themselves almost half that of the forereef *S. siderea* (−0.097; Figure 5b). This suggests that although there is a clear overall relationship between temperature and coral Li/Mg, the divergence of tropical corals from a single calibration highlights that accurate reconstructions still require site- and species-specific calibrations.

To demonstrate the importance of these site- and species-specific calibrations, the multispecies calibration (Figure 5a and equation (1)) was applied to the downcore Li/Mg ratios and reconstructed temperatures are compared to historic HadISST data (Figure 8). The forereef SSTs reconstructed by using the multispecies calibration (equation (1)) are mostly within error of HadISST, with the exception of the 1922 and 1923 summertime SSTs, which are slightly overestimated. However, backreef SSTs reconstructed in the same manner are consistently lower than HadISST temperatures (Figure 8).

5. Conclusions and Recommendations

The sea surface temperature calibrations presented here demonstrate that the Li/Mg-SST proxy is equal to, and in some locations, more precise than the more commonly used Sr/Ca-SST proxy for the species *S. siderea* (±1.5°C versus ±1.6°C in forereef coral FR-12). By combining elemental ratios to form multiproxy SST calibrations, the precision of the SST reconstructions is further improved. Both single elemental ratios (Sr/Ca and Li/Mg) in the backreef locality were found to be less sensitive to temperature, indicating that a secondary, non-SST variable impacts the uptake of these elements in the skeletal aragonite of *S. siderea* in these environments. As a test of reliability, reconstructed temperatures from 1921 to 1926 in both reef zones were compared to the HadISST record. Reconstructed forereef temperatures using the Li/Mg, Sr/Ca and the combined Li/Mg-Sr/Ca and Li/Ca-Mg/Ca-Sr/Ca proxies were not significantly different from each other, and these SSTs were also found to be within error of the HadISST data. Reconstructed temperatures from the backreef were found to be substantially offset from forereef reconstructions and HadISST data, and recorded anomalously high temperatures approaching 35°C (presumably damaging or fatal to coral), confirming their inaccuracy.

These results demonstrate that in some regions, Li/Mg, when used in isolation or in combination with other elemental ratios as part of a multiproxy approach, is a suitable addition to the temperature reconstruction tool-box of *S. siderea*. It remains unclear why our backreef reconstructions using Sr/Ca and/or Li/Mg are compromised, but this may be related to spatial variability in linear extension rates of *S. siderea* documented in this region, and for these samples in particular, by *Castillo et al.* [2011]. Nonetheless, in light of the more precise SST reconstructions that result from the multiproxy calibrations, we encourage their use over single elemental ratio proxies as a means of quantifying local surface ocean warming from elemental ratios within the coral *S. siderea*. While further investigation of the non-SST controls on SST proxies, such as Li/Mg, is required, it is clear from our study that the most reliable coral-based reconstructions of sea surface temperatures are obtained through combining multiproxy records that are calibrated in the same region to which they are applied.

Acknowledgments

This research was funded by the Natural Environment Research Council UK (Studentship number NE/K500926/1 to S.E.F.) and the National Oceanography Centre Southampton Graduate School. The collection and preparation of the coral cores were funded by NOAA award NA13OAR4310186 (to J.B.R. and K.D.C.) and NSF award 1437371 (to J.B. R.). Permits for collection and export were granted by the Belize Fisheries Department, Government of Belize. Reynolds data sets are freely available from www.nhc.noaa.gov/sst/ and listed in the supplementary Table S1. Hadley Centre's HadISST1 data are freely available from KNMI Climate Explorer (http://climexp.knmi.nl/) and are also listed in Tables S1 and S5. Supporting analytical data are included as three tables in a supporting information file, and data from other coral studies are cited and referred to in the reference list. Many thanks are extended to the B-team, Andy Milton, and Matt Cooper for their assistance in the clean chemistry and plasma labs. We are also grateful to Caroline Lear and Anabel Morte-Ródenas of Cardiff University for their supplying the multielement bracketing standard. We thank the anonymous reviewers for their constructive comments which improved this manuscript.

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