

*Paleoceanography*

Supporting Information for

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

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**Additional Supporting Information (Files uploaded separately)**

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**Introduction**

The information included in the supporting tables includes information about the composition of consistency standards, raw elemental ratios data from the coral samples, and historic and modern temperature data from loggers, Reynolds, or HadISST1. The raw coretop elemental and interpolated temperature data will allow any user to recreate the calibrations generated in this study. The raw downcore elemental data (Table S4) will allow users to recreate the temperature reconstructions seen in this study, or offer the chance to test other calibrations on these historic samples, and compare such reconstructions against the HadISST compilation (Table S5).

**Text**

**Text S1**

The standard set-up for the Element ICP-MS at the University of Southampton includes an additional ammonia (NH3) gas introduced into the spray chamber at a flow rate of 0.07 ml min-1 simultaneously with the sample gas to make the internal environment more basic [*Al-Ammar et al.*, 2000; *Ni*, 2006]. This is necessary for obtaining precise, reproducible B/Ca ratios (although these are not the subject of this particular study) by facilitating instrumental B-wash out [*Al-Ammar et al.*, 2000; *Ni*, 2006].

Whilst the addition of NH3 gas improves the B-washout it introduces an additional interference on 7Li by 14N++. This however can be adequately resolved in low resolution mode by moving the analyte mass window to focus on a section of the 7Li+ peak where the interference is reduced. The peak center was chosen to be a mass (typically ~7.015 amu) which would allow for some minor drift (Figure S1). Combined with careful background determination this ensured a minimal impact of 14N++ on 7Li.

**Text S2**

To determine if our cleaning protocol alters the trace element ratios of coral, a cleaning test was performed on JCp. Four 5 mg samples of JCp were subjected to the full coral cleaning procedure (section 2.3.2), and an additional four 5 mg samples were directly dissolved in 0.5 M HNO3. The trace elemental composition of these samples were determined using the Element ICP-MS (section 2.3.3), and bracketed against the external standard BSGS [*Ni*, 2006; *Ni et al.*, 2007]. To correct for the mean difference between JCp bracketed against BSGS or the external standard used in this study, the Li/Ca and Mg/Ca ratios were decreased by 3.6% and 6.12% respectively, and the Li/Mg and Sr/Ca ratios were increased by 3.42% and 0.79% respectively. As stated in the main text, the Li/Ca and Mg/Ca ratios declined 25% as a result of cleaning, but the Li/Mg ratios are not impacted by this procedure and equally, the Sr/Ca ratios are consistent between cleaned and uncleaned samples (Figure S2).

**Figures**

**Figure S1**



**Figure S1.** Schematic of the isobaric interference on 7Li from 14N++. A typical 7Li peak (green dotted curve) has ~20,000cps (0.1 ppb) when 115In and 138U sensitivity is 200 x 103 cps per 0.1 ppb. The red dotted curve reveals the 14N++ isobaric interference located at the left (lower mass) of the 7Li peak with an intensity of ~90,000 cps for the same tuning conditions as above, when additional gas (NH3) is set to 0.070 ml min-1. The area where these overlap causes a 7Li+14N++ spike. Note that the 7Li blank is insignificant compared to the signal (typically ~200 cps or 1 ppt).



**Figure S2.** Results of JCp-1 elemental analysis after samples were either cleaned (open circles) or directly dissolved in 0.5 M HNO3 without being cleaned. (a) Li/Ca and (b) Mg/Ca ratios are lower in cleaned samples, in contrast to (c) Li/Mg and (d) Sr/Ca ratios which are unaffected by the cleaning process. Error bars represent the 2σ external precision based on long term measurements of JCp-1 bracketed against the Cardiff University multi-element standard.

**Tables**

Table S1. Inner reef and outer reef data logger temperature, and Reynolds sea surface temperature composites for the forereef and backreef regions, and HadISST1 (2002-2008).

Table S2. Gravimetric elemental ratios and average measured elemental ratios of the University of Southampton consistency standards.

**Table S3.** Coretop Li/Mg and Sr/Ca ratios from the forereef (FR-12) and backreef (BR-06) corals used to make the Li/Mg- and Sr/Ca-SST calibrations. The backreef Li/Mg ratio for July 2008 was not included in the calibration.

**Table S4.** Downcore (1921-1926) Li/Mg and Sr/Ca ratios in both the forereef (FR-12) and backreef (BR-06) corals, and the resulting sea surface temperature reconstructions.

**Table S5.** Historic HadISST1 data, encompassing the forereef and backreef zones between 1921 and 1926.

Al-Ammar, A. S., R. K. Gupta, and R. M. Barnes (2000), Elimination of boron memory effect in inductively coupled plasma-mass spectrometry by ammonia gas injection into the spray chamber during analysis, *Spectrochimica Acta Part B*, *55*, 629-635.

Ni, Y. (2006), Evaluation of boron isotopes and trace abundances in planktonic foraminifers as palaeo-oceanographic proxies, 217 pp, University of Bristol, University of Bristol.

Ni, Y., G. L. Foster, T. Bailey, T. Elliott, D. N. Schmidt, P. Pearson, B. Haley, and C. Coath (2007), A core top assessment of proxies for the ocean carbonate system in surface‐dwelling foraminifers, *Paleoceanography*, *22*(3).