

Geochemical Records from *Porites* Corals: Ocean Circulation, Pollution, and Climate

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STATEMENT OF ORIGINALITY

The work described in this thesis was carried out while I was a full-time student at the Research School of Earth Sciences, at the Australian National University between March 2017 and June 2021. Except where mentioned in the text, the research described here is my own. No part of this thesis has been submitted to any other university or similar institution.

Yang Wu

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Abstract

Oceanic variables and human impacts on coastal environments are not well-understood. My PhD study has extracted the environmental information preserved in the skeletons (CaCO_3) of *Porites* corals to understand the long-term effects of these influences. *Porites* corals are ideal biomonitors because they are long-lived and during the process of calcification, chemical signatures are incorporated into the skeletal aragonite providing time histories of impacts to the corals and reef systems. This thesis is aimed at (1) using coral radiocarbon (^{14}C) to understand the seasonal to decadal scale ocean circulation and climatic variability in the South China Sea (SCS) and in the Great Barrier Reef (GBR) and (2) developing and applying multiple elemental ratios in coral skeletons to evaluate the century-long environmental changes (temperature and water quality) in the GBR.

The SCS radiocarbon study showed that Pacific water intrudes into the eastern SCS as reflected by the detection of ‘early radiocarbon bomb peak’ in late 1955 and that the circulation in the SCS is more affected by East Asian Monsoon than previously thought. The GBR radiocarbon study showed that GBR seawater ^{14}C is mainly affected by the East Australian Current. The extended GBR ^{14}C record also provides insights into the long-term overturning of the ^{14}C reservoirs. In both study sites, climatic variabilities such as El Niño-Southern Oscillation were found to be correlated with abnormally higher or lower ^{14}C signals tracking surface water circulation.

Multiple coral cores were collected from the nearshore GBR to assess the robustness of sea surface temperature (SST) proxies (Li/Ca, B/Ca, Mg/Ca, Sr/Ca, U/Ca). Results showed that U/Ca was more robust than other elemental ratios in these GBR corals. An improvement of Li/Ca and B/Ca as SST proxy can be made by normalizing Li/Ca and B/Ca to Mg/Ca which eliminates the impacts of vital effects. The empirical calibrations established in this study have

contributed to the site-specific SST calibrations in the GBR and have been used to revisit a universal model to reconstruct the SST.

The Gladstone Harbour region of Queensland is a major port for coal and alumina export. It is also subjected to major port expansion and dredging events. Corals were collected around the Gladstone Harbour to test if they are good indicators of environmental pollution throughout the historical development of the Gladstone Harbour. Results showed that a few heavy metals (Al, Ti, V, Mn, Cu, Zn, Pb) were elevated in coral skeletons during the post-industrial era (1950-present). These contaminants were mainly delivered to the coastal seawater by river runoff, but other modes of delivery also exist.

Corals subjected to nearshore river runoff can record terrigenous input. Corals were collected from the Central and Southern GBR to cover different hydrological conditions. Results showed that coral Ba/Ca are effective tracers of river runoff over the longer timescale, but the seasonal-scale variations of Ba/Ca can be terrigenous, temperature-dependent and/or bio-regulated depending on their geographic locations. The quantification of terrestrial runoff can be made from coral Ba/Ca ratios, but this approach should be preceded by careful site selection.

Publications and conference talks during candidature

Publications

- (1) **Wu, Y.**, Fallon, S.J., Cantin, N.E., & Lough, J.M. (2021). Assessing multiproxy approaches (Sr/Ca, U/Ca, Li/Mg, and B/Mg) to reconstruct sea surface temperature from coral skeletons throughout the Great Barrier Reef. *Science of The Total Environment*, p.147393. <https://doi.org/10.1016/j.scitotenv.2021.147393>
- (2) **Wu Y.**, Fallon S., Cantin N., & Lough J (2021). Surface ocean radiocarbon from a *Porites* coral record in the Great Barrier Reef: 1944-2017. *Radiocarbon* 1-11. <https://doi.org/10.1017/rdc.2020.141>
- (3) **Wu Y.**, & Fallon S. (2020). Prebomb to postbomb ¹⁴C history from the west side of Palawan Island: Insights into oceanographic changes in the South China Sea. *Journal of Geophysical Research: Oceans*, 125, e2019JC015979. <https://doi.org/10.1029/2019JC015979>
- (4) Lough J. M., Cantin N.E., Fallon S., & **Wu Y.** (2020) Summary Report: Potential of coral geochemical Tracers to record environmental histories within the Fitzroy River Basin. Report prepared for BHP Billiton. Australian Institute of Marine Science, Townsville, Qld. (163 pp)
- (5) Lough J.M., Fallon S., **Wu Y.**, & Cantin N.E. (2020) Project: Geochemical histories from coral cores adjacent to the Fitzroy River Basin. Report prepared for BHP Billiton Pty Ltd. Australian Institute of Marine Science, Townsville, Qld.
- (6) Cantin, N., **Wu, Y.**, Fallon, S., & Lough, J. (2019). Historical records of terrestrial sediment and flood plume inputs to the Whitsunday Island region from coral skeletons: 1861-2017. Australian Institute of Marine Science, Townsville, Qld. (30pp).
- (7) Cantin N.E., Fallon S., **Wu Y.** & Lough J.M. (2018) Project ISP019: Calcification and geochemical signatures of industrial development of the Gladstone Harbour from century old coral skeletons. Report prepared for Gladstone Healthy Harbour Partnership. Australian Institute of Marine Science, Townsville, Qld. (40 pp).

Conference talks

- (1) **Wu Y.**, Fallon S., Cantin N., & Lough J. Examining Ba/Ca, Y/Ca, rare earth elements as proxies for terrestrial runoff in the Great Barrier Reef. Virtual Goldschmidt. 21-26 June, 2020.
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(3) **Wu Y.**, Fallon S., Cantin N., & Lough J. Responses and records from *Porites* corals-Spatio-temporal environmental changes in the Gladstone Harbour. ACRS conference, Morten Island, Brisbane, Australia. May 7-10, 2019.

(4) **Wu Y.**, & Fallon S. Pre to post-bomb ^{14}C history from a coral in western Philippine Sea, AMS14, Ottawa, Canada. 14-18 August, 2017.

Table of Contents

Abstract.....	iv
List of Figures.....	xi
List of Tables	xvi
Chapter 1: Introduction	1
1.1 Coral structure and calcification.....	3
1.2 Coral radiocarbon.....	4
1.2.1 Radiocarbon production and coral uptake.....	4
1.2.2 Pre-bomb coral $\Delta^{14}\text{C}$ Records (before C.E. 1955).....	5
1.2.3 Post-bomb coral $\Delta^{14}\text{C}$ Records (after C.E. 1955).....	8
1.2.4 Ocean circulation.....	10
1.2.5 Climate information.....	11
1.3 Trace elements in corals.....	12
1.3.1 Coral SST proxies.....	13
1.3.2 Terrestrial runoff proxies.....	18
1.3.3 Pollution and Heavy Metals (Al, Cu, Zn, Fe, Cd, Pb, V).....	21
1.4 Objective and Chapter Summaries.....	22
Chapter 2: Methods	25
2.1 Coral collection and cutting.....	25
2.2 X-ray and ultra-violet analysis.....	26
2.3 Isotope analysis	27
2.3.1 Accelerator Mass Spectrometer theory.....	27
2.3.2 $\Delta^{14}\text{C}$ calculation from AMS data	29
2.3.3 Sample preparation for ^{14}C and stable isotopes (^{13}C , ^{18}O)	30
2.4 LA-ICP-MS.....	30
2.4.1 Sample preparation for LA-ICPMS	31
2.4.2 LA-ICP-MS analysis	31
2.4.3 Laser data processing	34
2.4.4 Analytical Uncertainty	38
2.4.5 Reproducibility.....	38
2.5 Developing coral age model	44
Chapter 3: Pre to post-bomb ^{14}C history from the west side of Palawan Island: insights into oceanographic changes in the South China Sea	46
3.1 Introduction.....	48
3.2 Materials and Methods.....	52
3.2.1 Coral location	52
3.2.2 Sample preparation for ^{14}C and stable isotopes	52
3.2.3 Age model.....	54
3.2.4 Additional coral locations for comparison and their age models	54
3.3 Results.....	55
3.4 Discussion	57
3.4.1 Pre-bomb era and early bomb intrusion.....	58
3.4.2 Post bomb era	60
3.4.3 Seasonal variation	62
3.4.4 South China Sea circulation	64

3.5 Conclusion	65
Chapter 4: Surface ocean radiocarbon from a Porites coral record in the Great Barrier Reef: 1945-2017	72
4.1 Introduction.....	74
4.2 Materials and Methods.....	75
4.2.1 Coral location, preparation and age model	75
4.2.2 ^{14}C analysis	77
4.3 Results	77
4.4 Discussion	78
4.4.1 Radiocarbon time series in the Southern GBR and regional variations	78
4.4.2 Seasonal and interannual variability.....	80
4.4.3 Long-term oceanic ^{14}C uptake	82
4.4.4 Utilizing GBR coral ^{14}C records as a dating reference series.....	84
4.5 Conclusion	85
Chapter 5: Assessing multiproxy approaches (Sr/Ca, U/Ca, Li/Mg, and B/Mg) to reconstruct sea surface temperature from coral skeletons throughout the Great Barrier Reef.....	87
5.1 Introduction.....	90
5.2 Methods.....	92
5.2.1 Study area and climate information.....	92
5.2.2 Sea surface temperature (SST).....	94
5.2.3 Sample preparation and LA-ICP-MS analysis	96
5.2.4 Age models and statistical analyses.....	98
5.3. Results.....	100
5.3.1 Elemental ratios	100
5.3.2 Periodicity and correlation.....	101
5.3.3 Principal Component Analysis	101
5.3.4 SST calibrations using elemental ratios	104
5.4. Discussion	106
5.4.1 Elemental ratio variability and temperature dependence	106
5.4.1.1 Sr/Ca	106
5.4.1.2 U/Ca.....	107
5.4.1.3 Mg/Ca	108
5.4.1.4 Li/Mg.....	109
5.4.1.5 B/Mg.....	110
5.4.2 Universal SST reconstruction model	112
5.4.3 Long-term trend and reconstruction	118
5.4.4 Summary of the Sr/Ca, U/Ca, Li/Mg, and B/Mg paleothermometer	121
5.5 Conclusion	122
Chapter 6: Coral records of spatio-temporal environmental changes in the Gladstone Harbour	144
6.1 Introduction.....	145
6.2 Research Methods.....	147
6.2.1 Study area	147
6.2.2 Geographic and hydrological setting	148
6.2.3 LA-ICP-MS	150
6.2.4 Age model.....	150
6.2.5 Statistical analyses.....	151

6.3 Results: time-series of individual coral cores	152
6.4 Discussion	160
6.4.1 <i>Spatial variability of trace elements</i>	160
6.4.2 <i>Pre-industrial periods vs post-industrial periods</i>	167
6.4.3 <i>Individual trace elements</i>	168
6.4.4 <i>Metal covariance and delivery pathways</i>	178
6.4.5 <i>Distribution coefficient (Kd)</i>	179
6.5 Conclusion	187
Chapter 7: Environmental and biological controls on seasonal to interannual Ba/Ca variations recorded in <i>Porites</i> corals from the Great Barrier Reef.....	189
7.1 Introduction	190
7.2 Study sites and methods	191
7.2.1 <i>Study area and sample collection</i>	191
7.2.2 <i>Geochemical analysis</i>	193
7.2.3 <i>Environmental data</i>	193
7.3 Results	194
7.4 Discussion	198
7.4.1 <i>Ba incorporation into coral skeletons</i>	198
7.4.2 <i>Spatially different timings of Ba/Ca peak and regional reproducibility</i>	199
7.4.3 <i>Long term Ba/Ca signals</i>	204
7.4.4 <i>Translating Ba signals</i>	206
7.4.5 <i>Implications from coral Mn/Ca and Y/Ca records</i>	208
7.5 Conclusion	210
Chapter 8: Conclusions and future directions	216
8.1 Coral radiocarbon	216
8.2 Coral trace elements (element/calcium ratio)	217
8.3 Future work	219
References.....	221

List of Figures

Figure 1.1 The overall structure of a polyp and the underlying skeleton.....	4
Figure 1.2 Locations of selected $\Delta^{14}\text{C}$ coral records in the Pacific Ocean and Atlantic Oceans.....	5
Figure 1.3 (a) Pre-bomb coral $\Delta^{14}\text{C}$ values for annual and biennial coral bands from the North Pacific; (b) Pre-bomb coral $\Delta^{14}\text{C}$ values for annual and biennial coral bands from the South Pacific; (c) Pre-bomb coral $\Delta^{14}\text{C}$ values for annual and biennial coral bands from the Atlantic.....	8
Figure 1.4 (a) Post-bomb coral $\Delta^{14}\text{C}$ values for annual and biennial coral bands from the North Pacific; (b) Post-bomb coral $\Delta^{14}\text{C}$ values for annual and biennial coral bands from the South Pacific; (c) Post-bomb coral $\Delta^{14}\text{C}$ values for annual and biennial coral bands from the Atlantic.....	9
Figure 1.5 Slopes and intercepts derived from the Sr/Ca-SST calibration equations.....	15
Figure 2.1 (a) and (b) underwater coral drilling (c) extracted coral core and (4) coral pieces for geochemical analysis.....	26
Figure 2.2 An example of X-ray positive print (left) and digitally enhanced photographs of luminescence (right) under ultra-violet light for Whitsunday Island (WHI84A).....	27
Figure 2.3 A typical set up to drill ^{14}C and stable isotope samples using the in-house Micromill.....	29
Figure 2.4 Laser ablation ICP-MS sampling unit (left), and samples and standards (NIST612, NIST614, Davies coral standard) in laser holder (right).....	33
Figure 2.5 An example of LA-ICP-MS time resolved data (counts/s) showing components of typical coral analysis produced by LAtools ‘data split’ command.....	36
Figure 2.6 LA-ICP-MS time resolved data (counts/s) of coral standard and sample HUM03A before and after de-spiking produced by LAtools ‘despike’ command.....	36
Figure 2.7 An example of background linear interpolation by LAtools.....	36
Figure 2.8 Calibration curves for ‘major’ trace elements using Davies coral standard.....	37
Figure 2.9 Calibration curves for ‘minor’ trace elements using NIST612 standard, with validation from NIST614 standard.....	38
Figure 2.10 Multiple daily measurements of the NIST614 calibrated by NIST612.....	41
Figure 2.11 Comparison of elemental ratios for RAT04A on replicate tracks.....	44
Figure 2.12 Overlay between U/Ca cycles and SST cycles for HUM03A.....	46

Figure 3.1 Coral locations from radiocarbon studies and ocean currents around southeast Asian archipelago.....	52
Figure 3.2 South China Sea surface currents during Northeast Monsoon (left, winter) and Southwest Monsoon (right, summer).....	53
Figure 3.3 X-ray images of Palawan coral.....	54
Figure 3.4 Complete $\delta^{18}\text{O}$ and Sea surface temperature curves for Palawan coral.....	55
Figure 3.5 Complete $\Delta^{14}\text{C}$ curves for Palawan coral.....	57
Figure 3.6 Comparison of $\Delta^{14}\text{C}$ records between Palawan (this study) and other selected sites.....	59
Figure 3.7 Close-up of early bomb intrusions and post-bomb values from selected sites.....	63
Figure 3.8 Comparison of $\Delta^{14}\text{C}$ seasonality, Palawan zonal velocity and Palawan sea surface salinity.....	65
Figure 4.1 General surface circulation in the Pacific and off northeast Australia.....	77
Figure 4.2 Comparison of $\Delta^{14}\text{C}$ records from Masthead Island (this study) and (a) southern GBR corals and (b) selected southern Pacific corals.....	79
Figure 4.3 Comparison between southern GBR surface ocean $\Delta^{14}\text{C}$ record, SST record and ONI (ocean Niño index).....	83
Figure 4.4 Comparison of $\Delta^{14}\text{C}$ records between Masthead Island (this study), atmospheric record and four north Pacific coral sites.....	86
Figure 5.1 Sample locations (red circles) for the coral cores from the Southern GBR (Gladstone region) and from the Central GBR (Whitsunday Islands).....	94
Figure 5.2 Results of elemental ratios vs distance (left panel) and power spectra analysis of Li/Ca, Li/Mg, B/Ca, B/Mg, Mg/Ca, Sr/Ca, Sr/Mg, U/Ca, and U/Mg (right panel).....	98
Figure 5.3 Rotated loadings of each element onto the first two principal components (PC) for HUM03A, HUM04B, MAS02C, SEN01C, SHW82C, and SMI81A.....	102
Figure 5.4 Scatter plots of elemental ratios (Li/Mg (blue), B/Mg (red), Sr/Ca (orange) and U/Ca (green)) for coral cores collected from Whitsunday Islands and Gladstone Harbour over a common assessment/calibration period (1990-2016).....	106
Figure 5.5 (a) Slopes and intercepts generated from the linear regressions between elemental ratios (Sr/Ca, U/Ca, Li/Mg, B/Mg) and SST; (b) Mathematic demonstration of the universal calibration of SST based on multi-trace elements.....	115

Figure 5.6 Comparison between UMTECS reconstructions and empirical SST reconstructions.....	117
Figure 5.7 Comparison between monthly HadISST and reconstructed SST for each coral core using four elemental ratios (Sr/Ca, U/Ca, Li/Mg, and B/Mg).....	120
Figure 6.1 Industrial development and port expansion history of Gladstone Harbour from 1917 to 2017.....	147
Figure 6.2 Coral sampling locations from the Gladstone Harbour and the main catchments in this region.....	148
Figure 6.3 Annual River flow ($\times 10^6$ ML) in (a) Fitzroy from 1915 to 2017 and in (b) Calliope from 1939 to 2017.....	149
Figure 6.4 Uranium seasonal cycles from the Gladstone Harbour corals.....	151
Figure 6.5 Geochemical time-series of Al/Ca, Ti/Ca, V/Ca, Mn/Ca, Cu/Ca, Zn/Ca, As/Ca, Y/Ca, Sn/Ca, La/Ca, Ce/Ca, Ba/Ca and Pb/Ca recorded in the <i>Porites</i> spp. skeleton from the Outer-Harbour Seal Rocks site (SEA10A) from 1959-2017.....	153
Figure 6.6 Geochemical time-series of Al/Ca, Ti/Ca, V/Ca, Mn/Ca, Cu/Ca, Zn/Ca, As/Ca, Y/Ca, Sn/Ca, La/Ca, Ce/Ca, Ba/Ca and Pb/Ca recorded in the <i>Porites</i> spp. skeleton from the Outer-Harbour Seal Rocks site (SEA11A) from 1952-2017.....	154
Figure 6.7 Geochemical time-series of Al/Ca, Ti/Ca, V/Ca, Mn/Ca, Cu/Ca, Zn/Ca, As/Ca, Y/Ca, Sn/Ca, La/Ca, Ce/Ca, Ba/Ca and Pb/Ca recorded in the <i>Porites</i> spp. skeleton from the Harbour Fringes Sable Chief Rocks site (SAB05A) from 1952-2017.....	155
Figure 6.8 Geochemical time-series of Al/Ca, Ti/Ca, V/Ca, Mn/Ca, Cu/Ca, Zn/Ca, As/Ca, Y/Ca, Sn/Ca, La/Ca, Ce/Ca, Ba/Ca and Pb/Ca recorded in the <i>Porites</i> spp. skeleton from the Middle Harbour zone at South End Curtis Island (SEN01C) from 1901-2017.....	156
Figure 6.9 Geochemical time-series of Al/Ca, Ti/Ca, V/Ca, Mn/Ca, Cu/Ca, Zn/Ca, As/Ca, Y/Ca, Sn/Ca, La/Ca, Ce/Ca, Ba/Ca and Pb/Ca recorded in the <i>Porites</i> spp. skeleton from the inshore control Hummocky Island (HUM02A) from 1902-2017.....	158
Figure 6.10 Geochemical time-series of Al/Ca, Ti/Ca, V/Ca, Mn/Ca, Cu/Ca, Zn/Ca, As/Ca, Y/Ca, Sn/Ca, La/Ca, Ce/Ca, Ba/Ca and Pb/Ca recorded in the <i>Porites</i> spp. skeleton from the inshore control Hummocky Island (HUM03A) from 1900-2017.....	159
Figure 6.11 Geochemical time-series of Al/Ca, Ti/Ca, V/Ca, Mn/Ca, Cu/Ca, Zn/Ca, As/Ca, Y/Ca, Sn/Ca, La/Ca, Ce/Ca, Ba/Ca and Pb/Ca (mol/mol) recorded in the <i>Porites</i> spp. skeleton from the offshore control Masthead Island (MAS01E) from 1890-2017..	160

Figure 6.12 Comparison of Al/Ca, Ti/Ca, V/Ca, Mn/Ca, Zn/Ca, Pb/Ca, Cu/Ca, Zn/Ca, Ba/Ca, Y/Ca, La/Ca and Ce/Ca elemental ratios in coral skeletons along the geographic gradients from near harbour sites to offshore sites.....	162
Figure 6.13 Comparison of trace element enrichment within the coral skeletons from five reef locations.....	168
Figure 6.14 Comparison of Al/Ca ratios at different coral sites, and their correspondence with major port development and floods.....	170
Figure 6.15 Comparison of Ti/Ca ratios at different coral sites, and their correspondence with major port development and floods.....	171
Figure 6.16 Comparison of V/Ca ratios at different coral sites.....	172
Figure 6.17 Comparison of Mn/Ca (mol/mol) elemental ratios at different coral sites.....	173
Figure 6.18 Comparison of Ba/Ca ratios at different coral sites, and their correspondence with major floods.....	175
Figure 6.19 Comparison of Y/Ca ratios at different coral sites, and their correspondence with major floods.....	175
Figure 6.20 Comparison of Cu/Ca (mol/mol) and Sn/Ca elemental ratios at different coral sites.....	176
Figure 6.21 Comparison of Zn/Ca (mol/mol) and Pb/Ca elemental ratios at different coral sites.....	178
Figure 6.22 Loading plots in rotated space for 16 elemental ratios in each coral core with Varimax rotation solution.....	179
Figure 7.1 Coral sampling sites in the Central GBR (purple rectangle, and purple circles) and in the Southern GBR (red rectangle and red circles) as well as satellite images for major rivers of influence.....	192
Figure 7.2 (a) Comparison between Fitzroy River discharge and rainfall in the study region (b) Comparison of annual River discharge from Fitzroy River, Pioneer River and the combination of Proserpine and O'Connell River.....	193
Figure 7.3 Coral Ba/Ca records from Hummocky Island (HUM02A&03A) and Humpy Island (HMP01B) to the north of Gladstone (Southern GBR).....	196
Figure 7.4 Coral Ba/Ca records from the Whitsunday Islands (Central GBR).....	197
Figure 7.5 Comparison of Ba/Ca, Mn/Ca and Y/Ca elemental ratios in coral skeletons from the Central GBR and Southern GBR.....	198
Figure 7.6 Monthly averages of coral Ba/Ca.....	201

Figure 7.7 Comparison of coral Ba/Ca profiles from Hummocky Island, Humpy Island and Keppel Island.....	202
Figure 7.8 Regional comparison of seasonal Ba/Ca cycles between SMI81A (this work) and North Molle Island (Lewis et al., 2012).....	204
Figure 7.9 Long-term coral Ba/Ca records from the Humpy Island (HMP01B, 1665-2000) and South Molle Island (SMI01C, 1860-1985).....	206
Figure 7.10 (a) Scatterplot of annual average Ba/Ca ratios from SMI01C_81A, HMP01B, HUM02A and HUM03A vs Fitzroy river discharge ($\times 10^6$ ML) from 1917-2017; (b) Scatterplot of annual average Ba/Ca ratios from SMI01C_81A vs Fitzroy River discharge, Pioneer River discharge and sum of Proserpine River and O'Connell River discharge ($\times 10^6$ ML) from 1917-2017.....	210

List of Tables

Table 1.1 Selected studies of Ba/Ca ($\mu\text{mol/mol}$) in <i>Porites</i> corals as environmental proxies.....	20
Table 2.1 Geographic locations of <i>Porites</i> coral cores.....	25
Table 2.2 The standard operation conditions for LA-ICP-MS.....	34
Table 2.3 Summary of LA-ICP-MS procedures.....	34
Table 2.4 Comparisons of overall uncertainty, limit of detection (LoD) and signal over background (bkg) counts for trace element.....	42
Table 3.1 Comparison of the early bomb intrusion values, timing and bomb-induced $\Delta^{14}\text{C}$ increases.	57
Table 5.1 Coefficients derived from elemental ratios (Sr/Ca (mmol/mol), U/Ca ($\mu\text{mol/mol}$), Li/Mg (mmol/mol) and B/Mg (mmol/mol)) vs SST ($p < 0.01$), root mean square error (RMSE) and long-term SST changes.....	103
Table 6.1 Geographic locations of <i>Porites</i> coral cores.....	148
Table 6.2 Comparison of average, minimum, maximum, median, standard deviation, first quartile and third quartile for selected elemental ratios in different coral sites.....	163
Table 6.3 Comparison of metal contents in <i>Porites</i> corals.....	164
Table 6.4 Factor loadings on rotated principal components for 16 elemental ratios in each coral core and the percentage variance explained by each component.....	165
Table 6.5 The mean concentrations of trace metals ($\mu\text{g}\cdot\text{g}^{-1}$) in coral skeletons from seven sites around the Gladstone Harbour and average trace metals ($\mu\text{g}\cdot\text{L}^{-1}$) in seawater from the Port Curtis.....	185
Table 6.6 Distribution coefficients (K_d) of selected metals in corals.....	186
Table 7.1 Geographic locations of <i>Porites</i> coral cores examined in this work.....	192
Table 7.2 Average annual skeletal growth and luminescence characteristics.....	195
Table 7.3 Correlations (r values, $p < 0.05$) between (a) coral annual luminescence range and annual river discharge (October-September), and (b) annual average coral Ba/Ca ratio and annual river discharge (October-September).....	195

Chapter 1: Introduction

The oceans play an important role in distributing heat, carbon and nutrients, and regulating our climate and weather conditions (Ganachaud and Wunsch, 2000; Ganachaud and Wunsch, 2003; Lau, 1978; Macdonald and Wunsch, 1996; Rahmstorf, 2002). The climatic and oceanic variations are reflected in the physicochemical properties of seawater, including the radiocarbon content, sea surface temperature (SST) and trace metal concentrations (Druffel, 2002; Druffel, 1997a; Grottoli and Eakin, 2007; Guilderson and Schrag, 1998). Understanding the structure of oceanic variabilities (e.g., ocean circulation and ocean geochemistry) is critical to accurately predicting future climatic and environmental changes.

Earth's climate and environment has undergone marked changes over the past centuries and many of these natural or anthropogenic alterations occurred prior to scientific observations (Blois et al., 2013; Crowley, 2000; Hodell et al., 1991; Lough, 2010; Thompson et al., 2006). In many regions, instrumental records and direct observations extend back only a few decades (Boer et al., 2000; Lough, 2010; Parker et al., 2000; Treble et al., 2003). These records are too short to fully explain the possible behaviours of Earth's climate and environment changes. The use of high-fidelity records (such as corals in paleoenvironmental studies) has emerged and appealed to many researchers in the past decades because the original isotopic and elemental signals have been preserved in the skeletons of marine calcifiers (Ainsworth et al., 2016; Beck et al., 1992; Crabbe, 2008; Druffel et al., 2007; Dunbar et al., 1994; Hoegh-Guldberg, 1999; Lough, 2010; Smith et al., 1997). These paleo-records offer an important window into understanding the preindustrial environment, and when coupled with other climate models (for example, General Circulation Models), can provide more insights into the mechanisms of climate change.

Human activities are the biggest threat to the health of the world's oceans. For example, since the middle of the 19th century, atmospheric carbon dioxide (CO₂) has been rising rapidly due to the massive emissions of fossil fuel CO₂ (Hook and Tang, 2013; Houghton, 1999; Houghton, 2003; Marland et al., 1985). This type of greenhouse gas has led to a long-term rise of the Earth's temperatures, which is commonly referred as global warming (Lashof and Ahuja, 1990). Global warming has adverse effects, such as sea level rise and altering ocean chemistry and many oceanic processes (Meinshausen et al., 2009; Raval and Ramanathan, 1989; Schneider, 1989). To infer the long-term sea surface temperature (SST) and CO₂ variations during the past, elemental ratios (e.g., B/Ca, Mg/Ca, Sr/Ca, U/Ca) and isotopic signatures ($\delta^{18}\text{O}$, $\delta^{13}\text{C}$, $\Delta^{14}\text{C}$) of corals, foraminifera and mollusk shells are widely used as recorders of climate conditions (Ainsworth et al., 2016; Beck et al., 1992; Crabbe, 2008; Druffel et al., 2007; Dunbar et al., 1994; Hoegh-Guldberg, 1999; Lough, 2010; Smith et al., 1997).

In addition to increasing CO₂ emissions and global warming, anthropogenic deterioration of seawater quality is a rising concern around the world because of the threat it poses to marine organisms and coastal ecosystems (Brodie and Waterhouse, 2012; Cooper et al., 2009; Haynes et al., 2007; Jones et al., 2015; Rossoll et al., 2012). Environmental modification from anthropogenic activities has been rising during the past century to support the needs of the booming population. Rapid coastal development and land use changes have increased nutrients, sediment loads and industrial metals in the ocean (Brodie and Waterhouse, 2012; Fallon et al., 2002; Inoue et al., 2014; Inoue et al., 2004; Kroon et al., 2020; Saha et al., 2019a). A few coral trace element ratios (e.g., Ba/Ca, Mn/Ca, and Y/Ca) have been applied to reconstruct terrestrial runoff, but the incorporation of these elements into coral skeletons is influenced by various environmental drivers with contradicting behaviours that obscure the interpretations of these geochemical signatures (Lewis et al., 2018; McCulloch et al., 2003; Saha et al., 2018a; Saha et al., 2018b). Also, only a few studies have utilized corals as marine biomonitors to track

environmental pollution such as Al, Fe, Cu, Zn, Pb, Mn, V, and Cd because of their lower abundance in corals (Bin Mokhtar et al., 2012; Fallon et al., 2002; Inoue et al., 2014; Lewis et al., 2012; Saha et al., 2019a; Saha et al., 2016).

In light of the increasing threats posed by climate change and anthropogenic activities, *Porites* sp. corals have been widely used to reconstruct ocean chemistry during the past. *Porites* corals can grow for several centuries and form continuous annual growth bands (Dodge and Vaisnys, 1975; Highsmith, 1979; Knutson et al., 1972; Shi et al., 2012). Annual growth bands can be seen in X-radiographs of coral skeletal slices cut along the growth axis. An accurate chronology can be constructed counting annual growth bands from a known collection date, prominent luminescent lines and/or SST proxies such as Sr/Ca and $\delta^{18}\text{O}$ (DeLong et al., 2007; DeLong et al., 2013; Lough, 2010). Using this chronology, geochemical values (extracted from the CaCO_3 skeleton), which reflect ambient seawater conditions, can be precisely matched to the coral's year of growth. Therefore, *Porites* corals serve as paleo-archive and are utilized in this study to provide a high-resolution spatial and temporal record of environmental and climatic changes in the South China Sea and the Great Barrier Reef.

1.1 Coral structure and calcification

Scleractinia corals consist of the living outer tissue layer and the underlying calcium carbonate skeleton. The tissue layer is composed of many polyps, which are located in a recessed calyx in the skeleton (called the corallite). The coral polyp has a simple structure consisting of a mouth encircled by feeding tentacles (Figure 1.1). Polyps use calcium (Ca^{2+}) and carbonate ions (CO_3^{2-}) in seawater to build a hard cup-shaped skeleton which is made of calcium carbonate (CaCO_3), which surrounds the body of the polyp.

Corals are thought to precipitate CaCO_3 from the extracellular calcifying fluid (ECF) (Gaetani and Cohen, 2006; McConnaughey, 1989; McCulloch et al., 2017; Sinclair, 2015). Corals also live in water and this is a leaky boundary to the ECF. The ion contents in the calcifying fluid are regulated by the coral. This process is partially attributed to the use of Ca-ATPase that removes protons in the calcifying fluid in exchange for Ca^{2+} ions from outside the calcifying fluid (Gaetani and Cohen, 2006; McCulloch et al., 2017).

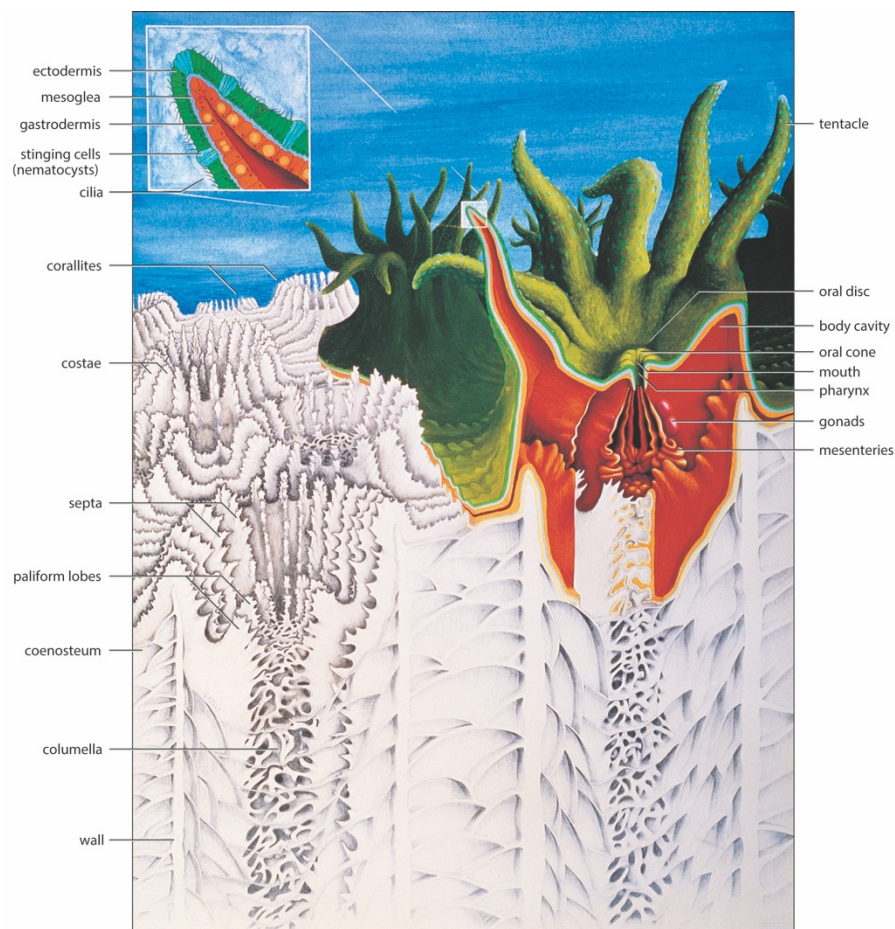


Figure 1.1 The overall structure of a polyp and the underlying skeleton. Drawing by Geoff Kelly. Veron J.E.N., Stafford-Smith M.G., Turak E. and DeVantier L.M. (2016). *Corals of the World*. Accessed 12 Oct 2020. <http://www.coralsoftheworld.org/page/structure-and-growth/> Permission granted by Corals of the World.

1.2 Coral radiocarbon

1.2.1 Radiocarbon production and coral uptake

Three isotopes of carbon are found in nature, with two nonradioactive isotopes (^{12}C and ^{13}C) and one radioactive isotope (^{14}C or radiocarbon). The half-life for ^{14}C is 5,730 years (Godwin,

1962; Johnson, 1965). Both the natural and artificial production of ^{14}C is through the reaction of thermal neutrons and nitrogen atoms in the upper atmosphere (i.e., $n + {}^{14}_7\text{N} \rightarrow {}^{14}_6\text{C} + p$). These ^{14}C atoms quickly react with O_2 to form radioactive $^{14}\text{CO}_2$. These atmospheric $^{14}\text{CO}_2$ molecules subsequently diffuse into seawater through air-sea gas exchange (Druffel and Linick 1978, Druffel and Suess 1983), and become a part of the dissolved inorganic carbon (DIC) pool. From there, the DIC is incorporated into coral skeletons during the calcification process (Druffel, 1997a). After the mass-dependent fractionation correction using coral $\delta^{13}\text{C}$, coral $\Delta^{14}\text{C}$ has been found to accurately record seawater $\Delta^{14}\text{C}$ DIC (Druffel, 1987; Fallon et al., 2003a; Guilderson and Schrag, 1998; Stuiver and Polach, 1977). $\Delta^{14}\text{C}$ in surface seawater and in coral skeletons is influenced by the input of bomb-produced radiocarbon, the burning of ^{14}C depleted fossil fuels (Tans et al., 1979) and ocean circulation such as vertical mixing and lateral advection of water masses (see sections below).



Figure 1.2 Locations of selected $\Delta^{14}\text{C}$ coral records in the Pacific Ocean and Atlantic Oceans. Detailed references for each site are listed in Figure 1.3 and Figure 1.4.

1.2.2 Pre-bomb coral $\Delta^{14}\text{C}$ Records (before C.E. 1955)

Pre-bomb $\Delta^{14}\text{C}$ values (-40‰ to -55‰) from the subtropical Pacific (e.g., Hawaii, Abraham Reef) were relatively higher than those (-80‰ to -65‰) from tropical regions (e.g., Galapagos, Mentawai) (Figure 1.3). The lower values in the equatorial zones were due to the upwelling

of ^{14}C depleted waters, while subtropical sites were dominated by downwelling and lateral advection (Druffel, 2002). Pre-bomb $\Delta^{14}\text{C}$ values in most subtropical Pacific sites have a narrow range, but some other sites such as Fiji and Fanning have oscillatory pre-bomb $\Delta^{14}\text{C}$ values due to their complex oceanographic conditions (Druffel, 1989; Druffel et al., 2001) (Figure 1.1). The North Atlantic was subject to regular convective mixing of surface and subsurface waters during the formation of 18°C-mode water, so pre-bomb $\Delta^{14}\text{C}$ values were more variable (Druffel, 1989) (Figure 1.1).

The Suess Effect refers to the decrease of atmospheric $^{14}\text{C}/^{12}\text{C}$ and $^{13}\text{C}/^{12}\text{C}$ ratios since 1850 due to the emission of fossil-fuel derived CO_2 , which is depleted in heavier isotopes of carbon (Suess, 1953). ^{14}C -free CO_2 is transferred into the ocean by gas exchange. The Suess Effect has been observed in some corals from the Atlantic and Pacific Oceans but with regional variations (Druffel, 1997a). Coral records from the northern subtropics revealed an expected Suess Effect (decrease of ~10‰, Figure 1.3) using a box diffusion model (Stuiver and Quay, 1981), whereas the Great Barrier Reef in the southwestern Pacific recorded a lower Suess Effect (Figure 1.3), potentially due to the non-steady state water mixing (Druffel and Griffin, 1993; Druffel and Griffin, 1999). The variations were caused by complex ocean dynamics which mixed seawaters containing different ^{14}C signatures. Therefore, coral records from more locations are needed to deconvolve the Suess Effect from the interannual-to-decadal scale of ocean circulations. Another marked change in atmospheric CO_2 was caused by the production of bomb ^{14}C in the stratosphere in the late 1950s and early 1960s. The dramatic rise of ^{14}C levels in the atmosphere during that period further masked the impact of the Suess Effect. Nevertheless, the unique ^{14}C signatures recorded in the coral skeletons provide a great opportunity to better understand ocean circulation and carbon cycle dynamics using ^{14}C labelled waters.

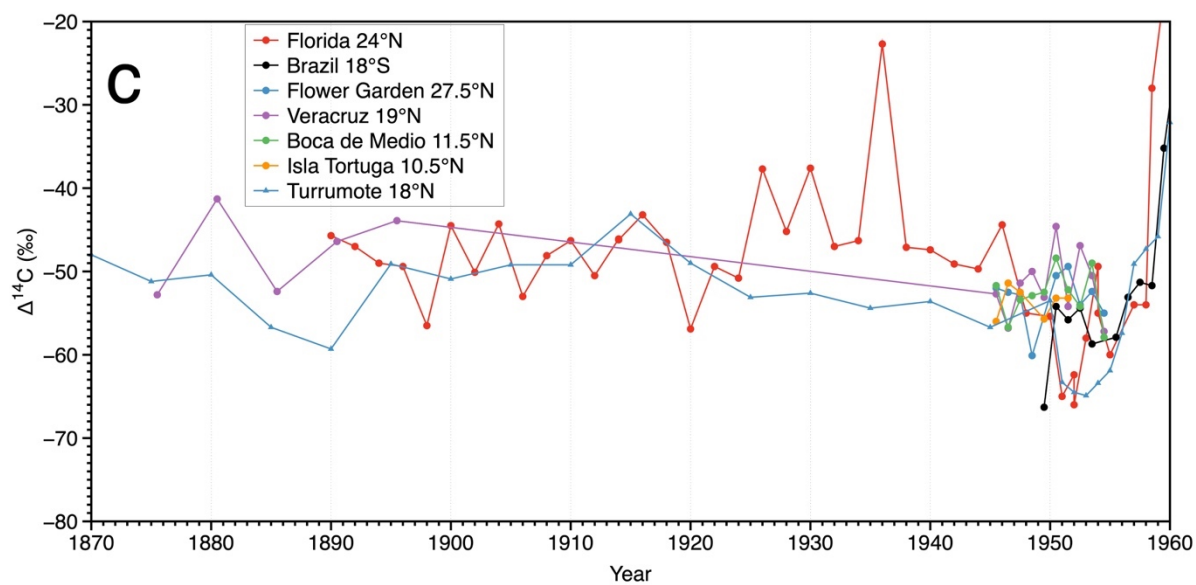
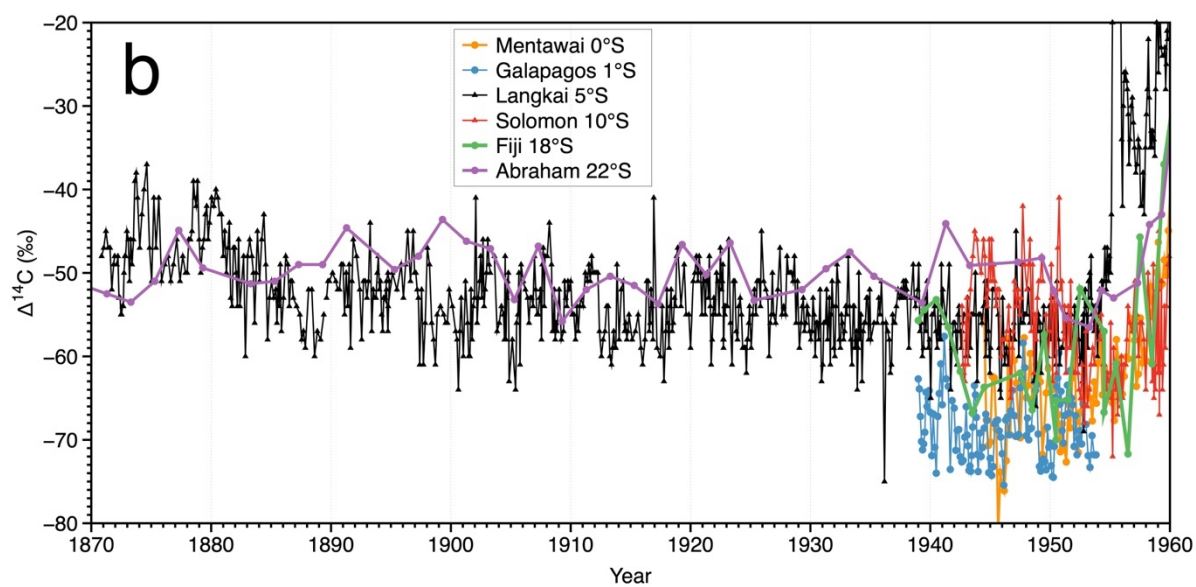
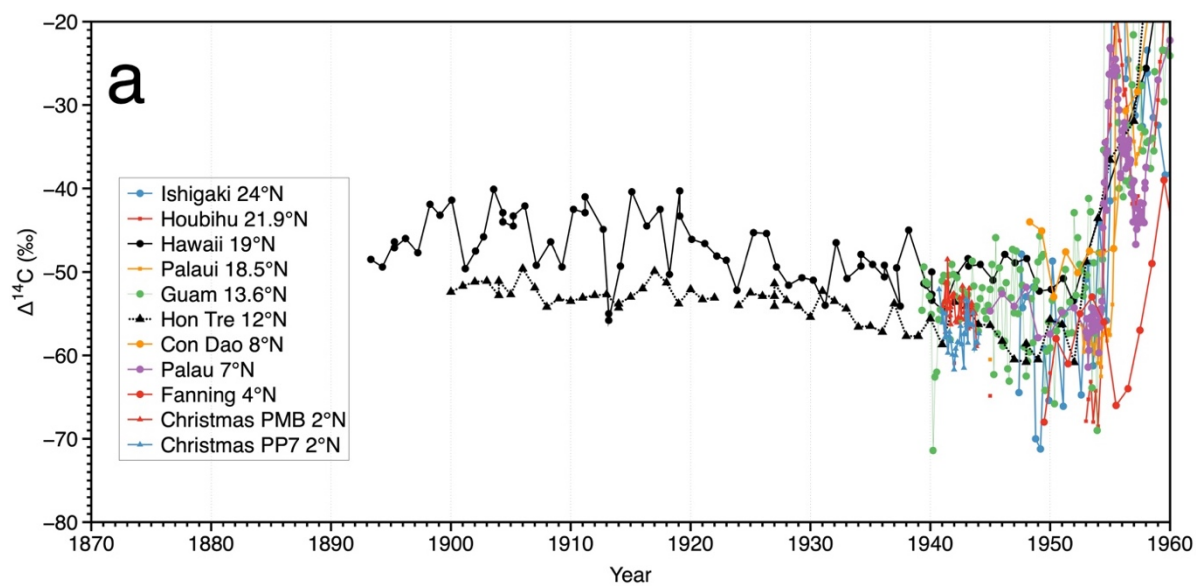


Figure 1.3 (a) Pre-bomb coral $\Delta^{14}\text{C}$ values for annual and biennial coral bands from the North Pacific; selected sites include Ishigaki (Hirabayashi et al., 2017a), Hawaii (Druffel et al., 2001), Guam (Andrews et al., 2016a), Hon Tre Island (Bolton et al., 2016), Con Dao (Mitsuguchi et al., 2007), Palau (Glynn et al., 2013), Christmas (Zaunbrecher et al., 2010), Houbihu and Palau Island (Ramos et al., 2019) and Fanning (Druffel, 1987); (b) Pre-bomb coral $\Delta^{14}\text{C}$ values for annual and biennial coral bands from the South Pacific; selected sites include Mentawai (Grumet et al., 2004), Galapagos (Guilderson and Schrag, 1998), Langkai (Fallon and Guilderson, 2008), Solomon (Guilderson et al., 2004), Fiji (Toggweiler et al., 1991), and Abraham (Druffel and Griffin, 1995; Druffel and Griffin, 1999); (c) Pre-bomb coral $\Delta^{14}\text{C}$ values for annual and biennial coral bands from the Atlantic; selected sites include Florida and Brazil (Druffel, 1997b), Flower Garden, Veracruz, Boca de Medio, and Isla Tortuga (Wagner et al., 2009), and Turrumote (Kilbourne et al., 2007) .

1.2.3 Post-bomb coral $\Delta^{14}\text{C}$ Records (after C.E. 1955)

Aboveground nuclear testing took place in a few regions around the world in the late 1950s and early 1960s and produced a large amount of atmospheric ^{14}C (Druffel, 1987; Nydal and Lovseth, 1983). The atmospheric ^{14}C doubled its amount and reached a peak in 1963 when the nuclear test ban treaty started (Graven, 2015; Levin et al., 1985; Pravalie, 2014). Seawater $\Delta^{14}\text{C}$ started to rise in the post-bomb era until it reached an equilibrium with atmospheric $\Delta^{14}\text{C}$ (normally ~ 10 years). The shape of the coral post-bomb $\Delta^{14}\text{C}$ timeseries is highly variable across the Pacific (Figure 1.4). The shape of the $\Delta^{14}\text{C}$ curves can provide insights into water mass movement, such as vertical mixing and lateral advection (Grottoli and Eakin, 2007). Generally, $\Delta^{14}\text{C}$ increased more rapidly in the gyre regions (e.g., Hawaii in the North Pacific gyre and Rarotonga in the South Pacific gyre) and reached the local maxima earlier (Figure 1.4) (Druffel et al., 2001; Guilderson et al., 2000). This was due to the longer residence time of surface water, thus maximizing the air-sea $^{14}\text{CO}_2$ exchange (Druffel et al., 2001; Guilderson et al., 2000). In contrast, corals from the Eastern Pacific such as Galapagos were shown to be susceptible to intense upwelling of lower $\Delta^{14}\text{C}$ water (Figure 1.4) (Guilderson and Schrag, 1998). The spatially different $\Delta^{14}\text{C}$ peak heights documented by the corals at Rarotonga, Tahiti and Viti Levu reflected the different atmospheric forcing and variable vertical mixing of surface waters with subsurface waters (Guilderson et al., 2000).

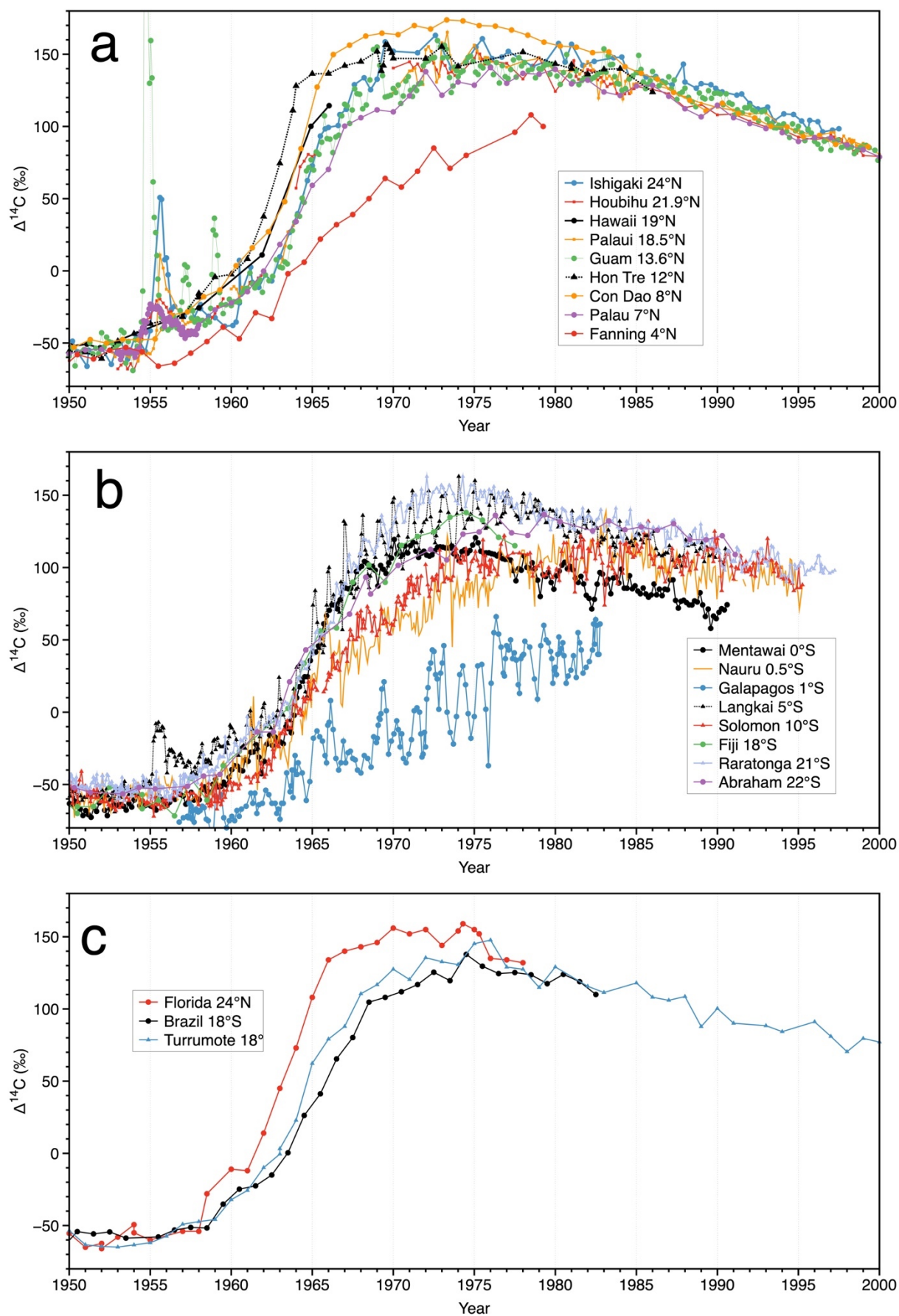


Figure 1.4 (a) Post-bomb coral $\Delta^{14}\text{C}$ values for annual and biennial coral bands from the North Pacific; selected sites include Ishigaki (Hirabayashi et al., 2017a), Hawaii (Druffel et al., 2001), Guam (Andrews

et al., 2016a), Hon Tre Island (Bolton et al., 2016), Con Dao (Mitsuguchi et al., 2007), Palau (Glynn et al., 2013), Houbihu and Palaui Island (Ramos et al., 2019), and Fanning (Druffel, 1987); (b) Post-bomb coral $\Delta^{14}\text{C}$ values for annual and biennial coral bands from the South Pacific; selected sites include Mentawai (Grumet et al., 2004), Nauru (Guilderson et al., 1998), Galapagos (Guilderson and Schrag, 1998), Langkai (Fallon and Guilderson, 2008), Solomon (Guilderson et al., 2004), Fiji (Toggweiler et al., 1991), and Abraham (Druffel and Griffin, 1995; Druffel and Griffin, 1999); (c) Post-bomb coral $\Delta^{14}\text{C}$ values for annual and biennial coral bands from the Atlantic; selected sites include Florida and Brazil (Druffel, 1997b) and Turrumote (Kilbourne et al., 2007).

1.2.4 Ocean circulation

The regionally different $\Delta^{14}\text{C}$ records, as revealed in both pre-bomb and post-bomb periods, were shown to be related to the circulation features and air-sea exchange of CO_2 , suggesting that coral $\Delta^{14}\text{C}$ can effectively track ocean circulation (Druffel, 1987; Druffel and Griffin, 1995; Druffel and Griffin, 1999; Fallon and Guilderson, 2008; Guilderson et al., 2009; Guilderson et al., 2000; Guilderson et al., 1998). For example, $\Delta^{14}\text{C}$ records can provide useful insights in lateral water mixing and transport such as current speed and pathway. Early bomb peaks in/around 1955 were detected in the coral records from Palaui, Houbihu, Ishigaki, Currimao, Guam, Palau and the Makassar Straits as a result of the immediate advection of ^{14}C -labelled seawater from the Marshall Islands where the United States of America conducted the thermonuclear weapon tests (Andrews et al., 2016a; Fallon and Guilderson, 2008; Glynn et al., 2013; Hirabayashi et al., 2017a; Hirabayashi et al., 2019; Ramos et al., 2019a). The timing of these early bomb peaks from different coral locations along the path of the North Equatorial Current (NEC) can be further utilized to estimate the speed of surface ocean currents (Andrews et al., 2016a; Hirabayashi et al., 2017a). The average speed of the NEC was estimated to be $\sim 0.1\text{-}0.2$ m/s calculated from the ^{14}C arrival time in Guam and the distance between Guam and Operation Castle (Andrews et al., 2016). A similar approach was applied by Hirabayashi et al. (2017a) to determine the speed of the Kuroshio Current based on the different timings of early bomb peaks between Guam and Ishigaki.

The early bomb ^{14}C signals in seawater were suggested to originate from the $\text{Ca}^{14}\text{CO}_3$ particulate fallout, because atmospheric $^{14}\text{CO}_2$ may be adsorbed onto CaO particles (produced by the vaporization of coral reefs due to high bomb energy) and form CaCO_3 (Andrews et al., 2016a; Druffel, 1987; Fallon and Guilderson, 2008). However, CaCO_3 is less likely to be transported a great distance due to its low solubility and its near neutral surface charge in seawater (the point of zero charge of CaCO_3 is around 8.5 (Kosmulski 2009)), and corals cannot accrete CaCO_3 directly regardless. Therefore, seawater was more likely to be labelled by dissolved CO_2 species in two ways: (1) adsorption of $^{14}\text{CO}_2$ to particulate fallout that then dissolved in seawater; (2) higher temperature and pressure resulting from nuclear fireballs augmenting the air-sea CO_2 exchange in the Marshall Islands where thermonuclear weapon tests occurred. Both processes may have taken place at the test sites, however, there is no direct evidence to prove which one might be dominant, even though the presence of bomb fallout has been shown by coral studies utilizing coral ^{90}Sr (Toggweiler and Trumbore 1985) and Pu (Benninger and Dodge 1986).

1.2.5 Climate information

The ocean is not in a steady state in respect to climatically important surface properties such as SST or the surface wind fields (Chao et al., 2000). Seasonal-interannual-decadal scale variability in coral $\Delta^{14}\text{C}$ can shed light on small- and large-scale oceanographic changes (e.g., monsoon strength and direction, Pacific Decadal Oscillation (PDO) and El Niño-Southern Oscillation (ENSO)) (Andrews et al., 2016a; Druffel, 1987; Guilderson and Schrag, 1998; Guilderson et al., 2000; Hirabayashi et al., 2017a; Hirabayashi, 2017b). For example, interannual variability of pre-bomb $\Delta^{14}\text{C}$ was evident in a coral from Hawaii, with changes in the range of 5-30‰ (Druffel et al., 2001). These changes were thought to be correlated with Northern Pacific SST and wind speed, indicating vertical water mixing and climatic forcing dictated the coral $\Delta^{14}\text{C}$ record (Druffel et al., 2001). In the Makassar Strait, seasonal

monsoon winds changed the proportion of North Pacific waters and upwelling dominated Banda Sea waters in different seasons, which resulted in seasonal $\Delta^{14}\text{C}$ variations in Langkai (Fallon and Guilderson, 2008; Guilderson et al., 2009).

ENSO events reoccur on interannual time scales, with its two components - sea surface temperature and atmospheric pressure - strongly correlated (Neelin et al., 1998). ENSO is caused by a low-latitude air-sea interaction, which is manifested as the Southern Oscillation in the atmosphere and the El Niño-La Niña transition in the ocean (Neelin et al., 1998; Wang, 2018; Zhong, 1990). Post-bomb $\Delta^{14}\text{C}$ records in the Pacific varied spatially in response to ENSO. In the central Pacific, Galapagos coral detected higher $\Delta^{14}\text{C}$ values during El Niño events as a result of the longer retention time of ^{14}C in surface water, decreased strength of upwelling and enhanced air-sea CO_2 exchange (Guilderson and Schrag, 1998). In contrast, it has been suggested that some El Niño events led to the displacement of low- $\Delta^{14}\text{C}$ waters into the southern GBR (southwestern Pacific), which lowered $\Delta^{14}\text{C}$ values at Abraham Reef (Druffel and Griffin, 1993; Druffel and Griffin, 1995). PDO and ENSO have same similar spatial patterns of sea surface temperature and winds, but PDO events occurred on longer decadal time scales (Newman et al., 2016). A phase change in PDO after 1976 was recorded by a coral $\Delta^{14}\text{C}$ record from Ishigaki suggesting the NEC bifurcation latitude may be linked to changes in physical oceanography (Hirabayashi et al., 2017a).

1.3 Trace elements in corals

Porites coral skeleton material is composed of aragonite (CaCO_3), but other trace elements (metals) can also be incorporated. Elemental ratios (element/Ca) in the skeletons of corals are sensitive to environmental changes. During coral growth, trace elements can be incorporated into the coral skeleton through various ways: substitution of dissolved metal ions for cation ion Ca^{2+} or anion ion CO_3^{2-} , trapping in skeletal defects, surface adsorption and combination with

organic tissues (Allison, 1996; Allison and Finch, 2007; Amiel et al., 1973; Barnard et al., 1974; Brown et al., 1991; Fallon et al., 2002; Linn et al., 1990; Saha et al., 2016; Shen and Boyle, 1988; Shen et al., 1991). Major trace elements (B, Mg, Sr, Ba, U) in coral skeletons are well documented as geochemical proxies for the reconstruction of the paleo-environment, such as SST and terrestrial runoff (Armid et al., 2011; Chen et al., 2015a; Correge, 2006; Cuny-Guirriec et al., 2019; D'Oliveo et al., 2018; DeCarlo et al., 2016; Fallon et al., 1999; Fowell et al., 2016; Jiang et al., 2017a; Lewis et al., 2012; Lewis et al., 2018; Lewis et al., 2007; McCulloch et al., 2002; Montagna et al., 2014; Moyer et al., 2012; Raddatz et al., 2013; Ross et al., 2019; Saha et al., 2016, 2018a; Walther et al., 2013; Zinke et al., 2019), while the abundance of other minor trace elements in coral skeletons can be utilized to monitor marine pollution (Ali et al., 2011; Brown et al., 1991; David, 2003; Esslemont et al., 2004; Fallon et al., 2002; Gissi et al., 2019; Guzman and Jarvis, 1996; Howard and Brown, 1984; Inoue et al., 2006; Inoue et al., 2014; Inoue et al., 2004; Lewis et al., 2007; Linn et al., 1990; Saha et al., 2019a; Shen and Boyle, 1988; Tanaka et al., 2013). Individual elements recorded in coral skeletons and their environmental relationship are discussed below.

1.3.1 Coral SST proxies

Elemental ratios (such as Sr/Ca, Mg/Ca, U/Ca, B/Ca, Li/Ca, and Li/Mg) in coral skeletons were found to correlate with sea surface temperature (SST) of the water where the coral grows, resulting in the utilization of these proxies for SST reconstruction in paleoclimate and paleoenvironment studies (Armid et al., 2011; Chen et al., 2015a; Correge, 2006; Cuny-Guirriec et al., 2019; D'Oliveo et al., 2018; DeCarlo et al., 2016; Fallon et al., 1999; Fowell et al., 2016; Montagna et al., 2014; Raddatz et al., 2013; Sadler et al., 2014; Ross et al., 2019; Zinke et al., 2019). The empirical calibration of temperature dependence for coral proxies is established by matching the seasonal variations of geochemical signals with the seasonal variations of instrumental SST. Among the studies exploring SST proxies, Sr/Ca and $\delta^{18}\text{O}$ were

usually considered to be the most robust temperature proxies (Beck et al., 1992; Gagan et al., 2012; McCulloch et al., 1994; McCulloch et al., 1999; Smith et al., 1979). A variety of SST proxies have been summarised below and more details can be found in chapter 5.

Strontium

Sr/Ca has been widely used as a reliable temperature proxy (Beck et al., 1992; Corregge, 2006; DeLong et al., 2013; Gagan et al., 2012; McCulloch et al., 1994; Pfeiffer et al., 2009; Quinn and Sampson, 2002; Schrag, 1999). The partitioning of Sr between seawater and aragonite has been found to be temperature dependent (Gaetani and Cohen, 2006). The Sr/Ca ratios in the coral skeletons are negatively correlated with SST (Alibert and McCulloch, 1997; Corregge, 2006). The Sr/Ca temperature proxy also has some limitations. For example, the temperature dependence of Sr/Ca derived from biogenic aragonites (-0.04 to -0.08 mmol/mol per $^{\circ}\text{C}$) is greater than the temperature dependence derived from abiogenic aragonite (~ -0.04 mmol/mol per $^{\circ}\text{C}$) (Cohen et al., 2002; Gaetani and Cohen, 2006; Gaetani et al., 2011; Smith et al., 1979; Zinke et al., 2019). In addition, the Sr/Ca-SST relationships can also be variable among colonies or sites (D'Olivo et al., 2018; Fallon et al., 2003b; Fowell et al., 2016; Saenger et al., 2008). These disparities are considered to be caused by 'vital effects' during coral biomineralization (DeCarlo et al., 2015; Gaetani and Cohen, 2006; Weber, 1973). Other environmental stresses, such as thermal stress, increased nutrients and decreased light intensity, can also have an impact on the Sr/Ca-SST relationship (Chen et al., 2015a; Marshall and McCulloch, 2002). Even though the intercepts and slopes generated from the Sr/Ca-SST calibrations are site-specific, they are themselves linearly correlated (Figure 1.5). A mathematical explanation is that the different regression lines derived from Sr/Ca-SST calibrations all pass through a 'centroid' (D'Olivo et al., 2018). This relationship has been explored in chapter 5 and has been found to be universal for other temperature proxies such as U/Ca and Li/Mg.

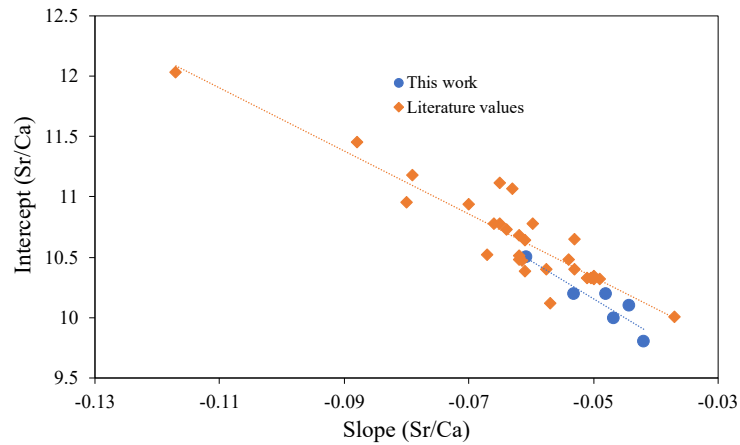


Figure 1.5 Slopes and intercepts derived from the Sr/Ca-SST calibration equations $\text{Sr/Ca}(\text{mmol/mol}) = b + k \times \text{SST}$ for *Porites* corals, where b and k are constants derived from linear regression fitting. b (intercepts) and k (slopes) are linearly correlated. Literature values and the associated references were listed in Table 1 in Sinclair (2015).

Magnesium

Mg^{2+} may not directly substitute for Ca^{2+} in aragonite (Finch and Allison, 2008). The aragonite lattice may be severely distorted by the comparatively small ion radius of Mg^{2+} . Therefore, Mg^{2+} is more likely to be enriched in amorphous calcium carbonate (ACC) or organics (e.g., Case et al., 2010; Sinclair et al., 2006), adsorbed on surface or loosely bound in the coral lattice (e.g., Case et al., 2010). The Mg/Ca ratio in coral has been proposed as a seawater temperature proxy in many studies (Armid et al., 2011; Chave, 1954; Fallon et al., 2003b; Fallon et al., 1999; Hart and Cohen, 1996; Mitsuguchi et al., 1996; Sinclair et al., 1998; Weber, 1974; Wei et al., 2000); however, in addition to seawater temperature, environmental variations (carbonate ion concentrations and possibly salinity), biological effects (microstructural entrapments and defects, skeletal growth rates, etc), and Rayleigh fractionation all have impacts on Mg/Ca incorporation (e.g., Armid et al., 2011; Case et al., 2010; Cross and Cross, 1984; Finch and Allison, 2008; Inoue et al., 2007; Meibom et al., 2004; Mitsuguchi et al., 2003; Reynaud et al., 2007; Sinclair et al., 2006; Watanabe et al., 2001).

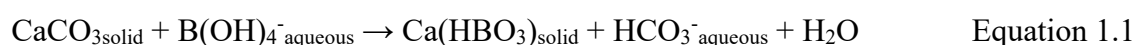
Uranium

U/Ca has been proposed as a temperature proxy in several studies because coral U/Ca ratios were found to be correlated with seawater temperature (Fallon et al., 2003b; Felis et al., 2009; Min et al., 1995; Ourbak et al., 2006; Quinn and Sampson, 2002; Shen and Dunbar, 1995; Sinclair et al., 1998; Wei et al., 2000). However, coral U/Ca ratios were also found to be related to carbonate ion concentration, pH, salinity and growth rate (DeCarlo et al., 2015; Gabitov et al., 2008; Inoue et al., 2011; Ourbak et al., 2006; Raddatz et al., 2014; Shen and Dunbar, 1995); therefore, the factors affecting U incorporation into the coral skeleton remain controversial. Previous studies showed that the highly negatively charged $[\text{UO}_2(\text{CO}_3)_3]^{4-}$ complexes were prevailing in seawater (e.g., Djogic et al., 1986; Kalin et al., 2005), but data from recent experiments revised the uranium speciation, shifting the consensus from $[\text{UO}_2(\text{CO}_3)_3]^{4-}$ to cation-balanced complexes (i.e., $\text{MgUO}_2(\text{CO}_3)_3^{2-}$ and/or $\text{CaUO}_2(\text{CO}_3)_3^{2-}$) (Endrizzi and Rao, 2014) as a result of the significantly higher Ca^{2+} and Mg^{2+} concentrations in seawater. Based on the uranium speciation under seawater conditions, uranium is more likely to be incorporated into coral skeletons by substituting for CO_3^{2-} as an anionic carbonate ion complex instead of Ca^{2+} (Reeder et al., 2000).

Boron

Boron (B) is a conservative element in seawater and has a long residence time (16-20 million years) in the oceans (Lee et al., 2010; Spivack et al., 1993). In seawater, boron has two major species, $\text{B}(\text{OH})_3$ and $\text{B}(\text{OH})_4^-$, which are controlled by the seawater pH. The speciation of boron is not only dependent on pH but also depends on temperature, with a decrease in the ratio of $\text{B}(\text{OH})_4^-$ to $\text{B}(\text{OH})_3$ as temperature increases (Hemming and Hanson, 1992). B/Ca ratios were found to mimic SST variations in a few sites (Fallon et al., 2003b; Fallon et al., 1999). In addition to temperature, other factors affect B/Ca incorporation into aragonite, such as coral growth rate and seawater carbonate chemistry (e.g., Holcomb et al., 2016; Mavromatis et al.,

2015; Wara et al., 2003). Relative to temperature, the B isotope is more of a well-established seawater pH proxy (Chen et al., 2019; Comeau et al., 2017; D'Olivo and McCulloch, 2017). Temperature may have an indirect influence on B isotopes or B concentration by changing B speciation and the calcifying solution. As a result, B/Ca ratios indicate more effectively for $[\text{CO}_3^{2-}]$ than surrounding seawater temperature (Holcomb et al., 2016). The mechanisms that control the B incorporation into coral are somewhat uncertain. A few work have suggested that B is incorporated as an anion in coral aragonite, with $\text{B}(\text{OH})_4^-$ suggested to be the dominant species (Hemming and Hanson, 1992; Hemming et al., 1995; Holcomb et al., 2016; Mavromatis et al., 2015; Yu and Elderfield, 2007):



Lithium

Lithium (Li^+) is conservative and has a quite low concentration in seawater (Huh et al., 1998). A few studies have implied that the potential of coral Li for recording environmental conditions (Correge, 2006; Hathorne et al., 2013; Marriott et al., 2004a). Li in both calcite and aragonite have been found to have a negative correlation with temperature and coral Li/Ca has a larger temperature dependence (5% per degree) than Sr/Ca (0.7% per degree) (Correge, 2006; Hathorne et al., 2013; Marriott et al., 2004a). In addition, Li/Ca in aragonite was found not to be influenced by salinity in a laboratory precipitation experiment (Marriott et al., 2004b). Heterovalent substitution of Li^+ for Ca^{2+} was inferred from the inorganic aragonite experiments because of the charge difference between Ca^{2+} and Li^+ (Marriott et al., 2004a; Okumura and Kitano, 1986). However, this hypothesis needs to be confirmed in corals grown in the field because the ionic size of Li^+ is small. Other processes, such as trapping of Li into defect sites may account for Li^+ incorporation (Amiel et al., 1973; Watanabe et al., 2001). Overall, the mechanisms responsible for the incorporation of Li into coral skeletons are not well understood. Recently, Li/Mg has been proposed to be a promising SST proxy due to the potentially universal

Li/Mg-SST relationship regardless of coral species across a wide range of seawater temperature (Bryan and Marchitto, 2008; Case et al., 2010; D'Olivo et al., 2018; Fowell et al., 2016; Hathorne et al., 2013; Montagna et al., 2014; Raddatz et al., 2013; Zinke et al., 2019). Li/Mg is considered to be mainly affected by Rayleigh fractionation and less affected by vital effects (Cuny-Guirriec et al., 2019) (see chapter 5 for details).

1.3.2 Terrestrial runoff proxies

Barium

Ba²⁺ is thought to be able to substitute for Ca²⁺ ions in the coralline aragonite even with its slightly larger ionic radius (Lea et al., 1989; Shannon, 1976; Zhong and Mucci, 1989). Since the concentration of Ba/Ca in the coral skeletons is in proportion to the seawater Ba concentration, Ba/Ca ratios in aragonitic coral skeletons have been widely used as various environmental proxies (Table 1.1).

The barium (Ba) concentration in seawater is more variable than previously discussed elements (Li, B, Mg, Sr, U), which are more conservative in seawater. Two major sources of seawater Ba are from upwelling of deeper water (Fallon et al., 1999; Lea et al., 1989; Montaggioni et al., 2006; Walther et al., 2013) and from terrestrial runoff (sediment loading and river discharge) (Alibert et al., 2003; Brenner et al., 2017; LaVigne et al., 2016; Lewis et al., 2018; McCulloch et al., 2003; Moyer et al., 2012; Sinclair, 2005b; Sinclair et al., 1998; Sinclair and McCulloch, 2004). Ba rapidly desorbs from particulate matter when freshwater is mixed with high ionic strength seawater by ion-exchange (Carroll et al., 1993; Edmond et al., 1985; Froelich et al., 1985). Estuarine studies suggested that Ba desorption mainly occurred at low salinities (<6‰), and then mixed conservatively at higher salinities (Carroll et al., 1993; Li and Chan, 1979; Sinclair and McCulloch, 2004). The desorption process can significantly increase the total dissolved Ba entering the seawater by 50% or more (Carroll et al., 1993; Li and Chan, 1979).

Coral Ba/Ca ratios remain difficult to interpret. Other than the terrestrial runoff and oceanic upwelling mentioned previously, coral Ba/Ca can also be influenced by temperature (Dietzel et al., 2004; Fallon et al., 2003b; Gaetani and Cohen, 2006; Gonneea et al., 2017; Grove et al., 2012) and biological factors such as surface ocean productivity (Saha et al., 2018b; Sinclair, 2005b). Temperature dependence of Ba/Ca has been suggested to be related to the distribution coefficient and precipitation efficiency (Gaetani and Cohen, 2006; Gonneea et al., 2017). Biotic Ba origins were found to be related to phytoplankton blooms (Saha et al., 2018b; Sinclair, 2005b).

Manganese

Similar to Ba^{2+} , Mn^{2+} in seawater can be proportionally incorporated into coral skeletons by substituting for Ca^{2+} (Alibert et al., 2003; Lewis et al., 2007; Saha et al., 2016; Wyndham et al., 2003). Manganese (Mn) concentration in seawater is affected by riverine manganese (in both dissolved and particulate forms), so coral Mn/Ca ratios have been used as proxies for terrestrial runoff and industrial contamination in a few studies (Chen et al., 2010; Fallon et al., 2002; Inoue et al., 2014; Moyer et al., 2012). However, seawater Mn concentrations are also influenced by climatic variations (Shen et al., 1991; Thompson et al., 2015), upwelling (Shen et al., 1991), aeolian inputs (Alibert et al., 2003), seawater temperature changes (Morris, 1974) and redox cycles initiated by sunlight and mediated by microorganisms (Alibert et al., 2003; Grove et al., 2013; Wyndham et al., 2004). For sampling sites that are away from major exogenous sources, seasonal variations of coral Mn/Ca have been documented which may be related to confounding factors such as redox cycles, temperature dependence or biological productivity (Lewis et al., 2018; Wyndham et al., 2004).

Table 1.1 Selected studies of Ba/Ca ($\mu\text{mol/mol}$) in *Porites* corals as environmental proxies

Baseline	Peak	$\Delta\text{Ba/Ca}$	Proxy	Location	Reference
3	6	3	Upwelling	Wadi Ayn, Oman, Red sea	Tudhope et al. (1996)
5	15	10	Upwelling	Marbat, Oman, Red Sea	Tudhope et al. (1996)
3.9	5.1	1.2	Upwelling	Shirigai Bay, Japan	Fallon et al. (1999)
4	12	8	River discharge	Havannah Island and Pandora Reef, GBR	McCulloch et al. (2003)
4.5	14	9.5	River discharge	Pandora Reef, GBR	Alibert et al. (2003)
3	6	3	River discharge	Davies Reef, GBR	Alibert et al. (2003)
4	15	11	River discharge	Havannah Island, GBR	Wyndham et al. (2004)
4	15	11	River discharge	Pandora Reef, GBR	Wyndham et al. (2004)
4	12	8	River discharge	King Reef, GBR	Sinclair and McCulloch (2004)
4	17	13	River discharge	Pandora Reef, GBR	Sinclair and McCulloch (2004)
4	13	9	Unknown	Cow Island, GBR	Sinclair (2005)
4	12	8	Unknown	Orpheus Island, GBR	Sinclair (2005)
4.3	21	16.7	Upwelling	Amedee Islet, New Caledonia	Montaggioni et al. (2006)
1.3	5.2	3.9	River discharge	Vata Ricaudy Reef, New Caledonia	Montaggioni et al. (2006)
4	50	46	Terrestrial runoff	Kenya	Fleitmann et al. (2007)
4	9.5	5.5	Terrestrial runoff	Kenya	Fleitmann et al. (2007)
4	25	21	Upwelling	New Ireland, Papua New Guinea	Alibert and Kinsley (2008)
3.5	7	3.5	River discharge	Round Top island, GBR	Jupiter et al. (2008)
4	6	2	River discharge	Keswick Island, GBR	Jupiter et al. (2008)
3	8	5	River discharge	Scawfell Island, GBR	Jupiter et al. (2008)
3.4	8	4.6	Sediment input	Kamalo, Molok'a Reef, Hawaii	Prouty et al. (2010)
5.5	10.2	4.7	Sediment input	One Ali'i, Molok'a Reef, Hawaii	Prouty et al. (2010)
2.8	21.6	18.8	Sediment input	Umpipa'a, Molok'a Reef, Hawaii	Prouty et al. (2010)
3	17.8	14.8	Sediment input	Pala'au, Molok'a Reef, Hawaii	Prouty et al. (2010)
6	15	9	Biological	Daya Bay, South China Sea	Chen et al. (2011)
6	15	9	Biological	Daya Bay, South China Sea	Chen et al. (2011)
4	7	3	Terrestrial runoff	Great Keppel, GBR	Saha et al. (2018a)
5	12	7	Terrestrial runoff	Nelly Bay, GBR	Lewis et al., (2018)
4	10	6	Terrestrial runoff	Pandora Reef, GBR	Lewis et al., (2018)
4	8	4	Terrestrial runoff	Havannah Island, GBR	Lewis et al., (2018)
4	6	2	Terrestrial runoff	Pelorus Island, GBR	Lewis et al., (2018)
4	7	3	Terrestrial runoff	Great Keppel, GBR	Saha et al. (2018a)

¹ $\Delta\text{Ba/Ca}$ shows the change in Ba/Ca concentration from baseline to peak values; ² Terrestrial runoff represents coupled impacts from river discharge and sediment input; ³ GBR abbreviates Great Barrier Reef

Yttrium and rare earth elements (REEs)

Rare earth elements (REEs) and yttrium (Y) (REEY hereafter) have great potential to track terrestrial inputs from rivers to coastal waters (Elderfield et al., 1990; Saha et al., 2018a; Saha et al., 2016; Saha et al., 2019b; Sholkovitz and Elderfield, 1988; Sinclair, 2005b; Sinclair and McCulloch, 2004; Wyndham et al., 2004) because these elements have different fractionations in river water and seawater (i.e., relatively enriched in river waters but depleted in seawaters). REEY come from chemical weathering of continental rocks and are subsequently carried by colloidal particles in catchment waterways (Byrne and Liu, 1996; Byrne et al., 1996). Light REEY are more resistant to dissolution and heavy REEY are more enriched in the solution phase (Moller et al., 2003; Sholkovitz and Shen, 1995). After normalization to shale standards, the fractionation of REEY patterns has been documented to effectively trace biogeochemical processes (Fallon et al., 2002; Nguyen et al., 2013; Saha et al., 2019b; Wyndham et al., 2004). REEY were suggested to be incorporated into coral lattices in close proportion to the concentration of the surrounding seawater (Akagi et al., 2004; Saha et al., 2019b; Sholkovitz and Shen, 1995; Wyndham et al., 2003; Wyndham et al., 2004); therefore, coral skeletal REEY are reliable proxies to investigate paleo-discharge in the nearshore marine environment (Saha et al., 2019b).

1.3.3 Pollution and Heavy Metals (Al, Cu, Zn, Fe, Cd, Pb, V)

Heavy metals have been examined in coral skeletons to investigate the impacts of anthropogenic activities in coastal regions (Ali et al., 2011; Brown et al., 1991; David, 2003; Esslemont et al., 2004; Fallon et al., 2002; Gissi et al., 2019; Guzman and Jarvis, 1996; Howard and Brown, 1984; Inoue et al., 2006; Inoue et al., 2014; Inoue et al., 2004; Lewis et al., 2007; Linn et al., 1990; Nguyen et al., 2013; Saha et al., 2019a; Shen and Boyle, 1988; Tanaka et al., 2013). For example, copper (Cu), manganese (Mn) and zinc (Zn) have been investigated to assess the impact of copper mining in Marinduque Island (Philippines) (David, 2003). Zn and

lead (Pb) were found to be elevated in coral skeletons at the time of gold mining and after the cessation of mining in Misima Island (Papua New Guinea) (Fallon et al., 2002). Vanadium (V) has been shown to be a potential proxy of historical oil pollution, catchment clearance and burning activity (Guzman and Jarvis, 1996; Saha et al., 2019a; Tanaka et al., 2013). These pollutant metals (in dissolved or particulate forms) can be incorporated into coral skeletons in various pathways. Dissolved Cu, Zn, Pb and Cd were suggested to be able to directly enter the coral lattice (Howard and Brown, 1984; Linn et al., 1990; Shen and Boyle, 1988). The incorporation mechanism of skeletal Fe remains unclear. Brown et al. (1991) proposed that Fe was deposited on skeletal spines during the tissue retraction and was calcified into skeletons when tissues grow back. Incorporation mechanisms of vanadate anions into the coral structures remains speculative. It is possible but very difficult for vanadate HVO_4^{2-} to directly substitute for CO_3^{2-} as the HVO_4^{2-} is much larger than the CO_3^{2-} (Saha et al., 2019a). Skeletal defects may provide potentially available sites to accommodate the large vanadate anion. These metals can also get into coral skeletons as particulate metals that can be trapped in skeletal cavities, incorporated during calcification, adsorbed onto surfaces or bound with organic tissues (Brown et al., 1991; Fallon et al., 2002; Saha et al., 2016).

1.4 Objective and Chapter Summaries

My PhD project revolves around reconstructing environmental perturbations using long-lived *Porites* corals collected from the South China Sea and the Great Barrier Reef. The South China Sea (SCS) was chosen because ocean circulation in the SCS is complicated and plays important role in climate change and local marine environments. *Porites* corals were also collected from inshore and offshore reefs in the central and southern Great Barrier Reef to investigate the long-term ocean dynamics and to better understand climatic and anthropogenic changes (e.g., variations of past SST, terrestrial runoff and nearshore processes such as dredging and mining activities) using ^{14}C and other coral-based trace element proxies.

Chapter 2 describes the study locations and analytical methods used for this research. The chapter starts by describing coral core collection, sample cleaning, cutting and preparation, and then describes the instruments and instrumental methods used to measure the radiocarbon, stable isotopes and trace elements in the coral skeletons.

Chapter 3 presents a new seawater radiocarbon (^{14}C) record reconstructed from a coral collected from the west side of Palawan Island (eastern South China Sea). This $\Delta^{14}\text{C}$ record spans the years 1947–1981, which covers the pre nuclear to post nuclear test period. The study region has various oceanographic characteristics as revealed by differences in the ^{14}C records of other corals across the Indo-Pacific. This chapter compares the Palawan radiocarbon record to other coral records in the SCS and Western Pacific Ocean and then relates the findings to ocean circulation and climate information. This chapter was published in *Journal of Geophysical Research: Oceans* (Wu and Fallon, 2020).

Chapter 4 presents a sub-annual coral $\Delta^{14}\text{C}$ record from Masthead Island in the southern Great Barrier Reef. The chapter compares the Masthead $\Delta^{14}\text{C}$ record to other published coral records in central and western Pacific, and then discusses variability in air-sea CO_2 exchange and regional ocean dynamics associated with climate change. This chapter has been published in *Radiocarbon* (Wu et al., 2021).

Chapter 5 examines the robustness of the geochemical proxies (Li/Ca, B/Ca, Mg/Ca, Sr/Ca, U/Ca) in reconstructing SST. Normalization of trace elements to Mg (e.g., Li/Mg, B/Mg) was explored and discussed. A universal calibration based on D'Olivo et al. (2018) was reproduced, modified and tested. Geochemical records from this work were also used for long-term SST

reconstruction. This chapter has been published in *Science of the Total Environment* (Wu et al., 2021).

Chapter 6 investigates the impacts of anthropogenic activities on coral reefs in the Southern GBR and provides new insights in the reproducibility of different coral cores from the same site. This work examines the accumulation of trace metals (e.g., Al, Ti, V, Mn, Cu, Zn, Pb) in corals in the Gladstone Harbour region, and links the metal spikes to industrial developments and natural climatic events.

Chapter 7 utilizes corals from the Whitsunday Islands and Gladstone Harbour (Fitzroy River catchment) linking Ba/Ca and luminescence bands to terrestrial runoff. Environmental and biological controls on the incorporation of Ba into coral skeletons were critically discussed. A quantitative reconstruction of terrestrial runoff was explored using coral Ba/Ca ratios in the studied regions.

Chapter 8 is a general conclusion, summarizing the main findings of the thesis and providing suggestions for future research.

Chapter 2: Methods

2.1 Coral collection and cutting

Coral cores were collected underwater with a combination of hydraulic and pneumatic air drills using SCUBA (Figure 2.1). Corals analyzed during the course of this research were collected from massive *Porites* bommies during three field trips: (1) 1-5 May 2017 & 26 August-3 September 2017 in the Gladstone Harbor Region & (2) February 2018 in the Whitsunday-Mackay Island region. Forty-nine coral cores were drilled from 23 coral colonies in the Gladstone region and 29 coral cores were drilled from 15 colonies at seven reef sites in and around the Whitsunday Island group. Most coral cores were collected from shallow water with the depth < 10 m. Coral cores with bio-erosion and bore holes were excluded for further analysis. A selection of coral cores that have been analyzed for geochemical and ^{14}C values is listed in Table 2.1.

Table 2.1 Geographic locations of *Porites* coral cores analysed during the course of this study

Site	Core ID	Latitude (°)	Longitude (°)	Record period
Western Palawan Island [†]	Palawan	+11.48333	119.01667	1947-1981
Rat Island	RAT02A	-23.76353	151.32203	n/a
Rat Island	RAT03A	-23.76353	151.32203	n/a
Rat Island	RAT04A	-23.76353	151.32203	n/a
Seal Rocks	SEA10A	-23.9569	151.4853	1959-2017
Seal Rocks	SEA11A	-23.9569	151.4853	1951-2017
South End Curtis Island	SEN01C	-23.7547	151.31693	1902-2016
Sable Chief Rocks	SAB05A	-23.81428	151.38417	1952-2017
Hummocky Island	HUM02A	-23.40341	151.14711	1902-2017
Hummocky Island	HUM03A	-23.40348	151.14716	1898-2017
Hummocky Island	HUM04B	-23.40239	151.146	1947-2017
Masthead Island	MAS01E	-23.53254	151.74602	1878-2017
Masthead Island	MAS02A	-23.53196	151.74033	1907-2017
Humpy Island	HMP01B	-23.219	150.968	1666-1999
Scawfell Island	SCF81B	-20.86196	149.6024	1956-2017
Shaw Island	SHW82C	-20.4796	149.0691	1947-2017
Whitsunday Island	WHI84A	-20.17447	148.9753	1979-2017
Stonehaven Bay	SNH84A	-20.0894	148.9076	1978-2017
Hook Island	HOO81A	-19.81582	149.1766	1978-2017
South Molle Island	SMI01C	-20.25878	148.8283	1860-1986
South Molle Island	SMI81A	-20.25878	148.8283	1975-2017

[†]Coral slab from the Western Palawan Island (eastern South China Sea) was generously provided by Bob Halley and Ryan Moyer from the USGS. Length to time conversion for RAT corals are not available due to the convoluted geochemical data and growth bands.

Coral slices were prepared at the Australian Institute of Marine Sciences (AIMS) Coral Core Archive using standard techniques (Lough and Barnes, 1990a; Lough and Barnes, 1990b). Core cores were air dried after collection. Dried coral cores were then mounted on aluminium trays using dental casting plaster, and a customized milling machine at AIMS was used to cut three ~6.5 mm thick slices parallel to a growth axis.

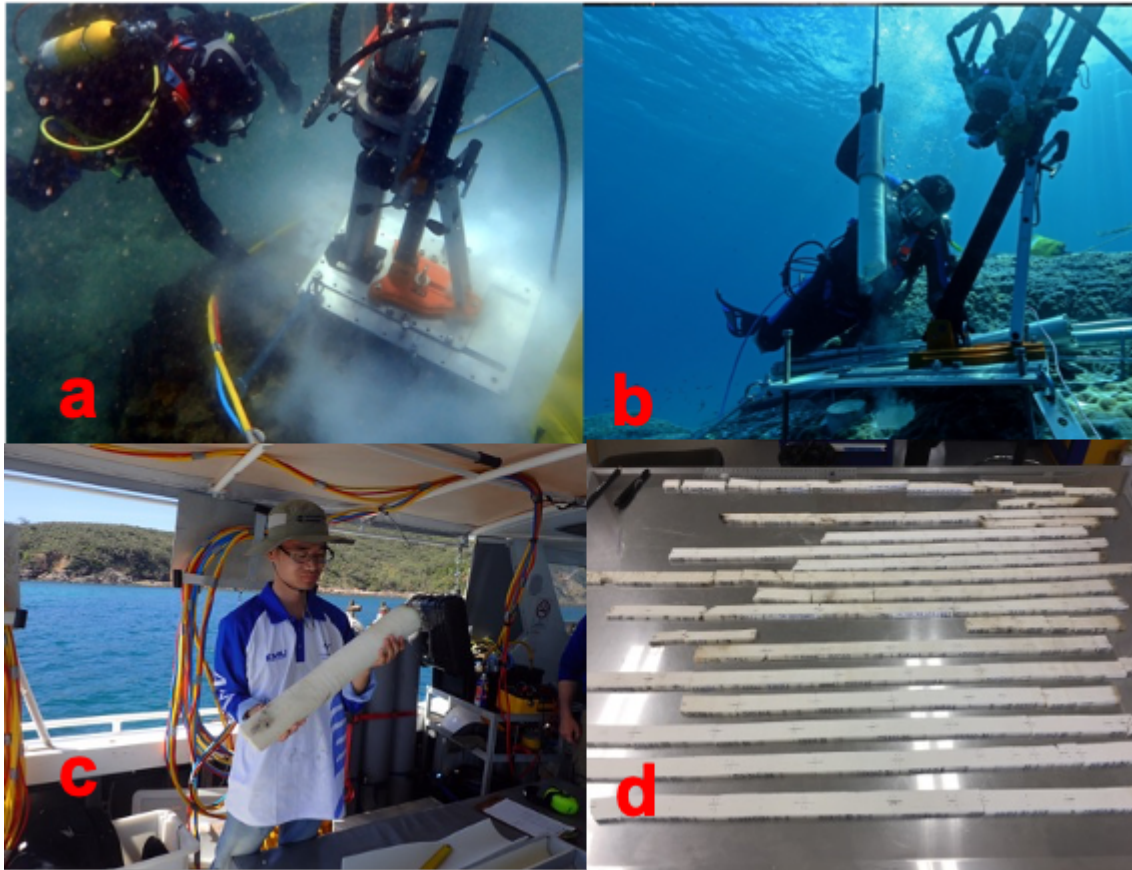


Figure 2.1 (a) and (b) underwater coral drilling (c) extracted coral core and (4) coral pieces for geochemical analysis

2.2 X-ray and ultra-violet analysis

Radiographic measurements (X-ray) and ultra-violet (UV) analysis on coral slices were carried out at AIMS. Coral slices were positioned on a table with a linear step motor for the concurrent measurements of skeletal density and luminescence at 0.254-mm increments. Density measurements used a γ -densitometer equipped with an ^{241}Am source and an optimized beam with 4 mm diameter (Chalker and Barnes, 1990; Lough and Barnes, 1990b). The X-radiograph

negative image was converted to a positive print to show the high-density, low-density and annual skeletal density bands (Figure 2.2). Details about the radiation source, counting equipment, density standards and the optimization can be found in Lough and Barnes (1990b). Luminescent lines were obtained by moving coral slices under UV light in a darkened room and recording the amount of visible light returned from the surface of the slice in the meantime (Figure 2.2) (Barnes et al., 2003; Lough et al., 2002).

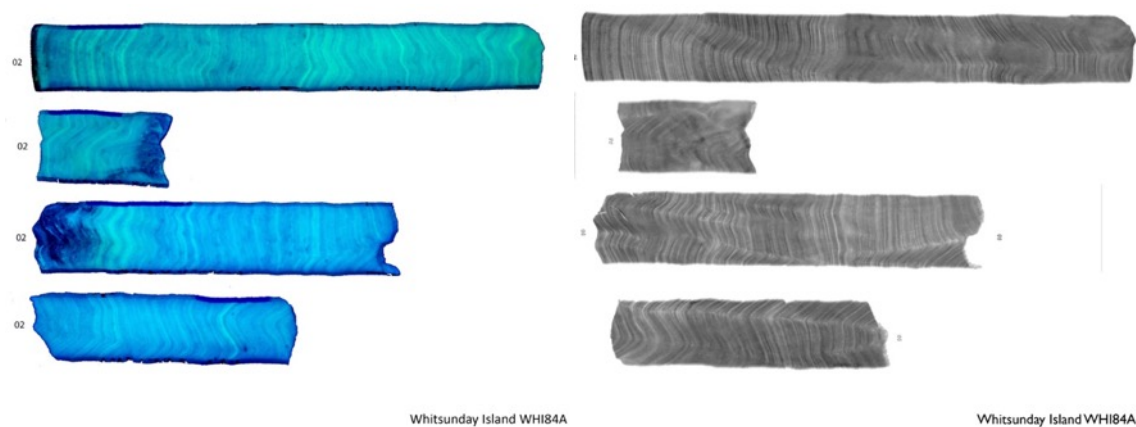


Figure 2.2 An example of X-ray positive print (left) and digitally enhanced photographs of luminescence (right) under ultra-violet light for Whitsunday Island (WHI84A). X-ray and luminescent images from other sites can be found in AIMS public publications (Cantin et al., 2018, 2019a, 2019b; Lough et al., 2020). The collection of corals is a group effort. Yang Wu assisted the coral collection in 2017 and was involved in the initial labwork to pre-treat the corals for geochemical study.

2.3 Isotope analysis

2.3.1 Sample preparation for ^{14}C and stable isotopes (^{13}C , ^{18}O)

Spatially high-resolution sampling was achieved by using an inhouse built micromill at the Radiocarbon Lab (Figure 2.3). The Micromill sampler is equipped with software designed by the RSES workshop which is able to pre-set the drilling transect and control other drilling parameters such as speed, width, depth and increments. Sample powders were drilled following the main growth axis of coral slabs (Alibert and McCulloch, 1997; DeLong et al., 2007; DeLong et al., 2013). The sampling increment was set to be 1.0 mm with the depth and width being 2.5 mm and 2 mm respectively. This sampling resolution roughly corresponds to 10 samples per year. Generated sample powders were deposited into 5 ml centrifuge tubes under vacuum. Any

residues were purged away to avoid cross-contamination. For radiocarbon analysis, approximately 5 mg of coral powders was weighed and loaded into 10 ml glass Vacutainer™ tubes. These tubes were then sealed and evacuated to $\sim 3 \times 10^{-3}$ Torr. Subsequently, 0.3 ml 85% orthophosphoric acid was injected via a gas tight syringe into the tubes. The acid reacted with CaCO_3 for ~ 2 hours at a temperature of 80°C . Generated CO_2 was cryogenically purified using dry ice and ethanol, the amount of CO_2 quantified and transferred using liquid nitrogen to a clean and baked $6 \times 50\text{mm}$ glass graphitization tube. Each glass tube was loaded with excess ($\sim 2.1 \times$) $\text{H}_2 : \text{CO}_2$ at 560°C using reduced iron as a catalyst (Vogel et al., 1984). Graphite samples were pressed and then measured by Single-Stage AMS at the Radiocarbon Laboratory, Australian National University for $^{14}\text{C}/^{12}\text{C}$, $^{14}\text{C}/^{13}\text{C}$, and $^{13}\text{C}/^{12}\text{C}$ ratios (Fallon et al., 2010). Age-corrected $\Delta^{14}\text{C}$ were reported for known-age geochemical samples (Stuiver & Polach, 1977). For stable isotope measurements, 1 mg sample powders were loaded into 3ml Exetainer™ vials. These vials were flushed with helium to remove inside air. 0.2ml $>100\%$ H_3PO_4 was then added to the vials to acidify carbonate powders. The acid hydrolysis was undertaken at 60°C for 4 hours. The resulting CO_2 was analysed for $^{13}\text{C}/^{12}\text{C}$ and $^{18}\text{O}/^{16}\text{O}$ on a SERCON 20-22 IRMS and carbonate device. Correction of stable isotope data were performed for aragonite due to acid-alpha fractionation (Kim et al., 2007). Stable isotope data are reported in delta notation relative to V-PeeDee Belemnite (Coplen, 1994; Coplen et al., 2006).

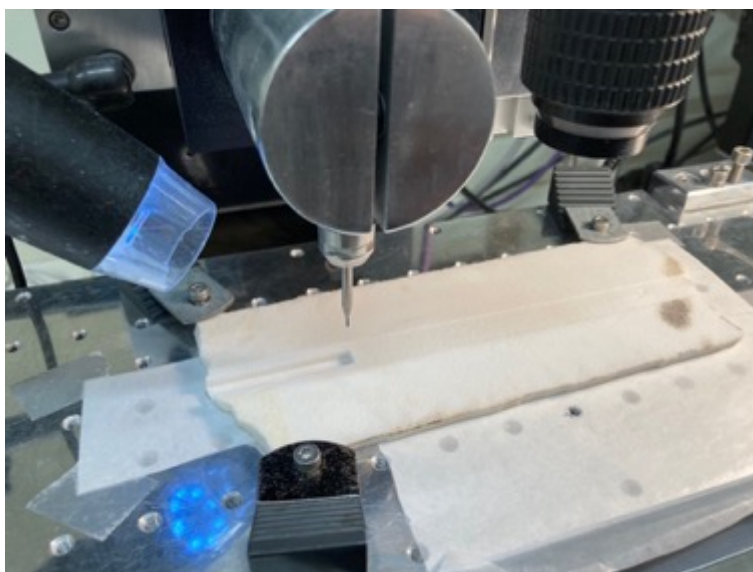


Figure 2.3 A typical set up to drill ^{14}C and stable isotope samples using the in-house Micromill

2.3.2 Accelerator Mass Spectrometer theory

A Single Stage Accelerator Mass Spectrometer (SSAMS) from National Electrostatics Corporation housed at the Research school of Earth Sciences, ANU was used to analyse $\Delta^{14}\text{C}$. The AMS consists of six major parts, starting with a caesium sputter ion source, low energy mass separation, accelerator (molecule dissociator), high energy mass spectrometer magnet, Faraday cups for stable ^{12}C , ^{13}C , and silicon barrier detector for ^{14}C atom counting. Briefly, negative ions are formed by the interaction of caesium ions with the iron graphite mixture during the first stage to discriminate ^{14}C from nitrogen. Subsequently, $^{12}\text{CH}_2$ and ^{13}CH from the negative ion beam will become dissociated during electron stripping to the C^{1+} charge state. Clean ^{14}C , ^{13}C and ^{12}C ion beams are then separated by mass. While Faraday cups measure the currents of ^{13}C and ^{12}C , ^{14}C atoms are collected and counted by a silicon barrier detector.

Although there are fifteen known isotopes for carbon, the most three common isotopes are ^{12}C , ^{13}C and the radioisotope ^{14}C which has a half-life of 5,730 years (Godwin, 1962; Johnson, 1965). Stable isotopic ratios of carbon are reported using a delta value. The standard for stable isotopes is a limestone called Pee Dee Belemnite (or PDB) originating from South Carolina. Currently,

other carbonates with a known and unchanging ^{13}C to ^{12}C ratio are used as a standard similar to PDB because PDB is no longer available.

2.3.3 $\Delta^{14}\text{C}$ calculation from AMS data

The first step to determine $\Delta^{14}\text{C}$ is a measure for sample $\delta^{13}\text{C}$ for a sample which is related to ratio of ^{13}C to ^{12}C . $\delta^{13}\text{C}$ can be calculated using the following equation:

$$\delta^{13}\text{C} = (R_S/R_{\text{VPDB}} - 1) * 1000,$$

where R stands for ratio, S stand for sample, VPDB stand for Vienna Pee Dee Belemnite, $R_S = ^{13}\text{C}/^{12}\text{C}$ of sample, and $R_{\text{VPDB}} = ^{13}\text{C}/^{12}\text{C}$ of standard.

Then fractionation is normalized/corrected through the following equations:

$$A_{\text{ON}} = 0.95 A_{\text{OX}} * 0.981^2 / (1 + \delta^{13}\text{C}_{\text{OX}}/1000)^2, \text{ normalized to } -19\text{‰ with regard to PDB};$$

$$A_{\text{SN}} = A_S * 0.975^2 / (1 + \delta^{13}\text{C}_S/1000)^2, \text{ normalized to } -25\text{‰ with regard to PDB},$$

For traditional methods, A_{OX} is the activity in counts per minute (cpm) of the modern standard; A_S is the equivalent cpm for the sample (Stuiver and Robinson, 1974, Stuiver and Polach, 1977).

For AMS, A_{OX} is based on the $^{14}\text{C}/^{12}\text{C}$ ratio of the standard and A_S is based on $^{14}\text{C}/^{12}\text{C}$ ratio of the unknown samples. Radiocarbon measurements were reported as fraction modern (F_m $^{14}\text{C} = A_{\text{SN}}/A_{\text{ON}}$) using measured $\delta^{13}\text{C}$. Radiocarbon age and $\Delta^{14}\text{C}$ can be calculated as following:

Radiocarbon age = $-8267 * \ln(F_m^{14}\text{C})$ years, where 8267 represents the mean lifetime of ^{14}C (8033 in Stuiver and Polach, 1977), and $\Delta^{14}\text{C} = (F_m * e^{\lambda(y-1950)} - 1) * 1000\text{‰}$, where $\lambda = 1/8267$ year.

2.4 LA-ICP-MS

Laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) at the Research School of Earth Sciences (RSES) was used to measure the abundance of the ‘major’ trace elements (^{11}B , ^{24}Mg , ^{84}Sr , ^{86}Sr , ^{137}Ba and ^{238}U) and ‘minor’ trace elements (^7Li , ^{27}Al , ^{47}Ti , ^{51}V , ^{55}Mn , ^{57}Fe , ^{60}Ni , ^{63}Cu , ^{66}Zn , ^{75}As , ^{89}Y , ^{118}Sn , ^{139}La , ^{140}Ce , ^{206}Pb , ^{207}Pb , ^{208}Pb) in corals. This

technique has been applied to a few coral studies and has provided relatively fast and high spatial resolution analysis while maintaining high accuracy and precision (Alibert et al., 2003; Fallon et al., 1999; Hathorne et al., 2011; Jupiter et al., 2008; Lewis et al., 2012; Lewis et al., 2018; Lewis et al., 2007; Sinclair et al., 1998; Wyndham et al., 2003). Depending on the selection of spot size, daily to weekly resolution environmental information can be resolved.

2.4.1 Sample preparation for LA-ICPMS

Coral slabs were sliced at AIMS (see section 2.1), and these slabs were then cut into ~95 x 25 mm pieces to match the size of laser sample (Figure 2.4). Skeletal material analysed is continuous (see chapter 5 for the cutting). Coral slabs for geochemical analysis were cleaned following standard procedures, similar to previous studies (Alibert and McCulloch, 1997; Fallon et al., 1999; Hathorne et al., 2011; Lewis et al., 2012; Lewis et al., 2007; Ramos et al., 2019b; Sayani et al., 2019; Watanabe et al., 2020; Wyndham et al., 2004). Coral pieces were first put in an ultrasonic bath with 18 Ω Milli-Q water for 30 mins to remove loose-bound materials and dirt from cutting. Both sides of the coral pieces were then cleaned 3 times using an ultrasonic probe to remove other debris inside the coral pieces. Cleaned coral pieces were placed on aluminium foils and oven-dried at 40 °C for a week before analysis. Plastic gloves were always worn to handle the samples to avoid contaminations. Optimal sampling tracks were selected along the main axis of growth based on X-ray images while avoiding problematic areas which have been suggested to cause the bias of geochemical signatures (Alibert and Kinsley, 2008; Alibert and McCulloch, 1997; DeLong et al., 2013). Fiducial marks were used to determine the laser tracks and facilitate the LA-ICPMS analysis.

2.4.2 LA-ICP-MS analysis

Analytical methods were similar to previous studies (Alibert et al., 2003; Fallon et al., 1999; Jupiter et al., 2008; Lewis et al., 2012; Lewis et al., 2018; Lewis et al., 2007; Sinclair et al., 1998; Wyndham et al., 2003). For each set up, two coral pieces were mounted in the sample

holder (Figure 2.4). The sample holder was inserted into a sealed aluminium chamber beneath the laser beam. The chamber is equipped with a DC motor which adjusts and maintains a constant scan speed. A 193 nm HelEx ArF MkII excimer laser was utilized to ablate coral samples. The ablation occurred under a helium atmosphere. The ablated materials in the chamber were purged by helium which was designed to improve the efficiency of sample removal and reduce the number of materials deposited on sample surfaces (Eggins et al., 1998; Sinclair et al., 1998). Before entering the ICP-MS, sample and gas mixture passes through a smoothing manifold which is designed to reduce signal fluctuations. The mixture is split into 8 streams when entering the manifold and recombines at the exit of manifold. Each stream has different residence time in the manifold. Then a Varian 820 single collector ICP-MS and later on a quadrupole ICP-MS (iCAP RQ) were used to detect the concentrations of samples sent from laser chamber. The standard operating conditions for laser cell and ICP-MS are given in Table 2.2. The ICP-MS was tuned using the NIST612 glass standard every morning before starting analysis to optimise sensitivity across the analyte range while keeping $\text{ThO}^+/\text{Th}^+ < 0.5\%$. The tuning conditions consist of: laser pulse repetition rate of 5Hz; spot size = 50 μm ; laser fluence > 10 J/cm^2 ; laser scan speed = 10 $\mu\text{m}/\text{s}$. The entire sampling routine is listed in Table 2.3. Detailed sampling procedures can be found in chapter 5. The slit size is set as a compromise between the sample resolution and the amount of material ablated. Data were averaged over 10 points resulting in each new data point corresponding to a resolution of $\sim 0.57\text{mm}$. The NIST SRM 612/614 glass standards (Horn et al., 1997; Pearce et al., 1997), which contain 61 elements, were utilized for ‘minor’ trace element calibration. Davies Reef coral standard from Great Barrier Reef (GBR) was utilized for ‘major’ trace element calibration as noted above (Fallon et al., 1999; Fallon et al., 2002; Lewis et al., 2018; Sinclair et al., 1998).

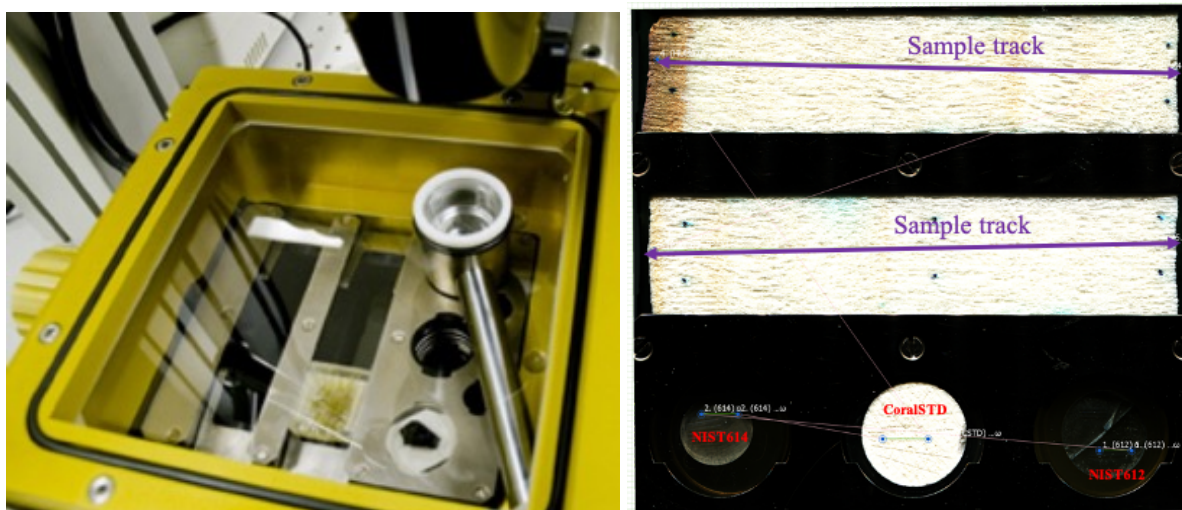


Figure 2.4 Laser ablation ICP-MS sampling unit (left), and samples and standards (NIST612, NIST614, Davies coral standard) in laser holder (right).

Table 2.2 The standard operation conditions for LA-ICP-MS

Equipment/parameter	Running condition
<i>Laser</i>	Lambda Physik LPF Pro 202
Gas Mix	ArF
Wavelength	193 nm
Helium flow rate	500 sccm
Laser Pulse rate	5 Hz (sampling) 10 Hz (cleaning)
Spot size	100*500 μm (sampling) 200*600 μm (cleaning)
High Voltage	10-20 kV
Scan speed	100 $\mu\text{m/s}$ (sampling) 200 $\mu\text{m/s}$ (cleaning)
<i>ICP-MS</i>	Varian 820 and iCAP RQ
Cool gas flow rate	13-14 l/min
Auxiliary gas flow rate	0.5-1 l/min
Nebulizer Ar flow rate	~1 l/min
Detector Mode	Calibrated mode (analogue and pulse counting)
Isotope dwell time	Varian 820: 20 ms dwell time iCap-RQ: 20 ms dwell time, 1 channel per element, 0.1 u spacing

Table 2.3 Summary of LA-ICP-MS procedures

Routine procedure to perform the LA-ICP-MS analysis	
1.	Clean laser cell, purge all lines, check cone and pre-condition ICP-MS
2.	Tune ICP-MS with NIST612: spot size 50 x 50 μm at 5Hz
3.	Pre-ablate coral samples to clean surface: spot size 200 x 600 μm at 10 Hz
4.	Wait for background to be stable and then collect ~200 s of background counts (laser off)
5.	Collect ~ 120 s of data from NIST 614 standard (laser on): spot size 100 x 500 μm at 5 Hz
6.	Collect ~ 120 s of data from NIST 612 standard (laser on): spot size 100 x 500 μm at 5 Hz
7.	Collect ~ 120 s of data from Davies Reef coral standard (laser on): spot size 100 x 500 μm at 5 Hz
8.	Collect data from coral samples (laser on): spot size 100 x 500 μm at 5 Hz:
9.	Repeat the procedures from 5-7 in a reversed order

2.4.3 Laser data processing

During each laser scanning, sample tracks were bracketed by NIST612, NIST614 and Davies coral standards. Data processing can be summarized as follows (1) signal de-spiking (removal of outliers), (2) background subtraction (measured with laser-off at the beginning and in the end), and (3) normalisation to internal standard and calibration to NIST glass standards and Davies coral standard including drift correction. The Python package (*LAtools*) was used to process the LA-ICP-MS data in this work (Branson et al., 2019). Python codes can be found in <https://latoools.readthedocs.io/en/latest/users/intro.html>. Detailed data processing steps from this approach are described below:

1. Raw data were imported to the program and then the data file was split according to laser sample orders. A regular sample list includes 8 sections: 'NIST614', 'NIST612', 'CoralSTD', 'Sample-A', 'Sample-B', 'CoralSTD', 'NIST612', 'NIST614' (Figure 2.5).
2. De-spiking was applied to remove outliers or instrumental artefacts which are physically unrealistic low or high values at certain time points. *LAtools* have two available de-spiking methods: `expdecay_despiker` to remove low outliers and `noise_despiker` to remove high outliers (Figure 2.6).

3. Data separation can be done by ‘auto-range’ function to identify the range of sample signals (laser-on) and background signals (laser-off) (Figures 2.6).
4. After identifying the signal and background, sample signals were background- corrected by first calculating the background underlying the signal regions and then subtracted the background from the sample signal. Background calculation has two choices of algorithms: `bkg_calc_interpld` and `bkg_calc_weightedmean` (Figure 2.7).
5. All isotopes were normalized to the internal standard, ^{43}Ca , and the resulting ratios were calibrated using the calibration curves based on the measurement of standards (Figure 2.8).

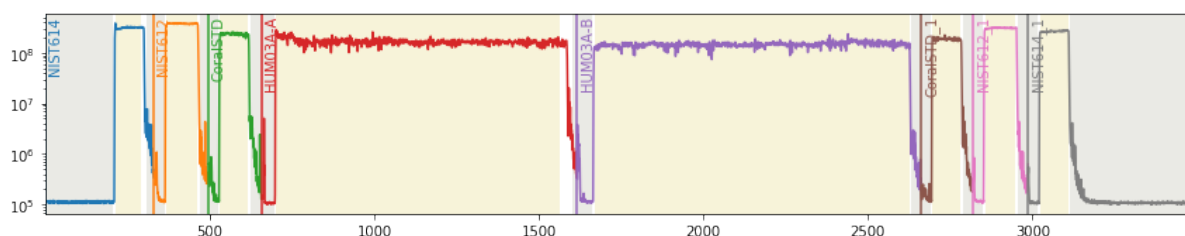


Figure 2.5 An example of LA-ICP-MS time resolved data (counts/s) showing components of typical coral analysis produced by *LAtools* ‘data split’ command. Gray regions are background during laser-off and yellow regions are samples and standards during laser on. Samples (e.g., HUM03A in the plot) are bracketed by standards (NIST614, NIST612 and Davies coral standard) and backgrounds.

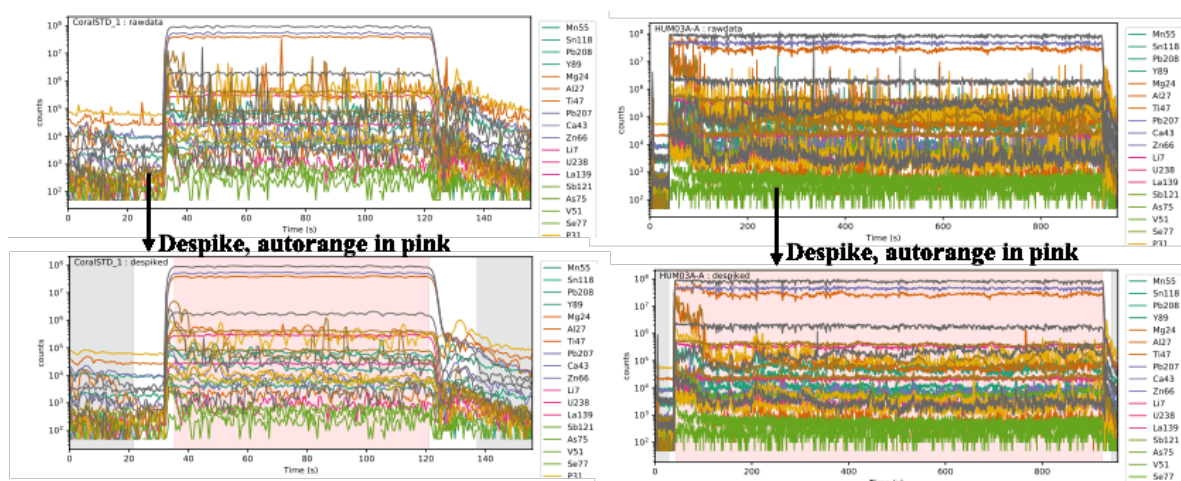


Figure 2.6 LA-ICP-MS time resolved data (counts/s) of coral standard and sample HUM03A before and after de-spiking produced by *LAtools* ‘despike’ command.

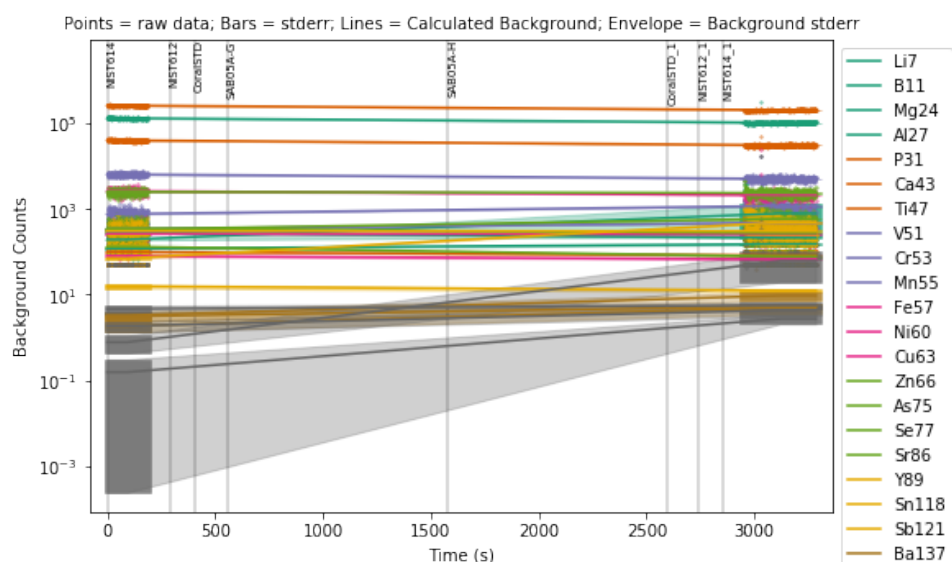


Figure 2.7 An example of background linear interpolation by *LAtools*.

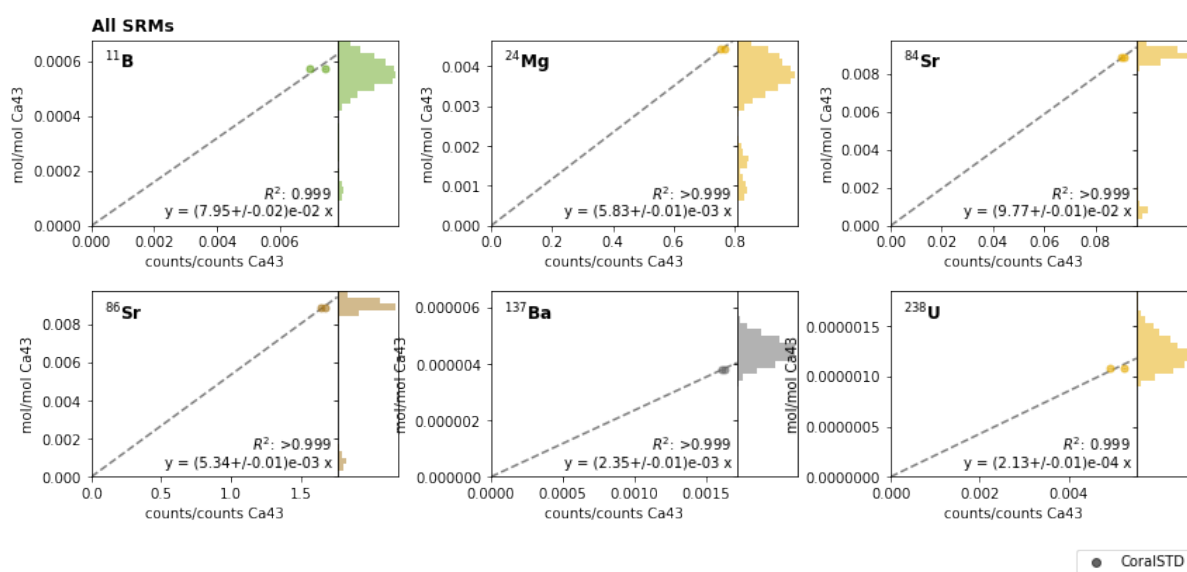


Figure 2.8 Calibration curves for ‘major’ trace elements using Davies coral standard.

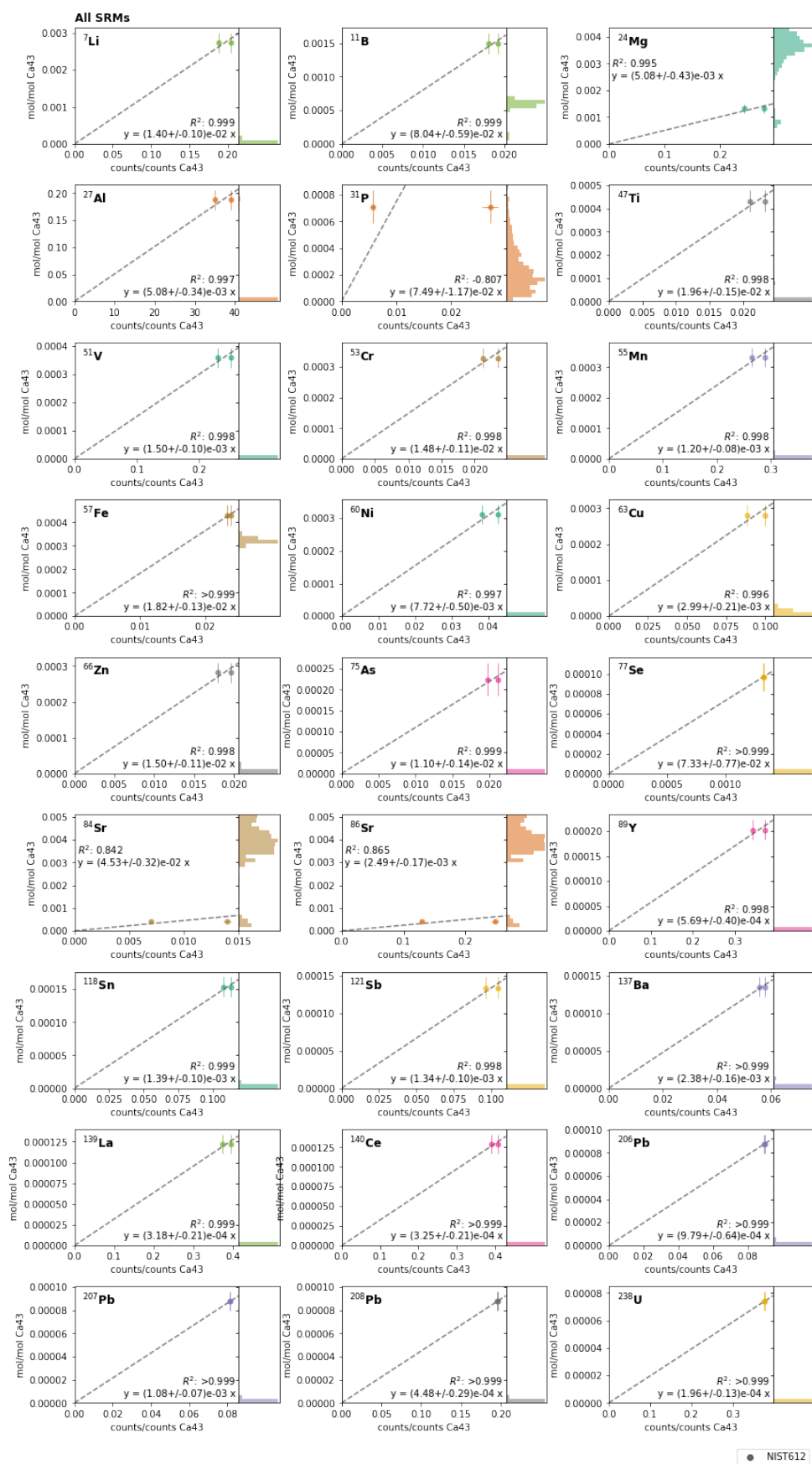


Figure 2.9 Calibration curves for ‘minor’ trace elements using NIST612 standard, with validation from NIST614 standard.

2.4.4 Analytical Uncertainty

The major component of the analytical uncertainty comes from the heterogeneity of the standards, and two minor components come from the counting statistics and the calibration of the standards. The overall uncertainty can be estimated from the following equation which combines these errors:

$$\sigma_{uncert} = \sqrt{\sigma_{count}^2 + \sigma_{calib}^2 + \sigma_{hetero}^2}$$

where σ_{uncert} is the overall uncertainty; σ_{count} is the standard deviation of the counting statistics estimated from the counts and dwell time; σ_{calib} is the standard deviation of the calibrations on the standard; σ_{hetero} is the standard deviation of ~120s scan on the standards.

The combined percentage standard deviation (uncertainty) and the limit of detection for element/calcium ratios are presented in Table 2.4. The overall uncertainty for the ‘major’ trace elements is 3.1% for B/Ca, 3.3% for Mg/Ca, 1.9% for Sr/Ca, 4.2% for Ba/Ca, and 4.6% for U/Ca. This aligns within the uncertainty obtained from other coral studies using LA-ICPMS technique (Fallon et al., 2003b; Fallon et al., 2002; Hathorne et al., 2011; Kawakubo et al., 2014; Prouty et al., 2010; Sinclair et al., 1998). The typical detection limits based on three times the standard deviation of blank are well below the concentrations of ‘major’ and ‘minor’ trace elements in corals. The low detection limits reflect high sensitivity and stable background counts during LA-ICP-MS analysis. Also, most elemental signals in NIST614, NIST612 and Davies coral standard were clearly resolved above background signals (Table 2.4).

2.4.5 Reproducibility

NIST614 standard has been measured as an unknown ‘sample’ and calibrated using NIST612 to test the long-term reproducibility. This process showed the measured trace element values of NIST614 agreed well with their accepted values and maintained a long-term stability (Table

2.4, Figure 2.10). Replicate tracks were also analysed on selected coral pieces to test the reproducibility of trace element records, especially when abrupt shifts in baseline values were noticed. The reproducibility from replicate tracks was quite high, showing mostly identical results (Figure 2.9). In general, the reproducibility across all ‘major’ trace elements was higher than the reproducibility for ‘minor’ trace elements. The slightly larger uncertainty for the ‘minor’ trace elements could result from the misalignment of sampling tracks, the complicated incorporation mechanisms for ‘minor’ trace elements and the low concentration of these ‘minor’ trace elements corals (Fallon et al., 2002) (see chapter 6).

Corals are often affected by diagenesis as a robust paleoenvironmental archive. The appropriate evaluation of diagenesis is important for the accurate reconstruction of the paleoenvironment. Diagenesis of coral reefs includes bioerosion, cementation, encrustation etc (Enmar et al., 2000). The diagenesis process can affect the original environmental information recorded by coral reefs. For example, even traces of cements for Sr and Mg can make major anomalies of geochemical signals. Therefore, attention should be made to understand the degree of influence of diagenesis which may restore the paleoenvironmental change process (Friedman et al., 1974; Ginsburg et al., 1967; Schroeder & Purser 1986; Webb et al., 2009, 2016).

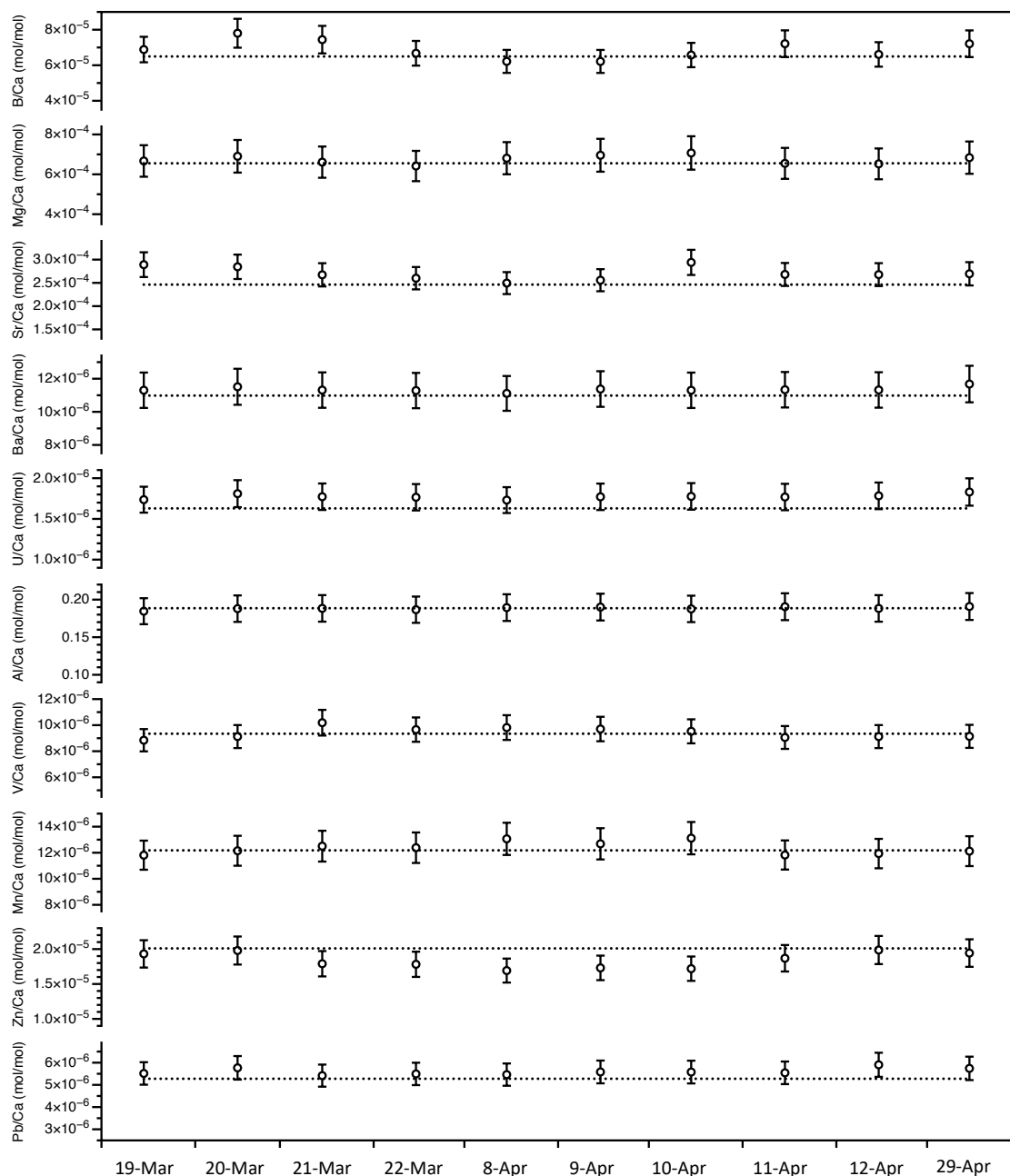


Figure 2.10 Multiple daily measurements of the NIST614 calibrated by NIST612 in 2019. Error bars are the analytical uncertainty. Dashed lines are the respective accepted values.

Table 2.4 Comparisons of overall uncertainty, limit of detection (LoD) and signal over background (bkg) counts for trace element in (a) Davies coral standard (CSTD) and (b) NIST612 and NIST614 obtained by LA-ICP-MS. Concentration values of trace elements are presented as element/Ca ratio (mol/mol). Note: Limit of detection was calculated using the equation: $LoD\ of\ metal\ \left(\frac{mol}{mol}\right) = \frac{3 * blank\ standard\ deviations\ (counts)}{Metal\ counts\ in\ Standards\ (counts)} * Metal\ concentration\ in\ Standard\ \left(\frac{mol}{mol}\right)$

(a)	Element/Ca	B/Ca	Mg/Ca	Sr/Ca	Ba/Ca	U/Ca
	Isotope	11	24	86	137	238
	Accepted value (mol/mol)	5.7E-04	4.4E-03	8.9E-03	3.8E-06	1.1E-06
	StDev (mol/mol)	1.8E-05	1.5E-04	1.7E-04	1.6E-07	4.9E-08
	Uncertainty (%)	3.1	3.3	1.9	4.2	4.6
	Lod	6.2E-07	5.2E-08	4.4E-06	1.4E-07	7.1E-11
	Signal/bkg	774	107337	38209	11363	765444
Davies Coral Standard (CSTD)	Measured value using NIST612 (mol/mol)	5.9E-04	4.4E-03	5.6E-03	3.7E-06	9.4E-07

(b)	Element/Ca	Li/Ca	B/Ca	Mg/Ca	Al/Ca	Ti/Ca*	V/Ca	Mn/Ca	Cu/Ca*	Zn/Ca	As/Ca	Sr/Ca	Y/Ca	Sn/Ca	Ba/Ca	La/Ca	Ce/Ca	Pb/Ca	U/Ca
	Isotope	7	11	24	27	47	51	55	63	66	75	86	89	118	137	139	140	208	238
NIST 612	Accepted value (mol/mol)	2.7E-03	1.5E-03	1.3E-03	1.9E-01	4.3E-04	3.6E-04	3.3E-04	2.8E-04	2.8E-04	2.2E-04	4.2E-04	2.0E-04	1.5E-04	1.3E-04	1.2E-04	1.3E-04	8.8E-05	7.4E-05
	StDev (mol/mol)	9.6E-05	4.3E-05	6.4E-05	3.3E-03	8.4E-06	6.8E-06	6.2E-06	2.3E-05	1.1E-05	7.8E-06	6.3E-05	4.9E-06	3.3E-06	3.2E-06	2.7E-06	2.6E-06	3.0E-06	3.5E-06
	Uncertainty (%)	3.5	2.9	4.9	1.8	1.9	1.9	1.9	8.3	3.8	3.5	14.9	2.4	2.1	2.3	2.2	2.0	3.4	4.8
	LoD	6.9E-07	4.7E-06	3.6E-07	8.5E-06	1.1E-06	2.0E-07	3.4E-07	1.3E-07	1.7E-06	5.2E-07	3.7E-07	1.2E-08	1.1E-07	1.8E-08	2.8E-09	3.7E-09	3.8E-09	4.4E-10
	Signal/bkg	6946	269	4620	1681	262	839	178	1459	66	369	459	47931	992	56227	306566	201667	141648	8432755
NIST 614	Accepted value (mol/mol)	1.1E-04	6.5E-05	6.6E-04	1.9E-01	3.6E-05	9.3E-06	1.2E-05	1.0E-05	2.0E-05	4.7E-06	2.5E-04	4.2E-06	6.7E-06	1.1E-05	2.4E-06	2.7E-06	5.3E-06	1.6E-06
	StDev (mol/mol)	4.5E-06	1.0E-05	3.4E-05	2.8E-03	4.3E-06	3.9E-07	3.7E-07	9.4E-07	1.5E-06	6.7E-07	4.7E-05	1.4E-07	3.0E-07	5.0E-07	8.1E-08	9.8E-08	1.7E-07	7.0E-08
	Uncertainty (%)	3.9	16.0	5.1	1.5	5.9	3.9	2.9	4.8	7.5	14.1	20.2	3.5	4.6	4.5	3.2	3.4	3.3	4.2
	LoD	7.9E-07	2.3E-06	3.1E-07	1.0E-05	3.6E-07	1.8E-07	2.8E-07	5.5E-08	1.5E-06	4.9E-07	2.2E-07	1.3E-08	6.7E-08	2.0E-08	2.8E-09	3.9E-09	4.5E-09	5.3E-10
	Signal/bkg	256	23	2673	1427	67	24	8	122	5	8	443	947	68	4086	5971	4056	7200	156478
	Measured value using NIST612 (mol/mol)	1.2E-04	6.5E-05	6.6E-04	1.9E-01	7.2E-05	9.9E-06	1.3E-05	2.0E-05	2.0E-05	4.8E-06	2.3E-04	4.1E-06	6.5E-06	1.1E-05	2.5E-06	2.8E-06	5.2E-06	1.6E-06

*Measured values for Ti/Ca and Cu/Ca of NIST614 calibrated from NIST612 are consistently higher than the NIST614 accepted values which suggest some interferences during ICP-MS analysis

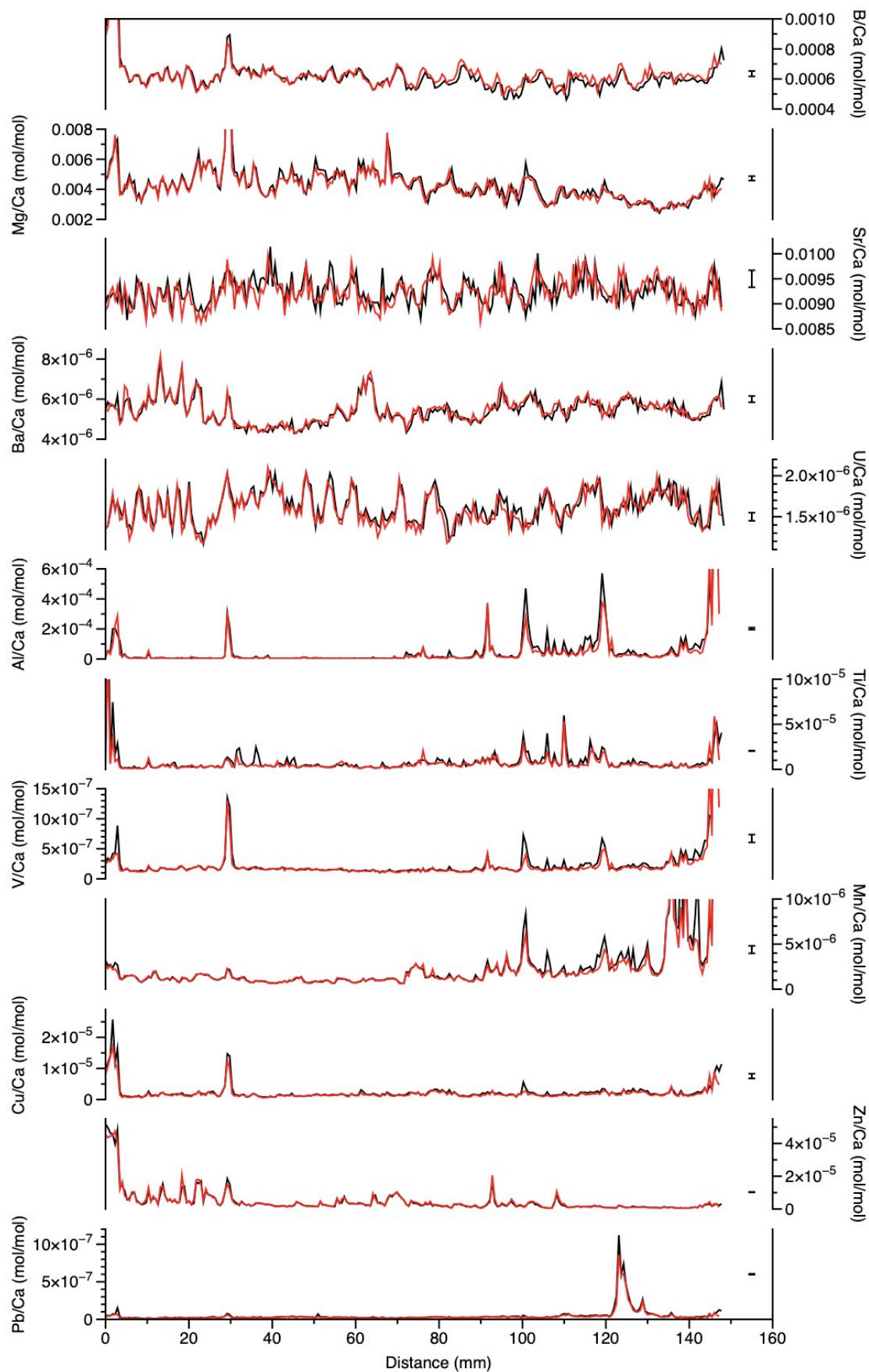


Figure 2.11 Comparison of elemental ratios (B/Ca, Mg/Ca, Sr/Ca, Ba/Ca, U/Ca, Al/Ca, Ti/Ca, V/Ca, Mn/Ca, Cu/Ca, Zn/Ca, Pb/Ca, Y/Ca) for RAT04A on replicate tracks.

2.5 Developing coral age model

To better compare and interpret temporal variations, coral isotope ratios and elemental ratios were translated from length (distance from core top) to time. Preliminary chronologies were constructed from counting annual high-low density bands and the markers of prominent luminescent lines (Figure 2.2). Then the age model was fine-tuned by comparing seasonal cycles of temperature proxies (e.g., U/Ca, see chapter 5) to the seasonal SST record (Figure 2.12). Sharp peaks of temperature proxies such as U/Ca and Li/Mg occurred in winters and broad wide peaks occurred in summers. A delicate relationship between elemental ratios and SST was constructed by pinning the U/Ca maxima to the seawater temperature minima, and by matching U/Ca minima to the seawater temperature maxima where appropriate (D'Olive et al., 2018; Fallon et al., 2003b; Kawakubo et al., 2017). Assuming coral growth to be linear between marker points, the re-sampling of geochemical data was made by linear interpolation using Analyseries 2.0.8 (Paillard et al., 1996). Weekly or monthly data were subsequently computed using Analyseries depending on the different needs of calibration and presentation.

Although linear interpolation between marker points has been widely used to establish time series, it should be noted that the growth of coral skeletons does not have simple linear extension and has seasonal changes. The inappropriate time-averaging of geochemical time series could lead to some data 'noise' (Nothdurft and Webb, 2007). Besides, the biosmoothing within the living coral tissue layer may attenuate geochemical signals (Gagan et al., 2012) even though the attenuation is normally <10% for most *Porites* corals (Alibert and McCulloch, 1997; Gagan et al., 1998). The tissue smoothing may also cause an offset up to 1.5 months to the seasonal signal (Barnes et al., 1995). Therefore, skeletal microstructure needs to be considered to interpret the time-series of coral geochemistry.

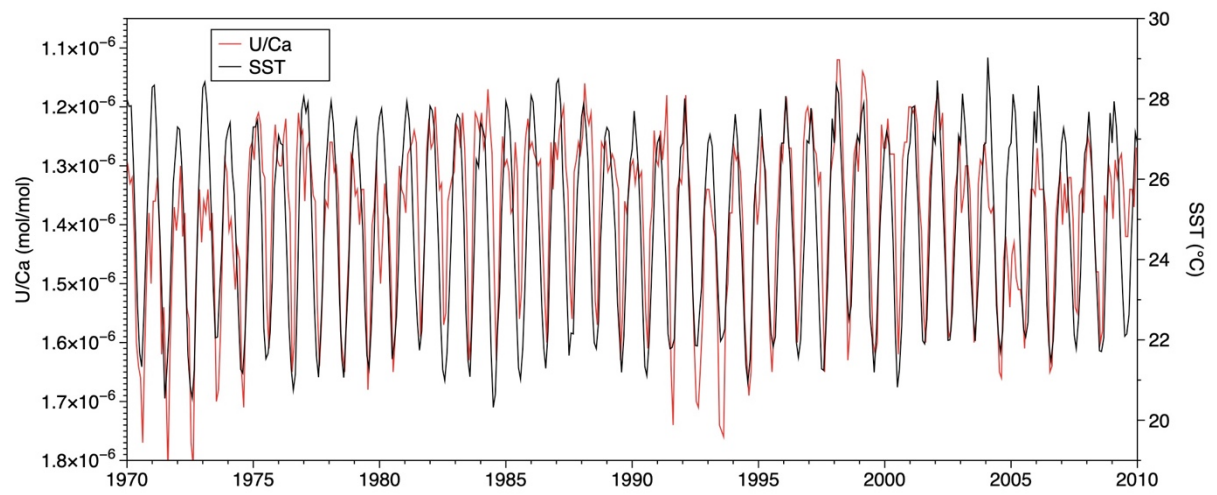


Figure 2.12 Overlay between U/Ca cycles and SST cycles for HUM03A from 1970 to 2010

Chapter 3: Pre to post-bomb ^{14}C history from the west side of Palawan

Island: insights into oceanographic changes in the South China Sea

Chapter overview

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Contribution by others in this chapter:

YW and SF designed the study. YW drilled the coral powder for analyses, prepared the graphite samples, performed the stable isotope analysis, interpreted the data and wrote the manuscript. SF ran the AMS analysis and edited the manuscript. Funding for the work was provided by the ANU Radiocarbon Laboratory.

Signatures:



Yang Wu



Stewart Fallon

Abstract

Compared to the natural production of ^{14}C , thermonuclear tests have produced a globally abnormal ^{14}C signal. To examine and reconstruct ocean circulation in the South China Sea (SCS), we generated a pre to post bomb ^{14}C time series from a *Porites lobata* coral from the west side of Palawan Island, Philippines. Results show a diluted early bomb ^{14}C intrusion in late 1955. We use this record to extend our understanding of the surface ocean circulation in and around the SCS by tracing ^{14}C labelled water from nuclear test sites. Our post-bomb $\Delta^{14}\text{C}$ peaked at 154 ‰ in 1975, which lags ~10 years from the atmospheric peak, consistent with other marine records. This coral record also displayed clear seasonal $\Delta^{14}\text{C}$ cycles indicating different surface waters passed the Palawan Island coral site due to seasonal variations of the East Asian Monsoon.

Plain Language Summary

We present a seawater radiocarbon record (^{14}C) reconstructed from a coral collected from the west side of Palawan Island. This $\Delta^{14}\text{C}$ record encompasses the years 1947-1981, which covers the pre to post nuclear test period. Firstly, our results display a rapid $\Delta^{14}\text{C}$ rise in the coral skeleton around 1955-1956, which is commonly called an “early bomb peak”. This early bomb intrusion results from the nuclear weapon testing in the Marshall Islands and then the direct transport of ^{14}C by ocean currents. Secondly, we observe a strong $\Delta^{14}\text{C}$ seasonality in this coral record which is dominated by East Asian monsoon forced ocean circulation. These results help fill in the gap of complete pre to post bomb $\Delta^{14}\text{C}$ data in the Eastern South China Sea and show that $\Delta^{14}\text{C}$ in the coral skeleton is a robust proxy for recording variations in ocean circulation.

Key Points:

- A complete pre to post bomb $\Delta^{14}\text{C}$ record (1947-1981) is generated from a *Porites* coral in the South China Sea
- An early bomb intrusion in late 1955 is observed in this study site but not as intense as some other sites
- Strong $\Delta^{14}\text{C}$ seasonality in this coral record is dominated by East Asian monsoon forced ocean circulation

3.1 Introduction

^{14}C can be produced in the atmosphere both naturally and artificially. Nitrogen atoms in the upper troposphere and stratosphere can absorb thermal neutrons which are generated by cosmic rays transforming ^{14}N into ^{14}C . Other neutron reactions, such as thermonuclear weapon explosions in the atmosphere, can also produce neutrons and therefore ^{14}C . Atmospheric nuclear weapon testing essentially doubled the amount of atmospheric ^{14}C with a peak in 1963 due to the start of the nuclear test ban treaty (Graven, 2015; Levin et al., 1985; Pravalie, 2014).

Atmospheric CO_2 enters into seawater by air-sea gas exchange when the CO_2 gas pressure in the atmosphere is higher than that in the surface ocean. As part of the global CO_2 , $^{14}\text{CO}_2$ enters the seawater becoming a component of the seawater dissolved inorganic carbon (DIC), which corals use for calcification (Druffel, 1997a). After correcting for the mass-dependent fractionation using coral $\delta^{13}\text{C}$, coral $\Delta^{14}\text{C}$ has been shown to directly track seawater $\Delta^{14}\text{C}$ DIC (Druffel, 1987; Fallon et al., 2003; Guilderson & Schrag, 1998; Stuiver & Polach, 1977). Physical processes occurring in the ocean (e.g., vertical mixing, advection of upper ocean waters), along with the Suess effect (burning of ^{14}C depleted fossil fuels (Tans et al., 1979) and

bomb-produced radiocarbon (nuclear tests), play major roles in affecting $\Delta^{14}\text{C}$ values in surface seawater.

The radiocarbon isotopic signature (^{14}C) in coral skeletons is useful for tracing ocean circulation (Druffel, 1987; Druffel & Griffin, 1995, 1999; Fallon & Guilderson, 2008; Guilderson et al., 2009; Guilderson et al., 2000; Guilderson et al., 1998). Currimao, Houbihu, Palau, Ishigaki, Palau, Guam and Makassar Straits have detected an early bomb intrusion in/around 1955 which is due to the immediate advection of ^{14}C labelled water from nuclear test sites (Andrews et al., 2016; Fallon & Guilderson, 2008; Glynn et al., 2013; Hirabayashi et al., 2017a; Hirabayashi et al., 2019; Ramos et al., 2019). All these sites are in the path of North Equatorial Current (NEC) or its bifurcated currents. Different timings of early bomb intrusions from various coral locations can be used to determine the speed of surface ocean currents (Andrews et al., 2016; Hirabayashi et al., 2017a). Andrews et al. (2016) calculated the average speed of NEC to be $\sim 0.1\text{-}0.2$ m/s by dividing the distance between Operation Castle and Guam by ^{14}C arrival time in Guam. According to the different timing of early bomb intrusions between Ishigaki and Guam, Hirabayashi et al. (2017a) estimated the Kuroshio current to be 0.21 m/s.

Interannual to decadal variability of coral $\Delta^{14}\text{C}$ can also provide insights into other small to large scale oceanographic changes (e.g., surface seawater $\Delta^{14}\text{C}$ can respond to upwelling, Pacific Decadal Oscillation (PDO), ENSO and ocean winds) (Andrews et al., 2016; Druffel, 1987; Guilderson & Schrag, 1998; Guilderson et al., 2000; Hirabayashi et al., 2017a; Hirabayashi et al., 2017b). PDO and ENSO behave quite similarly in the Pacific by affecting the sea surface temperature (SST) and surface winds (Newman et al., 2016; Pierce et al., 2001; Schneider & Cornuelle, 2005). For example, inter-annual upwelling and seasonal vertical upwelling were documented by a coral in Galapagos and a coral in Rarotonga respectively,

which coincided with ENSO and PDO (Guilderson & Schrag, 1998; Guilderson et al., 2000). In most cases, higher $\Delta^{14}\text{C}$ values were observed during El Niño events, due to the increased retention time of ^{14}C in surface water, decreased upwelling and enhanced air/sea CO_2 exchange (Guilderson & Schrag, 1998). In the Makassar Strait (Indonesian Throughflow), seasonal monsoon winds vary the contribution of North Pacific waters in boreal winters and Banda Sea waters in boreal summers, resulting in seasonal $\Delta^{14}\text{C}$ cycles in Langkai and Lombok Strait (Fallon & Guilderson, 2008; Guilderson et al., 2009).

The South China Sea (SCS) is surrounded by Malaysia, Philippines, China and Vietnam, with its average and maximum water depth being 1212 m and 5559 m respectively. The northern boundary of SCS connects to the East China Sea through the Taiwan Strait, the southern boundary connects to the Java Sea through Karimata Straits, and it connects to the Pacific Ocean on the northeast through the Luzon Strait (Figure 3.1) (Qu et al., 2009). General circulation models (GCM) have suggested the SCS may connect to the Sulu Sea through Mindoro Strait (Figure 3.1) (Qu et al., 2006; Qu et al., 2009). North Equatorial Current (NEC) water travels westward towards the Philippines and bifurcates into the northward Kuroshio Current (KC) and the southward Mindanao Current (MC) (Figure 3.1), which plays an important role in the ocean circulation in the Philippine Sea (Qiu & Lukas, 1996). KC/Pacific water intrudes into the SCS through Luzon Strait and continuously flows toward the Java Sea (Figure 3.1). Kuroshio current water can intrude into the SCS throughout the year, with more significant flow during winter (Qu et al., 2009; Yuan et al., 2006; Yuan et al., 2014).

Ocean circulation in the SCS is very complex and is dominated by the East Asian monsoon (Hu et al., 2000; Wei et al., 2016). The winter monsoon leads to a southwesterly water flow (Hu et al., 2000), which is sourced from Pacific water in the east and the East China Sea water from the north (Figure 3.2). This circulation also forms a counterclockwise gyre between the

Philippines and Vietnam (Figure 3.2). The summer monsoon drives a reversed circulation, and delivers water from the south to the SCS (Figure 3.2) (Chu et al., 1999; Hu et al., 2000).

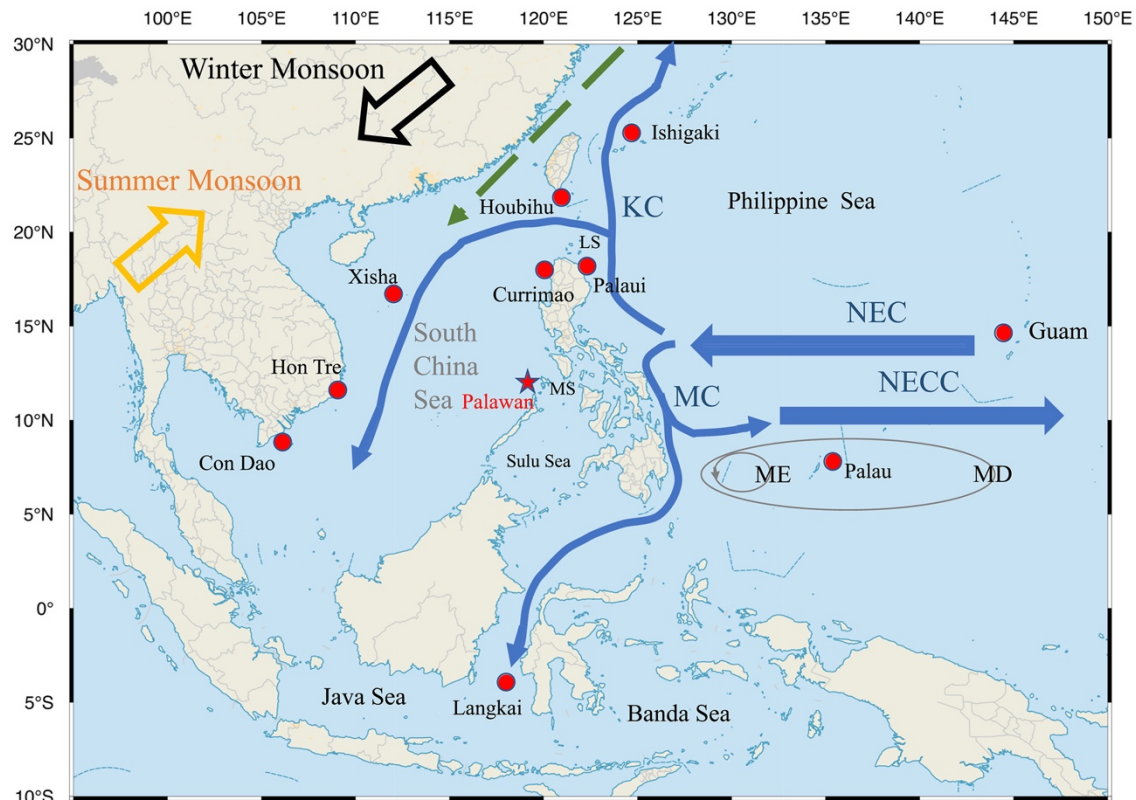


Figure 3.1 Coral locations from radiocarbon studies and ocean currents around southeast Asian archipelago. *KC* is short for Kuroshio current, *MC* is short for Mindanao Current, *NEC* is short for North Equatorial Current, *NECC* is short for North Equatorial Countercurrent, *LS* is short for Luzon Strait, *MS* is short for Mindoro Strait, *ME* is short Mindanao Eddy, *MD* is short for Mindanao Dome. Blue lines represent water from Pacific Sea water, green dash line represents water from East China Sea water, red pentagram represents the sampling site in this study, red solid circles represent the sampling sites in other coral radiocarbon studies. This map was produced using Qgis.

In situ measurements of the surface water processes in the northeastern South China Sea are limited, complicating our understanding of the seasonal and interannual variations. Comparison between coral-based reconstruction of surface water radiocarbon, observational data and ocean modelling results (e.g., Simple Ocean Data Assimilation) can further constrain the ocean circulation in the northeastern South China Sea. In this study, we developed a 34-year record of seawater $\Delta^{14}\text{C}$ reconstructed from a *Porites lobata* coral collected from the west side of Palawan Island (eastern side of the SCS). Results from this study were placed in context with other coral records in the SCS and Western Pacific Ocean in order to use the movement

of bomb-produced ^{14}C as a tracer for ocean circulation in the SCS. This study details seasonal variations in SCS ocean circulation resulting from reversals of the East Asian Monsoon.

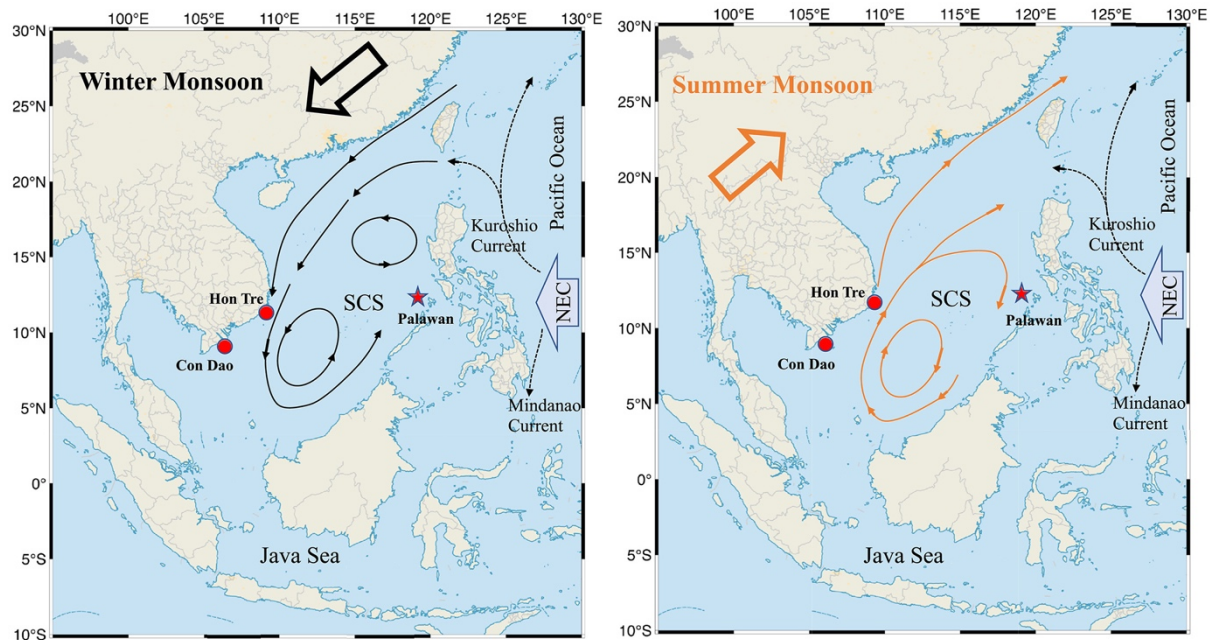


Figure 3.2 South China Sea surface currents during Northeast Monsoon (left, winter) and Southwest Monsoon (right, summer). Winds are shown in large arrows. SCS is short for South China Sea.

3.2 Materials and Methods

3.2.1 Coral location

The study site is located in the South China Sea, which is a semi-enclosed water body of the Western Pacific Ocean. A core was drilled from a *Porites lobata* coral colony off the west side of El Nido Bay, Palawan Islands (11°29' N; 119°01' E) in May 1981 by the US Geological Survey (Figure 3.1). The coral will be hereby named Palawan.

3.2.2 Sample preparation for ^{14}C and stable isotopes

The coral core was sliced into ~7mm slabs parallel to the axis of growth (Figure 3.3), and subsamples were drilled along its main growth axis (Alibert & McCulloch, 1997). In order to maintain sampling on a main growth axis, two parallel transects with clear growth bands were selected including an overlapping area 40 mm long (Figure 3.3). A sampling increment of 1.0 mm was milled, roughly corresponding to 10 samples per year. Approximately 5 mg of coral

sample powder was loaded into 10 ml glass Vacutainer™ tubes, evacuated and acidified with 85% orthophosphoric acid (0.3 ml) at 80°. Generated CO₂ was cryogenically purified and transferred to a graphite line where excess H₂ reacted with CO₂ at 560 °C using reduced iron as a catalyst (Vogel et al., 1984). Graphite samples were then measured by Single-Stage AMS at the Radiocarbon Laboratory, Australian National University for ¹⁴C/¹²C, ¹⁴C/¹³C, and ¹³C/¹²C ratios (Fallon et al., 2010). The data are reported as age-corrected Δ¹⁴C for known-age geochemical samples (Stuiver & Polach, 1977). One sample every two mm was measured for ¹⁴C and stable isotopes (¹³C and ¹⁸O). Stable isotope samples were loaded into 3ml Exetainer™ vials, flushed with helium and acidified with 0.2ml >100% H₃PO₄. The acid hydrolysis was undertaken at 60 °C. The resulting CO₂ was analyzed for ¹³C/¹²C and ¹⁸O/¹⁶O on a SERCON 20-22 IRMS and carbonate device. Stable isotope data were acid-alpha fractionation corrected using a value of 1.00939 for aragonite (Kim et al., 2007). Results are reported in delta notation relative to V-PeeDee Belminite (Coplen, 1994; Coplen et al., 2006).

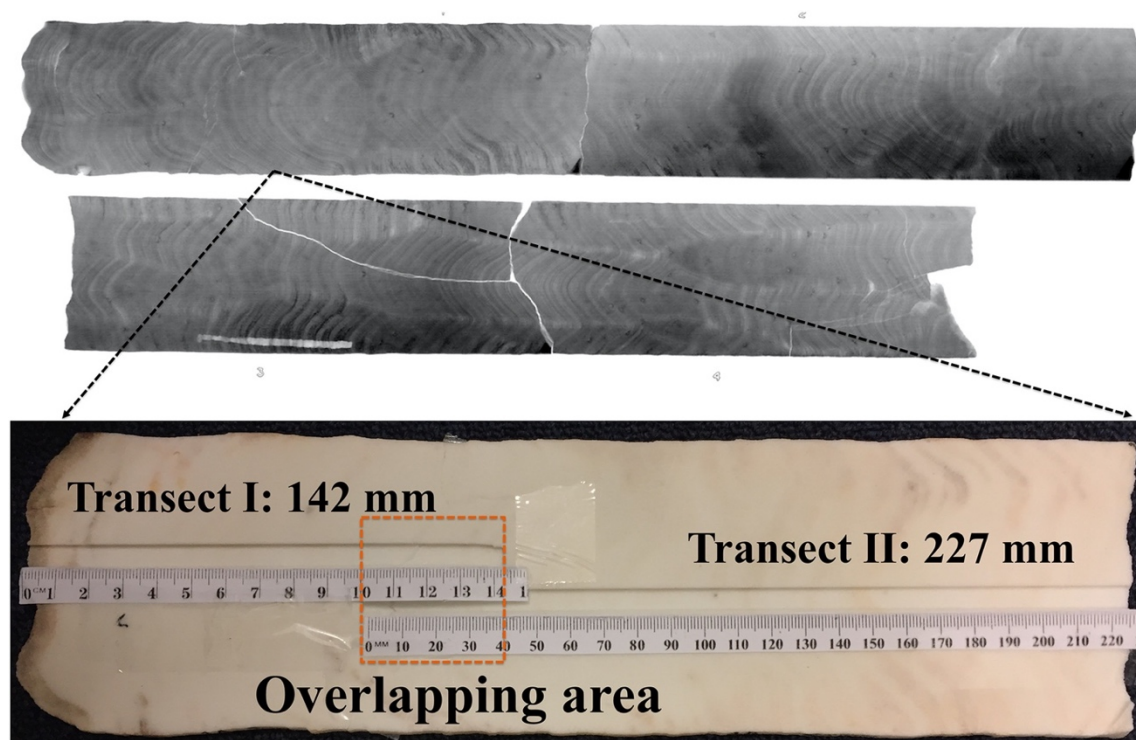


Figure 3.3 X-ray images of Palawan coral. The image reveals the annual growth bands, and two drilling transects with overlapping area.

3.2.3 Age model

$\delta^{18}\text{O}$ in corals has been shown to be negatively correlated with sea surface temperature (SST) and is often used to develop age models (Druffel, 1987; McCulloch et al., 1994). In this study, we used annual density bands and fine-tuned the age model by matching the $\delta^{18}\text{O}$ maxima to the winter SST minimum (Figure 3.4). SST records were retrieved from IGOSS LDEO climate data website (<http://iridl.ldeo.columbia.edu>). Age model error is estimated to be ± 2 months in this work.

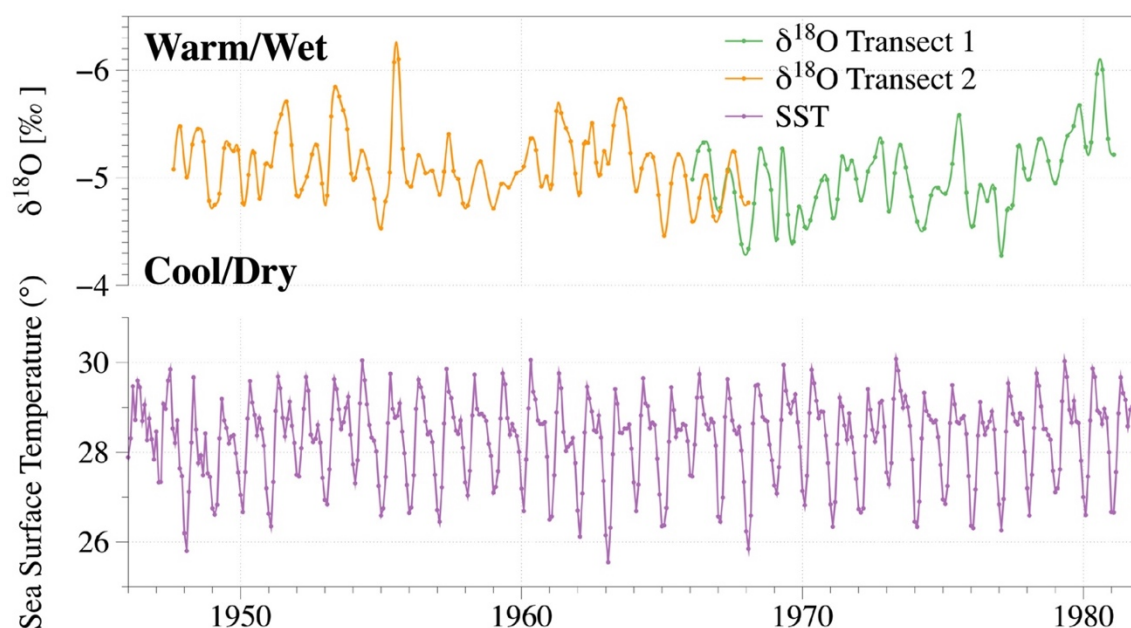


Figure 3.4 Complete $\delta^{18}\text{O}$ and Sea surface temperature curves for Palawan coral. Full link to retrieve SST

(<http://iridl.ldeo.columbia.edu/SOURCES/.GOSTA/.gisst22/.sst/dataselection.html?limit.X.value=119E&limit.Y.value=11.5N&limit.T.value=Jan+1940+to+Dec+1994>) for the 1-degree latitude by longitude box centered on 11.5N, 118.5E. Line has been spline smoothed in Datagraph.

3.2.4 Additional coral locations for comparison and their age models

Coral records from Con Dao and Hon Tre Islands are located in the southwestern SCS. Coral record from Currimao is located off northwest Luzon Island. Coral records from Ishigaki, Houbihu, Palaui, Palau and Guam Islands are located in the Western Pacific Ocean, where Guam is nearest to the nuclear test sites (Figure 3.1). Coral record from Langkai Island is located at the southern exit of Makassar Strait. $\Delta^{14}\text{C}$ time series in the locations (Figure 3.1)

which we compared to Palawan data were validated in various ways. The Con Dao coral age model was based on luminescent and density bands, and was confirmed by Sr/Ca seasonal cycles (Mitsuguchi et al., 2007). Hon Tre and Ishigaki coral age models were made by pinning seasonal Sr/Ca extremes to local SST (Bolton et al., 2016; Hirabayashi et al., 2017a). Palau and Guam coral age models are based on seasonal cycles of $\delta^{18}\text{O}$ similar to this study (Andrews et al., 2016; Glynn et al., 2013). The Langkai coral age model was made by assigning the minimum $\delta^{13}\text{C}$ to February, and finetuned using $\delta^{18}\text{O}$ maxima and SST minima. Currimaos, Houbihu and Palaui coral age models were based on annual density bands and Sr/Ca seasonal cycles (Hirabayashi et al., 2019; Ramos et al., 2019). Typically, age model uncertainties developed by the above proxies ($\delta^{18}\text{O}$, $\delta^{13}\text{C}$, Sr/Ca) are ± 2 months (Fallon & Guilderson, 2008; Guilderson et al., 2009).

3.3 Results

A total of 173 samples were measured in the Palawan coral for $\Delta^{14}\text{C}$, spanning the years 1947-1981 (Figure 3.5). The coral $\Delta^{14}\text{C}$ shows the typical ocean bomb pulse pattern due to the increase in atmospheric $^{14}\text{CO}_2$ and subsequent $^{14}\text{CO}_2$ invasion into the surface ocean as a result of atmospheric nuclear tests. The average (1947-50) pre-bomb $\Delta^{14}\text{C}$ is -59.9‰ with some clear seasonal cycles, the maximum $\Delta^{14}\text{C}$ is +154‰ with an overall amplitude of 214‰ (Table 3.1). The first rapid rise of coral $\Delta^{14}\text{C}$ from -54‰ to -29‰ starts in 1955, and is consistent with early bomb intrusions described by previous studies (Ishigaki (Hirabayashi et al., 2017a), Guam (Andrews et al., 2016), Palau (Glynn et al., 2013), Okinawa (Konishi et al., 1981), Langkai (Fallon & Guilderson, 2008), and Houbihu and Palaui (Ramos et al., 2019)). The coral $\Delta^{14}\text{C}$ then plateaus at ~ -32 ‰ until 1960 when values increase gradually displaying a 10-15‰ seasonal cycle. Another rapid increase in $\Delta^{14}\text{C}$ (~ 90 ‰) due to the long-term air-sea diffusion of CO_2 starts in 1965 with clear seasonal cycles of ~ 30 ‰ until the end of the coral record in 1981 (Figure 3.5).

Due to variations in the growth axis of the coral a second transect was needed. Figure 3.5 also shows the high reproducibility in the overlapping section between the two parallel transects. Agreement between overlapping $\Delta^{14}\text{C}$ transects reveals good repeatability of coral $\Delta^{14}\text{C}$ records.

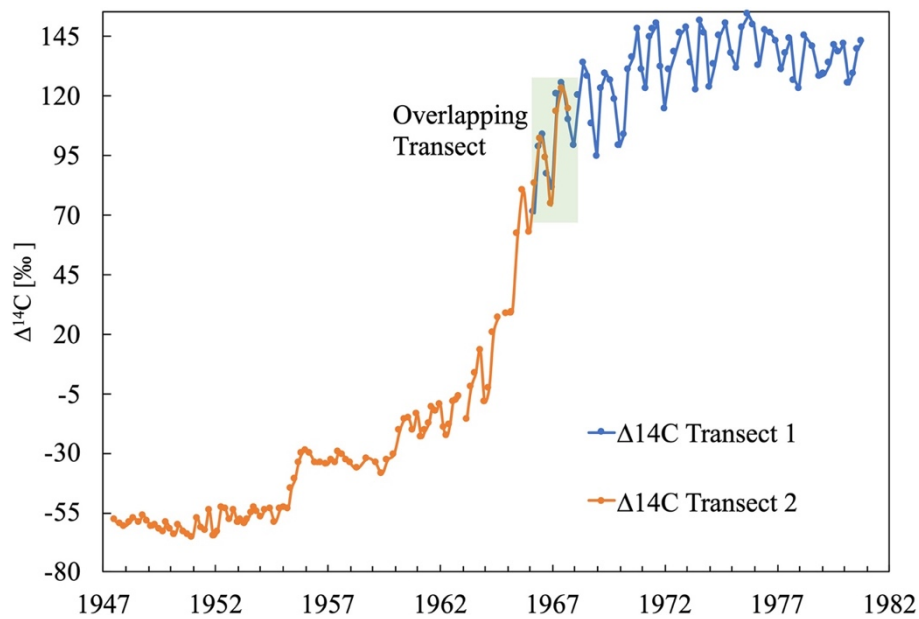


Figure 3.5 Complete $\Delta^{14}\text{C}$ curves for Palawan coral

Table 3.1 Comparison of the early bomb intrusion values, timing and bomb-induced $\Delta^{14}\text{C}$ increases

Location		Mean $\Delta^{14}\text{C}$ from 1948-1952 (‰)	Post bomb maximum (‰)	Bomb- induced Increase (‰)	Early bomb intrusion (‰)	Timing of early bomb intrusion
	n	Mean $\pm$ Std				
Guam	32	-54.1 $\pm$ 5.5	160	214	937.6	1954.7
Palau	6	-55.6 $\pm$ 2.3	142	198	-26.4	1955
Langkai	60	-57.0 $\pm$ 2.6	163	220	-7.6	1955.5
Ishigaki	12	-59.5 $\pm$ 7.6	163	223	50.7	1955.6
Palau	4	-58.2 $\pm$ 2.2	165	223	11	1955.6
Houbihu	1	-62.1	151	213	-19.6	1955.6
Currimao	10	-55.8 $\pm$ 6.0	183	239	-4.9	1956
Palawan	27	-60.0$\pm$3.6	154	214	-29.3	1956
Con Dao	5	-48.0 $\pm$ 3.7	173	221	n/a ^a	n/a
Hon Tre	6	-58.8 $\pm$ 2.3	156	215	n/a	n/a

Note. Selected sites in this table are Palawan (in bold, This Study), Guam (Andrews et al., 2016), Palau (Glynn et al., 2013), Langkai (Fallon & Guilderson, 2008), Ishigaki (Hirabayashi et al., 2017a), Palau and Houbihu (Ramos et al., 2019), Currimao (Hirabayashi et al., 2019), Con Dao (Mitsuguchi et al., 2007), and Hon Tre (Bolton et al., 2016).

^an/a represents no early bomb intrusion detected or not noted in the study

3.4 Discussion

Coral records in the SCS are limited. Three published complete pre to post bomb data sets were from corals collected at Con Dao Island (Mitsuguchi et al., 2007), Hon Tre Island (Bolton et al., 2016) and Luzon Island (Hirabayashi et al., 2019) (Figure 3.1). Con Dao Island and Hon Tre Island are located in the southwestern SCS whereas this study site is located on the eastern side of the SCS (Figure 3.1, Figure 3.2). The Con Dao and Hon Tre coral $\Delta^{14}\text{C}$ values are consistently higher than other tropical regions (e.g., Guam, Palau, Langkai) (Figure 3.6), and similar to subtropical regions (e.g., Okinawa, Currimao) (Figure 3.6). Because of the isolation from other major ocean currents (e.g., NEC) and the enhanced air-sea CO_2 gas exchange by East Asian monsoon, the Con Dao coral record displays a more rapid rise and higher maximum corresponding to greater air/sea exchange of CO_2 (Mitsuguchi et al., 2007). The overall slope and peak values of $\Delta^{14}\text{C}$ in this study are identical to Langkai and similar to the other locations outside of the SCS (Figure 3.6) but distinct from that of Con Dao Island or Hon Tre Island (Figure 3.6a), confirming the eastern side of SCS is influenced by Pacific seawater.

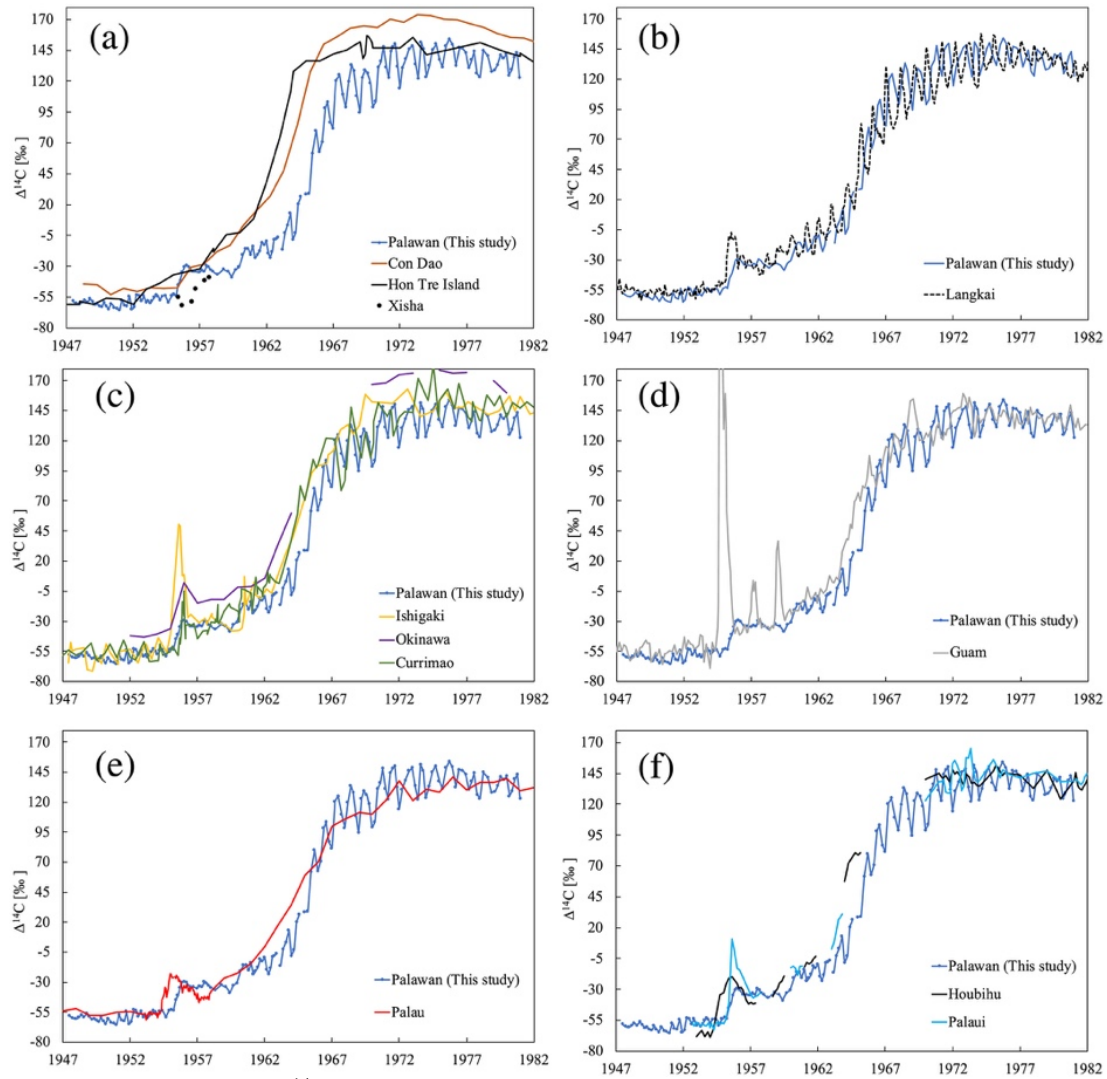


Figure 3.6 Comparison of $\Delta^{14}\text{C}$ records between Palawan (this study) and other selected sites. (a) Con Dao (Mitsuguchi et al., 2007), Hon Tre (Bolton et al., 2016) and Xisha (Southon et al., 2002), (b) Langkai (Fallon & Guilderson, 2008), (c) Ishigaki (Hirabayashi et al., 2017a), Okinawa (Konishi et al., 1981), and Currimao (Hirabayashi et al., 2019, Hirabayashi, 2017b), (d) Guam (Andrews et al., 2016), (e) Palau (Glynn et al., 2013), (f) Houbihu and Palaui (Ramos et al., 2019).

3.4.1 Pre-bomb era and early bomb intrusion

Bomb radiocarbon was generated by a series of thermonuclear weapon tests in the 1950's and early 1960's. The worldwide nuclear tests resulted in a prolonged increase in atmospheric ^{14}C which peaked in late 1963 in the northern hemisphere (Hua & Barbetti, 2004; Hua et al., 2013; Nydal & Lovseth, 1983). In general, the atmospheric ^{14}C in the southern hemisphere lagged behind that in the northern hemisphere (where the majority of tests took place), because bomb radiocarbon was gradually mixed to the southern stratosphere (Hua & Barbetti, 2004; Hua et al., 2013).

The pre-bomb $\Delta^{14}\text{C}$ value in Palawan is statistically different (not different) from Guam, Con Dao, Palau Currimao and Langkai (Hon Tre, Ishigaki, and Palau) over a consistent period 1948-1952 (*t*-test statistics in Table S3.2). Among all records, the Con Dao coral has a significantly higher pre-bomb $\Delta^{14}\text{C}$ due to shallow water and intensive air-sea CO_2 diffusion (Mitsuguchi et al., 2007).

The coral records from in and around the SCS display a distinctive early bomb intrusion signal that arrives ~ 1955 (Figure 3.6) (Andrews et al., 2016; Fallon & Guilderson, 2008; Glynn et al., 2013; Hirabayashi et al., 2017a; Hirabayashi et al., 2019; Ramos et al., 2019). This signal displays itself differently in the different locations, variations in arrival time and amplitude suggest competing water sources and mixing from different locations (Table 3.1, Figure 3.7a). Sites outside the SCS (e.g., $\Delta^{14}\text{C}$ in the coral from Langkai increased by 40‰ from -50‰ to -10‰ in 3 months) have earlier arrival and higher $\Delta^{14}\text{C}$ compared to the Palawan coral which shows a more gradual increase from -53.7 ‰ in April/May 1955 to -29.4 ‰ in December 1955/January 1956 (Figure 3.6). Based on the ‘peak’ values from Palawan ($F^{14}\text{C}=0.9714$) and Guam ($F^{14}\text{C}=1.9387$), a simplistic calculation can be done to estimate the relative fraction (*f*) of non-NEC waters that have been laterally entrained during transit of the ‘first bomb intrusion’ from Guam to the SCS using the following mass balance equation (1):

$$f \cdot F^{14}\text{C}(\text{non-NEC waters}) + (1-f) \cdot F^{14}\text{C}(\text{Guam}) = F^{14}\text{C}(\text{Palawan}), \quad (1)$$

$F^{14}\text{C}$ for non-NEC waters was chosen by averaging pre-bomb values from South China Sea and North Pacific (Table 3.1, Table S3.2), which equals 0.94. Result shows a fraction of 0.97 of non-NEC waters and a fraction of 0.03 of NEC (Guam) water can lead to the Palawan early bomb signal.

The early bomb rise in the Palawan coral is consistent with the timing of the Kuroshio current intrusion (usually November to March) into the SCS via Luzon Strait when the winter northeast monsoon is dominant (Nan et al., 2015). Unlike other early bomb intrusions, the signal in the Palawan coral is less intense even with its high temporal resolution, and lags behind coral records of Ishigaki and Langkai by several months (Table 3.1, Figure 3.7a). The lower intrusion value indicates water mass (depleted in ^{14}C) mixing in/near this coral site with the Kuroshio current, resulting in a dilution of the early intrusion. Hirabayashi et al. (2017a) noticed their first ^{14}C intrusion in the Ishigaki coral was almost one year delayed compared with the Guam coral, but identical to the coral record of Langkai. They attributed their delay to the long travel distance from the Marshall Islands to Ishigaki (Hirabayashi et al., 2017a). This is consistent with the Palawan ^{14}C delay because the Kuroshio current needs to travel further down to the South China Sea (SCS) to reach the Palawan Island (Figure 3.1, Figure 3.2). The different timing and magnitude of early bomb intrusions suggest the preservation of ^{14}C in coral skeletons is affected by their locations and distance between sites (Ramos et al., 2019). However, we cannot rule out Pacific water seeping through the Philippine Islands and mixing with SCS water causing the dilution of ^{14}C and the timing delay. Modeling by Andrews et al. (2016) shows ^{14}C labelled water particles entering the Sulu Sea in late 1954 and mixing into the Palawan region ~1956.

3.4.2 Post bomb era

After the early bomb intrusion, $\Delta^{14}\text{C}$ values in the Palawan coral dropped slightly but levelled off at $\sim -32\text{‰}$ for nearly 2 years suggesting slow transport and/or storage of the labelled Pacific water via the Sulu Sea into the Palawan region (Figure 3.5, Figure 3.7a). This is in contrast to the coral locations outside the SCS (e.g., Guam, Langkai, Ishigaki, (Andrews et al., 2016; Fallon & Guilderson, 2008; Hirabayashi et al., 2017a) which exhibited higher peak values

followed by a rapid decrease owing to the continuous input of unlabeled fresh Pacific water (Figure 3.7a).

The quick rise from 1959 to 1960 may be the delayed arrival of other ^{14}C labelled water as the rise follows closely after the 1959 ^{14}C peak in Guam (Figure 3.6d, Figure 3.7a). This is similar to the 1956 rise in Palawan which also follows the large ^{14}C peak in Guam in 1955 (Figure 3.6d). After 1960, Palawan coral record shows the biggest similarity with that of Langkai in timing and amplitude (Figure 3.6b), except the peaks and valleys are opposite in boreal summer (July, August, September) and winter seasons (Figure 3.6b, Figure 3.8).

From 1960-1970, the Palawan coral exhibited a slower and delayed increase compared to Currimao, Ishigaki and Guam (Figure 3.6c and 3.6d). After 1970, summer $\Delta^{14}\text{C}$ values from the Palawan coral are marginally higher than those in Guam (Figure 3.6d), indicating water coming from the western margin of the SCS was more dominant in these years. ENSO was found to significantly influence the lateral exchange rate in the Luzon Strait, with increased water transport into the SCS corresponding to El Niño periods (Ramos et al., 2019). Additionally, there is more consistency in $\Delta^{14}\text{C}$ values between Palawan and Guam in 1972/1973 and after 1976/1977 (Figure 3.6d), potentially due to the strong El Niño in 1972/1973, changing PDO regime and changing NEC bifurcation latitude in 1976/1977. These episodes favored the intrusion of Pacific water via Luzon Straits (Qu et al., 2009). Palawan coral $\Delta^{14}\text{C}$ is higher than that of Palau in the 1970s (Figure 3.6e), especially during El Niño years. Interannual variability of the Mindanao eddy is strongly related to ENSO, displaying increasing (decreasing) strength during El Niño (La Niña) (Zhao et al., 2013), suggesting that the Palau coral $\Delta^{14}\text{C}$ is influenced by the Mindanao eddy (Hirabayashi et al., 2017a). Increasing the strength of the Mindanao eddy intensifies vertical mixing in the Palau region, leading to upwelling of ^{14}C depleted water. Because the Mindanao Dome is geographically close to the

NEC bifurcation point, it's also possible that the change in NEC bifurcation latitude may have led to relatively low $\Delta^{14}\text{C}$ in Palau. The post 1976 $\Delta^{14}\text{C}$ records from Palawan, Palau, Guam, and Langkai become more consistent (Figure 3.6) because air-sea diffusion became the dominant influence on Pacific water $\Delta^{14}\text{C}$.

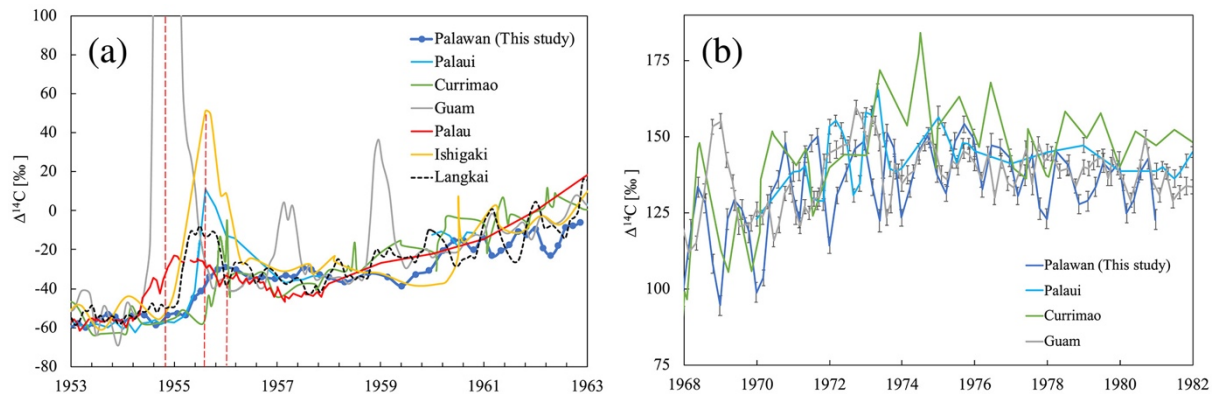


Figure 3.7 Close-up of (a) early bomb intrusions captured in Palawan (this study), Langkai (Fallon & Guilderson, 2008), Guam (Andrews et al., 2016), Ishigaki (Hirabayashi et al., 2017a), Currimao (Hirabayashi et al., 2019), Palaui (Ramos et al., 2019) and Palau (Glynn et al., 2013) showing different arrival times due to travelling distance (b) post-bomb values from selected sites (Palaui, Currimao, Guam) and Palawan (this study). Red dashed lines in panel (a) are used to help identify the timing of peak values.

3.4.3 Seasonal variation

High resolution $\Delta^{14}\text{C}$ data is essential to reconstruct seasonal changes, however few coral radiocarbon records display clear seasonality regardless of the sampling resolution (e.g., Guam, Currimao, or Ishigaki (Andrews et al., 2016; Hirabayashi et al., 2017a; Hirabayashi et al., 2017b)). Two coral radiocarbon records that exhibit strong seasonality are Palawan and Langkai (Fallon & Guilderson, 2008) (Figure 3.6b, Figure 3.8). Coincidentally, both are influenced by the East Asian monsoon which leads to the seasonal mixing of different water masses (Hu et al., 2000; Schneider, 1998; Wei et al., 2016). The seasonal maximum $\Delta^{14}\text{C}$ in Palawan typically occurs during boreal summers (July, August, September) while the minimum $\Delta^{14}\text{C}$ occurs in boreal winters (December, January, February). This observation is consistent with coral $\Delta^{14}\text{C}$ from Currimao (Hirabayashi et al., 2017b), geographically close to Palawan (Figure 3.1). There are several possible drivers to the low winter coral $\Delta^{14}\text{C}$ in

Palawan. Firstly, the northeast monsoon favors the transport of Pacific water to the west side of Palawan Island during winter bringing water with a lower ^{14}C signature than the surrounding SCS. Secondly, the Luzon Strait area is subject to stronger mesoscale eddies caused by the Kuroshio intrusion, which lowers the $\Delta^{14}\text{C}$ values by vertical mixing (Soeyanto et al., 2014). Thirdly, a stronger winter East Asian monsoon (Hsin et al., 2012) might induce some local upwelling by removing surface water and upwelling deep ^{14}C depleted water. Possible but weak evidence for upwelling as the cause of lower surface water $\Delta^{14}\text{C}$ is that the Palawan coral has the lowest $\Delta^{14}\text{C}$ values most of the time during post-bomb period (Figure 3.6, Figure 3.7b). However, it should be noted that $\Delta^{14}\text{C}$ values in some sites (e.g., Palau) have been smoothed due to lower-resolution sampling. Higher surface water $\Delta^{14}\text{C}$ at Palawan is more easily explained by the southwest monsoon (Boreal summer) delivering higher ^{14}C water due to enhanced air-sea CO_2 exchange from the southwestern SCS. The high SCS ^{14}C is evidenced by the coral records from Can Dao and Hon Tre Island (Figure 3.6a).

Secular or sub-decadal changes in winds may affect the magnitude of $\Delta^{14}\text{C}$ seasonality in Palawan, because the SCS circulation is mainly controlled by the East Asian monsoon. Relative to the summer monsoon, the East Asian Winter Monsoon (EAWM) has a stronger impact. To test the influence of EAWM, we calculated the Palawan summer-winter $\Delta^{14}\text{C}$ difference and compared it with EAWM speed (Song et al., 2012). Results show $\Delta^{14}\text{C}$ seasonal differences were positively correlated to the monsoon velocity especially after 1973 (Figure S3.4), similar with the finding by Hirabayashi et al. (2017b). However, the decreasing $\Delta^{14}\text{C}$ seasonal differences is more likely to be related to the decreasing air-sea gradients after the post-bomb peak.

In summary, the East Asian monsoon drives ocean circulation in the SCS (Figure 3.2) (Hu et al., 2000), and is the cause of higher $\Delta^{14}\text{C}$ in summers and lower $\Delta^{14}\text{C}$ in the winters (Figure

3.8). Anticyclonic monsoon during summers favors the transport of higher ^{14}C water from Con Dao (the southern SCS) to the west side of Palawan Island whereas cyclonic monsoon in winters bring more ^{14}C diluted water from Luzon Strait or the Pacific Ocean. Heavy winds during the winter may also stir the surface water and induce localized upwelling which contributes to the vertical water mass mixing and lower ^{14}C (Figure 3.7b).

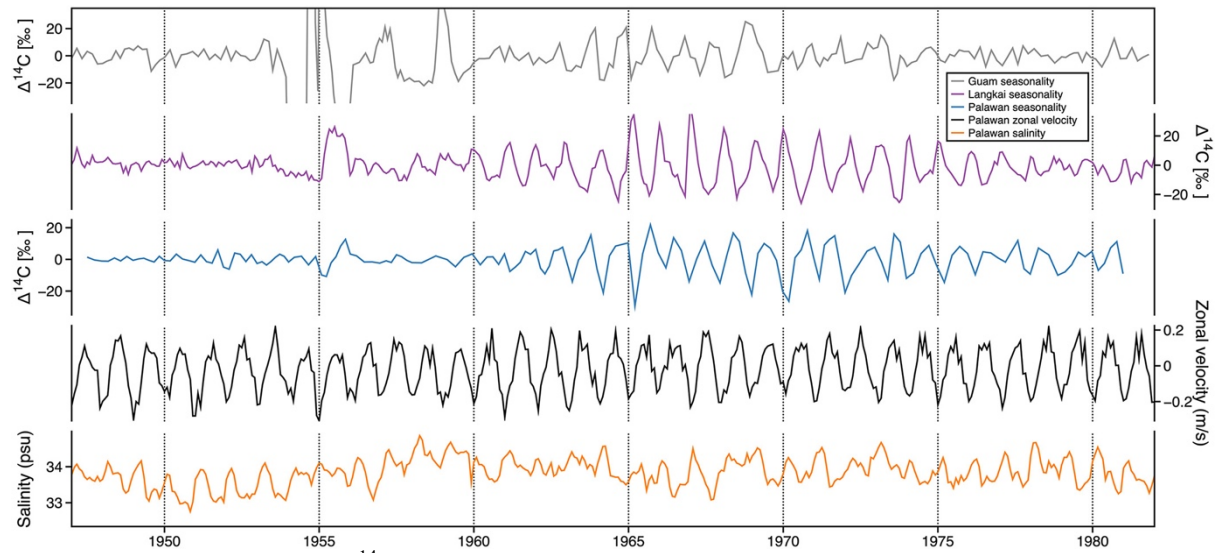


Figure 3.8 Comparison of $\Delta^{14}\text{C}$ seasonality in Palawan (this study), Langkai (Fallon & Guilderson, 2008), Guam (Andrews et al., 2016), Palawan zonal velocity and Palawan sea surface salinity. For seasonality, each data point was normalized to the relevant annual $\Delta^{14}\text{C}$ average to remove the long-term trend.

3.4.4 South China Sea circulation

To integrate the Palawan observations and better understand the water transport in the SCS, we synthetically explored the Con Dao $\Delta^{14}\text{C}$ record using a simple 1-D box model (Figure S3.2) (Druffel, 1989, 1997b; Grumet et al., 2004; Ramos et al., 2019; Stuiver & Braziunas, 1993; Stuiver et al., 1986; Stuiver & Quay, 1981). The model has an atmospheric box (tree ring $\Delta^{14}\text{C}$), a subsurface box and a lateral box (e.g., Palawan coral $\Delta^{14}\text{C}$). Coral $\Delta^{14}\text{C}$ in Con Dao can be calculated using the following equation (2):

$$\text{ConDao}_{t+\Delta t} = \text{ConDao}_t + [\Delta t * k_{\text{Lat}} * (\text{Palawan}_t - \text{ConDao}_t)] + [\Delta t * (k_{-1} * A_{t+\Delta t} - k_1 * \text{ConDao}_t)] + \Delta t * W * (\text{Subsurface}_{t+\Delta t} - \text{ConDao}_t), \quad (2)$$

where ConDao_t is the coral $\Delta^{14}\text{C}$ at time t , Palawan_t is the coral $\Delta^{14}\text{C}$ at time t , k_{Lat} is the lateral exchange rate, k_{-1} (or k_1) is the rate of $^{14}\text{CO}_2$ input from the atmosphere (or the ocean), A is atmospheric ^{14}C , and W is the vertical exchange rate. For simplicity, k_{Lat} is assumed to be 0.37 (Ramos et al., 2019). Detailed estimation and explanation of these variables can be found in the supporting information. Regardless of the model caveats, results indicate a lateral contribution from northeastern SCS water (labelled with an early bomb intrusion signal) is an essential component to account for the rapid $\Delta^{14}\text{C}$ rise in Con Dao from 1955-1960 (Figure S3.3). Model-calculated surface $\Delta^{14}\text{C}$ at Con Dao were well correlated to the observed $\Delta^{14}\text{C}$ between 1950 and 1966 using the average wind speed of 5.64 m/s (Figure S3.3). The weaker correlation after 1966 may be attributed to poor constraints on subsurface ^{14}C values, vertical exchange rate (W) and lateral exchange rate (k_{Lat}).

3.5 Conclusion

This study provides a complete pre to post $\Delta^{14}\text{C}$ bomb curve in the South China Sea (SCS) spanning from 1947 to 1981, which is distinctly different from the coral records at Con Dao Island or Hon Tre Island from the southwestern SCS (Bolton et al., 2016; Mitsuguchi et al., 2007). An early bomb ^{14}C intrusion signal arrived in late 1955 from the immediate transport of $\Delta^{14}\text{C}$ labelled water from the Pacific proving ground nuclear test site but not as intense as other sites. The shape of the $\Delta^{14}\text{C}$ bomb curve and the strong seasonality recorded in the Palawan coral is a result of water mass mixing induced by the variability of East Asian Monsoon. This study has improved our understanding of the connection between Pacific Ocean and the SCS, and provides a potential evidence that the SCS surface water exchanges with the Sulu Sea through the Mindoro Straits.

Acknowledgments

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3.6 Supplementary Information

This supporting information provides additional text, figures, and tables to help interpret the data and discussion in the main text. Figure S3.1 shows the SST reconstruction using $\delta^{18}\text{O}$. Text S3.1 describes the box model and discusses the model results. Figure S3.2 is the schematic diagram of 1-D box model. Figure S3.3 compares the model results using different variables. Figure S3.4 shows a close-up of post-bomb values from selected sites from 1968-1982. Figure S3.5 compares seasonal $\Delta^{14}\text{C}$ difference of Palawan coral to the average winter monsoon wind velocity from December to February (Song et al., 2012). Table S3.1 describes different variables which are used for model calculation. Table S3.2 shows *t*-test results of pre-bomb coral $\Delta^{14}\text{C}$ in and around the South China Sea.

Text S3.1

We explored the Con Dao record using a simple 1-D box model (Druffel, 1989; Druffel, 1997b; Grunet et al., 2004; Ramos et al., 2019a; Stuiver and Braziunas, 1993; Stuiver et al., 1986; Stuiver and Quay, 1981). Based on the model (Fig. S2), coral $\Delta^{14}\text{C}$ in Con Dao can be calculated using equation:

$$\text{ConDao}_{t+\Delta t} = \text{ConDao}_t + [\Delta t * k_{\text{Lat}} * (\text{Palawan}_t - \text{ConDao}_t)] + [\Delta t * (k_{-1} * A_{t+\Delta t} - k_1 * \text{ConDao}_t)] + \Delta t * W * (\text{Subsurface}_{t+\Delta t} - \text{ConDao}_t), \text{ where:}$$

$$k_1 = I / (Z * \Sigma \text{CO}_2 \text{ yr}^{-1})$$

$$I = V_p * 0.019 \text{ mM} * 365\text{-day yr}^{-1}$$

$$V_p = \text{WS} * 0.9995 - 3.47 \text{ (Druffel, 1989; Druffel, 1997b; Grunet et al., 2004; Ramos et al., 2019a)}$$

$$k_{-1} = F1 * k_1 / 0.983 \text{ yr}^{-1}$$

$$F1 = [\Delta^{14}\text{C}_a / 0.983 - \Delta^{14}\text{C}_s * p\text{CO}_{2s} / p\text{CO}_{2a}] / (\Delta^{14}\text{C}_a / 0.983 - \Delta^{14}\text{C}_s), \text{ here we assume } p\text{CO}_{2s} = p\text{CO}_{2a} \text{ (Druffel, 1989; Druffel, 1997b; Grunet et al., 2004), therefore } F1=1$$

Description of the variables can be found in Table S1. Wind speeds were estimated to be 5.64 m/s from 2003 to 2019, and 6.2 m/s from 1950 to 1982. Using the following links:

<https://iridl.ldeo.columbia.edu/SOURCES/.COAD>

<http://apdrc.soest.hawaii.edu/las/v6/constrain?var=12985>

Pre-bomb fraction modern values used in the above equations are: $A=0.975$; $k_{Lat} = 0.37$; $ConDao_{pre-bomb}=0.95$, $Palawan_{pre-bomb}=0.945$, and $Subsurface_{pre-bomb}=0.925$. Water mass renewal rate (W) in Con Dao was solved using the steady state pre-bomb $\Delta^{14}C$ values at Con Dao and Palawan sites. Post-bomb subsurface values were linearly interpolated using measured $\Delta^{14}C$ from Geochemical Ocean Section (GEOSECS, 1973) and World Ocean Circulation Experiment (WOCE, 1993 to 1995). A few variables have been tested to examine their impacts on the Con Dao $\Delta^{14}C$ records. For example, if there is no lateral contribution, model-calculated coral $\Delta^{14}C$ from 1955-1960 are much lower than the observed data (Fig. S3). Lateral contribution from Palawan (or north-eastern SCS) to Con Dao seem to be an essential component to account for the rapid $\Delta^{14}C$ rise from 1955-1960. Gas exchange piston velocity was sensitive to wind speed. If the wind speed is 6.2m/s, model-calculated coral $\Delta^{14}C$ are consistently higher than the observed data (Figure S3, right panel). if the wind speed is 5.64m/s, model-calculated surface $\Delta^{14}C$ in Con Dao can well correlate with observed $\Delta^{14}C$ between 1950 and 1966. The weaker correlation after 1966 may be attributed to poor constraints on subsurface $\Delta^{14}C$, vertical exchange rate (W) and lateral exchange rate (k_{Lat}).

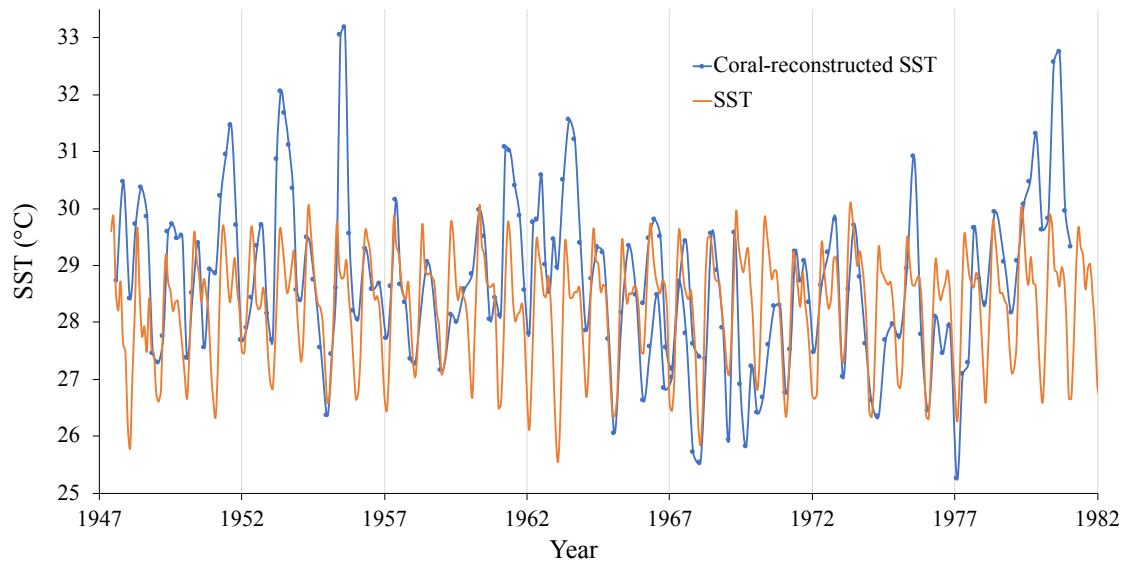


Figure S3.1 Comparison between local SST and oxygen isotope reconstructed SST

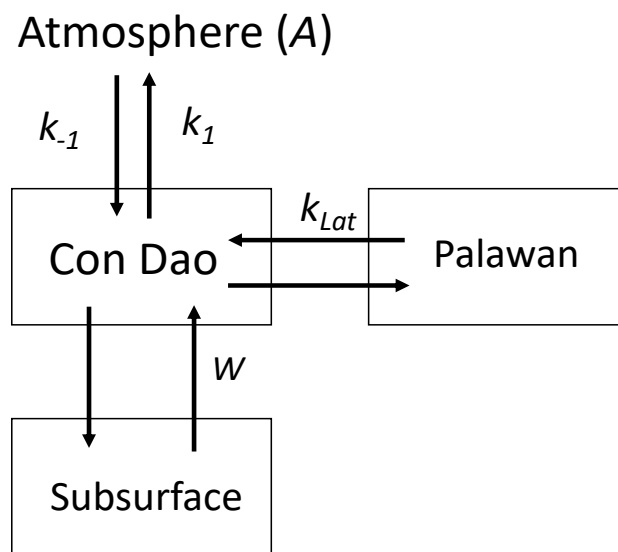


Figure S3.2 Schematic box model to calculate the Con Dao coral $\Delta^{14}\text{C}$

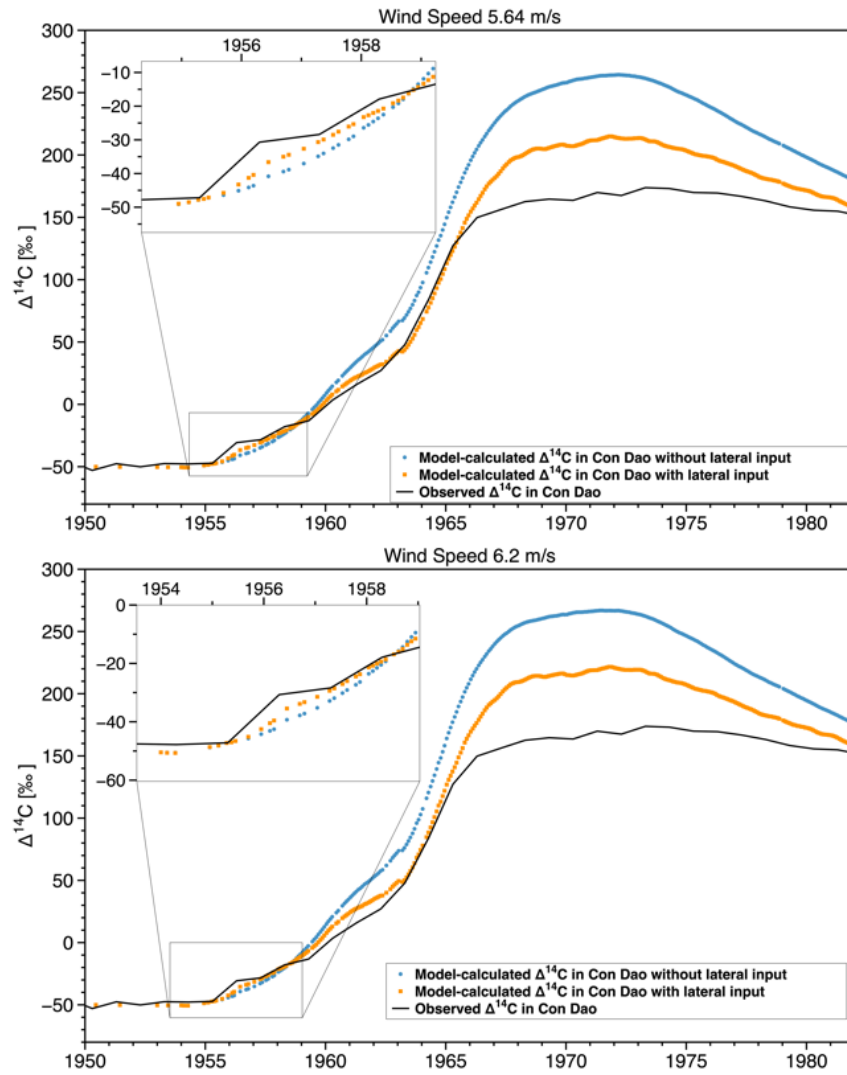


Figure S3.3 Box model results of the forward calculations using different lateral exchange rates (k_{Lat}) and wind speeds. Observed Con Dao $\Delta^{14}C$ were plotted for comparison.

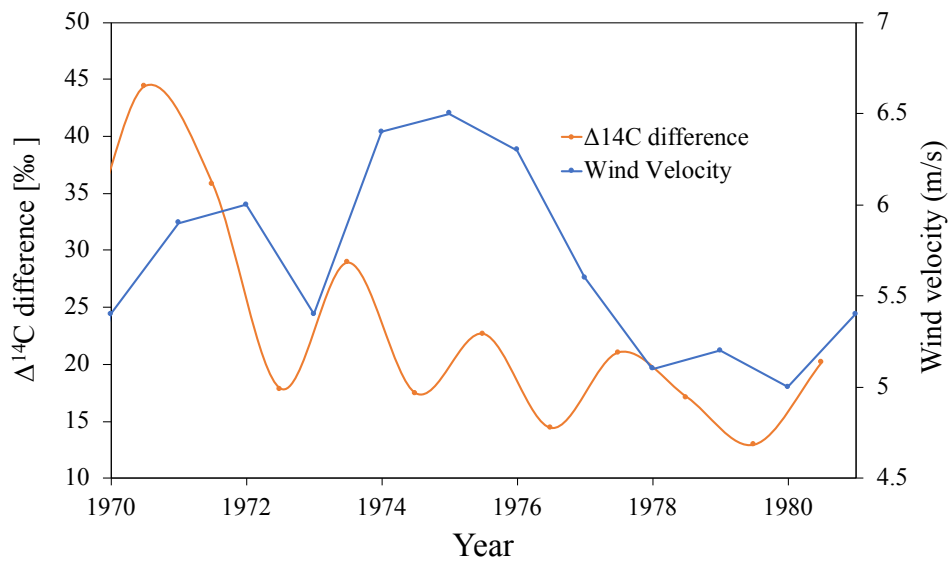


Figure S3.4 Comparison of seasonal $\Delta^{14}C$ difference of Palawan coral and the average winter monsoon wind velocity from December to February (Song et al., 2012)

Table S3.1 Description of the variables for calculating the forward model

Variable	Description	Value	Units
WS	wind speed		m s ⁻¹
Vp	gas exchange piston velocity		m day ⁻¹
Z	mixed layer depth	50	m
ΣCO ₂	total CO ₂ dissolved in seawater	2.06	mol m ⁻³
CO ₂ (aq)	dissolved CO ₂	0.019	mol m ⁻³
k ₋₁	rate of ¹⁴ CO ₂ input from the atmosphere		yr ⁻¹
k ₁	rate of ¹⁴ CO ₂ input from Con Dao to the atmosphere		yr ⁻¹
k _{Lat}	rate of ¹⁴ CO ₂ input from Palawan to Con Dao	0.37	yr ⁻¹
W	rate of ¹⁴ CO ₂ input from Subsurface to Con Dao		yr ⁻¹

Table S3.2 Statistic *t*-test results of pre-bomb coral Δ¹⁴C in and around the South China Sea

Period 1948- 1952	n	Mean	Std. Devi ation	Std. Error Mean	t	df	Sig. (2- tailed)	Mean Diffe rence	Std. Error Diffe rence	95% Confidence Interval of the Difference	
										Lower	Upper
Hon Tre	6	-58.8	2.3	1.0	0.7	31	0.4	1.2	1.6	-2.0	4.3
Palawan	27	-60.0	3.6	0.7							
Ishigaki	12	-59.5	7.6	2.2	0.2	37	0.8	0.4	1.8	-3.2	4.0
Palawan	27	-60.0	3.6	0.7							
Guam	32	-54.1	5.5	1.0	4.6	57	0.0	5.8	1.2	3.3	8.3
Palawan	27	-60.0	3.6	0.7							
Con Dao	5	-48.0	3.7	1.6	6.8	30	0.0	12.0	1.8	8.4	15.6
Palawan	27	-60.0	3.6	0.7							
Palau	6	-55.6	2.4	1.0	2.8	31	0.0	4.4	1.6	1.2	7.5
Palawan	27	-60.0	3.6	0.7							
Langkai	60	-57.0	2.6	0.3	4.3	85	0.00	3.0	0.7	1.6	4.3
Palawan	27	-60.0	3.6	0.7							
Palau	4	-58.1	2.1	1.1	0.9	29	0.33	1.9	1.9	-2.0	5.7
Palawan	27	-60.0	3.6	0.7							

Chapter 4: Surface ocean radiocarbon from a *Porites* coral record in the Great Barrier Reef: 1945-2017

Chapter overview:

This chapter has been published in *Radiocarbon*. Wu Y., Fallon S., Cantin N., & Lough J (2021). Surface ocean radiocarbon from a *Porites* coral record in the Great Barrier Reef: 1944-2017. *Radiocarbon* 1-11. <https://doi.org/10.1017/rdc.2020.141>. The content in this chapter is reproduced entirely in the exact same format of the published manuscript except that the references are merged into the thesis references.

Contribution by others in this chapter:

YW and SF designed the study. YW drilled the coral powder for analyses, prepared the graphite samples, performed the geochemical analysis, interpreted the data and wrote the manuscript. SF ran the AMS analysis. NC collected the MAS01E coral core. YW, SF, NC and JL edited the final manuscript. Funding for the work was provided by the ANU Radiocarbon Laboratory, and the Gladstone Healthy Harbour Partnership Project ISP019.

Signatures:



Yang Wu



Stewart Fallon



Neal Cantin



Janice Lough

Abstract

We present a high-resolution seawater radiocarbon ($\Delta^{14}\text{C}$) record from a *Porites* coral collected from Masthead Island in the southern Great Barrier Reef (GBR) covering the years 1945-2017. The $\Delta^{14}\text{C}$ values from 1945-1953 (pre-bomb era) averaged -49‰. As a result of bomb-produced ^{14}C in the atmosphere, $\Delta^{14}\text{C}$ values started to rise rapidly from 1959, levelled off at ~131‰ in the late 1970s and gradually decreased to ~40.3‰ by 2017 due to the decrease in the air-sea ^{14}C gradient and the overturning of the ^{14}C ocean reservoir (i.e., surface ocean to subsurface ocean; atmosphere to surface ocean). The Masthead Island record is in agreement with previous ^{14}C coral records from the southern GBR. A comparison between surface ocean and atmospheric $\Delta^{14}\text{C}$ suggests that, since 2010, the main reservoir of bomb-derived ^{14}C has shifted from the atmosphere to the surface ocean, potentially resulting in reversed ^{14}C flux in regions where the CO_2 gradient is favourable. The high-resolution Masthead coral $\Delta^{14}\text{C}$ sheds light on long-term variability in air-sea exchange and GBR regional ocean dynamics associated with climate change and in conjunction with the previous records provides a robust seawater ^{14}C reference series to date other carbonate samples.

Key words: *Porites* coral, bomb- ^{14}C , Great Barrier Reef, oceanographic change

4.1 Introduction

Carbon exists as three isotopes in nature with two nonradioactive isotopes (^{12}C and ^{13}C) and one radioactive isotope (^{14}C or radiocarbon). Modern surface seawater radiocarbon is a combination of natural and bomb-produced radiocarbon. Natural radiocarbon originates from the collision of cosmic rays with nitrogen in the upper atmosphere, while bomb-produced radiocarbon derives from atmospheric nuclear weapon testing during the 1950s and 1960s (Druffel 1987, Nydal and Lovseth 1983). ^{14}C produced in the atmosphere quickly forms ^{14}CO then $^{14}\text{CO}_2$ after reacting with oxygen. This atmospheric $^{14}\text{CO}_2$ subsequently diffuses into seawater due to air-sea gas exchange (equilibration normally takes around 10 years) (Druffel and Linick 1978, Druffel and Suess 1983). The uptake of CO_2 and therefore $^{14}\text{CO}_2$ throughout the global ocean leads to the redistribution of bomb-derived ^{14}C .

Porites sp. corals are long-lived (up to 300+ years), and their skeletons record the ^{14}C content of the dissolved inorganic carbon (DIC) in the surrounding water (i.e., coral $\Delta^{14}\text{C}$ = sea water $\Delta^{14}\text{C}$, after correcting for mass-dependent fractionation). This provides an opportunity to examine oceanographic and climate variability using radiocarbon as a seawater tracer over multiple time scales. Many studies have used the ^{14}C in coral skeletons to track ocean circulation (Druffel 1987; Druffel and Griffin 1995, 1999; Fallon and Guilderson 2008; Guilderson et al. 1998; Guilderson et al. 2000; Guilderson et al. 2009; Andrews et al. 2016a; Hirabayashi et al. 2017a; Hirabayashi 2017b; Wu and Fallon 2020). Seawater ^{14}C has also been shown to be sensitive to large-scale climate phenomena such as the El Niño-Southern Oscillation (ENSO) due to the movement of ^{14}C labelled water (Druffel and Griffin 1993, 1995; Guilderson and Schrag 1998). Coral $\Delta^{14}\text{C}$ records can also be used as a temporal reference series to aid in dating marine organisms with calcified structures (Fallon and Guilderson 2005; Andrews et al. 2016b; Andrews et al. 2018).

Numerous coral $\Delta^{14}\text{C}$ records have been reported from the tropical Pacific Ocean, however, many of these records either have low temporal resolution or are relatively short in length, limiting the complete history of bomb ^{14}C uptake and decline. Water sampling programs such as the World Ocean Circulation Experiment (WOCE, (Key et al. 1996)) provide a low temporal resolution snapshot of seawater ^{14}C concentrations over the past decades but cannot inform seasonal and interannual variations of seawater ^{14}C . Long-term continuous coral $\Delta^{14}\text{C}$ records can add critical information to these water sampling programs by providing a detailed high-resolution history of oceanic ^{14}C uptake at the coral location. Such knowledge is essential to better understand the large-scale oceanic circulation.

Long records of coral $\Delta^{14}\text{C}$ from the southern GBR have been documented in several publications by Druffel and Griffin (1993, 1995, 1999). In this study, we provide an up to date seawater $\Delta^{14}\text{C}$ history from a *Porites* coral collected at Masthead Island, southern GBR (Figure 4.1). This bi-monthly $\Delta^{14}\text{C}$ record provides detailed information about the seasonal and interannual ocean circulation off northeast Australia on multiple time scales. The coral $\Delta^{14}\text{C}$ results imply that air-sea gradients have evolved to a new state, with surface seawater ^{14}C now higher than atmospheric $^{14}\text{CO}_2$, suggesting that the surface ocean can be a source of ^{14}C to the atmosphere in areas of CO_2 outgassing.

4.2 Materials and Methods

4.2.1 Coral location, preparation and age model

A modern *Porites* sp. coral core (MAS01E) was collected from Masthead Island ($23^\circ 31' 57''$ S, $151^\circ 44' 45''$ E) at a water depth of 4.5 m in August 2017 (Figure 4.1). Masthead Island is located 60 km from the Australian Coast and may occasionally be influenced by major river flood events (Cantin et al. 2018). Standard techniques were used to prepare the coral slices,

which are cut parallel to the axis of growth (Lough and Barnes 1990). Annual density banding from X-ray images were counted from the top (year of collection) to provide a preliminary age model. U/Ca seasonal cycles measured by Laser ablation–inductively coupled plasma–mass spectrometry (LA–ICP–MS) analysis were used to fine-tune this age model by matching U/Ca maxima to the winter sea surface temperature (SST) minima (Fallon et al. 1999). Age model errors are estimated to be ± 2 months from the geochemical analysis. Geochemical data for the age model were reported in Cantin et al. (2018).

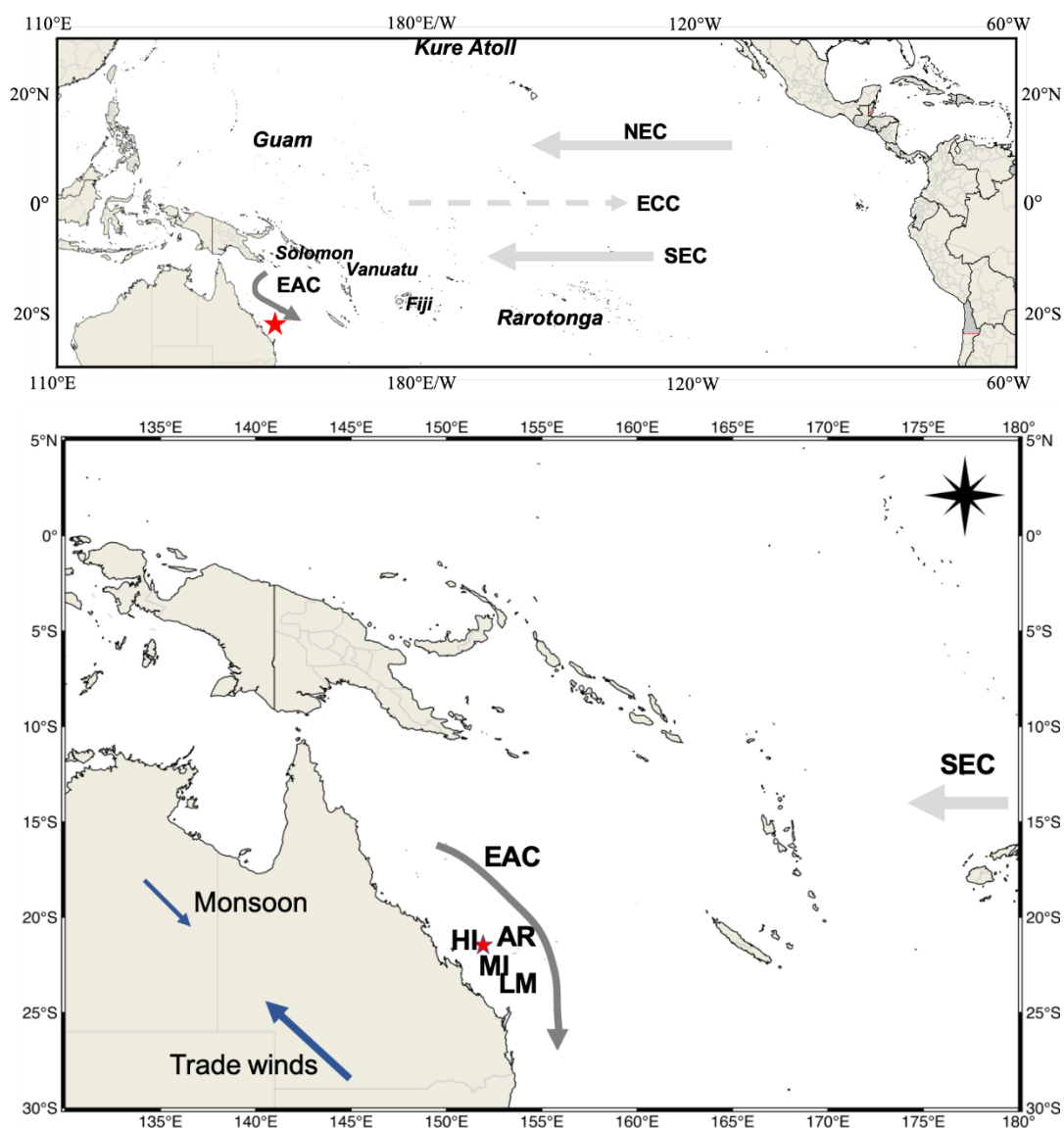


Figure 4.1 General surface circulation in the Pacific and off northeast Australia. The broad South Equatorial Current (SEC) flows westward and splits into two parts around latitude 15°S. The northern SEC branch forms the Hiri Current, and the southern branch forms the East Australian Current (EAC), which is the dominant current in the GBR region (Godfrey et al. 1980; Wijeratne et al. 2018; Oke et al. 2019). A red star represents sampling sites used in this study. MI, HI, LM and AR stand for Masthead

Island, Heron Island, Lady Musgrave and Abraham Reef, respectively. NEC is the North Equatorial Current and ECC is the Equatorial Counter Current. Blue arrows show the directions of southeast Trade winds from April to November and weaker northwest monsoons from December to March in northeast Australia (Steinberg 2007). This map was produced using Qgis.

4.2.2 ^{14}C analysis

Samples for ^{14}C analysis were drilled following the main growth axis. The pre-set track has a 2 mm width, 2.5 mm depth and 2 mm increment, which corresponds to ~5 samples per year. 5 mg of coral sample powders was placed in individual VacutainerTM tubes, evacuated, heated and acidified with 0.2 ml 85% orthophosphoric acid at 80°C. Generated CO_2 was purified and reduced to graphite by excess H_2 using Fe as a catalyst. Graphite samples were pressed into targets and measured by the single-stage Accelerator Mass Spectrometer (SSAMS) at the Australian National University (Fallon et al. 2010). All results are background corrected using ^{14}C -free marble and corrected using AMS online $\delta^{13}\text{C}$. ^{14}C results are reported as decay-corrected $\Delta^{14}\text{C}$ (Stuiver and Polach 1977).

4.3 Results

Figure 4.2 shows the surface ocean $\Delta^{14}\text{C}$ values as recorded in the Masthead Island coral, spanning the years 1945-2017. $\Delta^{14}\text{C}$ values averaged -49‰ in the pre-bomb period (1945-1953), with a linear decrease of 0.82‰ per year from 1945 to 1953, revealing a moderate Suess effect (Tans et al. 1979). $\Delta^{14}\text{C}$ values increased steadily from 1959 to 1970 as a result of the atmospheric bomb ^{14}C signal. $\Delta^{14}\text{C}$ values reached the post-bomb peak plateau in the late 1970s, and then $\Delta^{14}\text{C}$ values decreased gradually to ~40.3‰ by 2017, approximately corresponding to a linear decrease of 2.9‰ per year ($R^2=0.97$, linear regression calculated from 1982 to 2017).

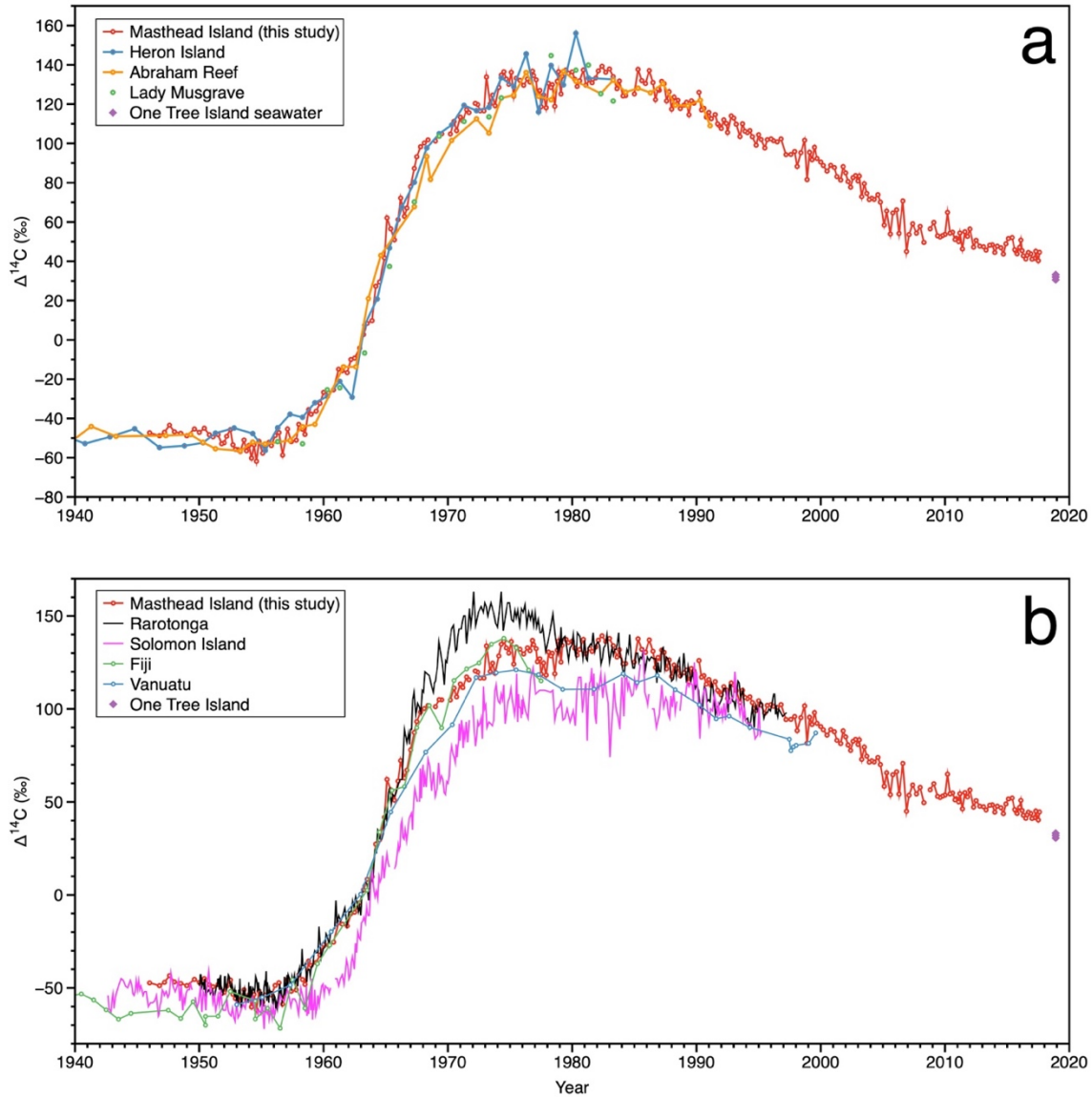


Figure 4.2 Comparison of $\Delta^{14}\text{C}$ records from Masthead Island (this study) and (a) southern GBR corals (Heron Island, Lady Musgrave, Abraham Reef (Druffel and Griffin 1993, 1995, 1999)), and (b) selected southern Pacific corals (Fiji (Toggweiler et al. 1991), Vanuatu (Fallon et al. 2003), Solomon Island (Guilderson et al. 2004), Rarotonga (Guilderson et al. 2000)).

4.4 Discussion

4.4.1 Radiocarbon time series in the Southern GBR and regional variations

Figure 4.2a shows a comparison between Masthead Island $\Delta^{14}\text{C}$ record and records from the other southern GBR corals which only extend through the 1980s (Heron Island, Lady Musgrave, Abraham Reef (Druffel and Griffin 1993, 1995, 1999)). The Masthead Island $\Delta^{14}\text{C}$ record is similar to other coral records in the southern GBR (Figure 4.2a) in general, confirming the East

Australian Current (EAC) as the primary water mass that feeds the central and southern GBR. However, some short-scale variations are also evident. The Masthead Island post-bomb $\Delta^{14}\text{C}$ values are similar to Heron Island but slightly higher than Lady Musgrave and Abraham Reef. Druffel and Griffin (1995) attributed lower values in Abraham Reef to the nearby shelf break (Andrews and Gentien 1982) which upwells low $\Delta^{14}\text{C}$ water to Abraham Reef. Although Masthead Island and Heron Island are physically close to each other (Figure 4.1), $\Delta^{14}\text{C}$ values from the two locations show small differences in late 1970s, with two measurements from Heron Island showing high $\Delta^{14}\text{C}$ values not reproduced in the Masthead Island coral (Figure 4.2a).

Figure 4.2b compares the Masthead Island $\Delta^{14}\text{C}$ record to other southern Pacific coral records (Fiji (Toggweiler et al. 1991), Vanuatu (Fallon et al. 2003), Solomon Island (Guilderson et al. 2004), Rarotonga (Guilderson et al. 2000)) which are all influenced by the South Equatorial Current (SEC). The Solomon Island record has the lowest $\Delta^{14}\text{C}$ values for all these locations (Figure 4.2b), representative of lower ^{14}C waters from the equatorial branch of the SEC due to equatorial upwelling. $\Delta^{14}\text{C}$ records from Masthead Island and Fiji are nearly identical (Figure 4.2b) for the post-bomb period, revealing that both sites are fed by the southern branch of the SEC (higher ^{14}C waters). For the pre-bomb period when $\Delta^{14}\text{C}$ was weakly controlled by air-sea exchange, the $\Delta^{14}\text{C}$ record from Fiji is lower (Figure 4.2b), Toggweiler et al. (1991) attributed this to older water from Peru upwelling. The Masthead Island $\Delta^{14}\text{C}$ values are mid-way between the values from Rarotonga and Vanuatu from 1967 to 1978 (Figure 4.2b). The elevated post-bomb peak recorded in Rarotonga reflects a strong air-sea exchange due to longer residence time of surface water in the south Pacific gyre (Guilderson et al. 2004). The Rarotonga record converges with the Masthead Island record in the late 1970s as the

atmospheric ^{14}C record is decreasing sharply reducing the air-sea ^{14}C gradient while the Masthead Island record displays the regional seawater ^{14}C .

4.4.2 Seasonal and interannual variability

A high-pass filter was subjected to the $\Delta^{14}\text{C}$ time series to extract the seasonal (2.5-year window, frequency ranging from 0.1-0.5) and interannual (20-year window, frequency ranging from 0.012-0.5) $\Delta^{14}\text{C}$ variations to compare with SST and ENSO records (Figure 4.3). Results show that the Masthead Island $\Delta^{14}\text{C}$ exhibits clear seasonal and interannual variability throughout the entire length of the time series. The amplitude varies from 2–10‰, with small amplitude (<5‰) being dominant. Masthead Island $\Delta^{14}\text{C}$ is in phase with SST most of the time during post-bomb period. Synchronous changes between $\Delta^{14}\text{C}$ and SST suggest seasonally different water masses bathed this location. The Masthead Island $\Delta^{14}\text{C}$ seasonal and interannual variability may result from seasonal latitudinal shifts of the SEC bifurcation and/or seasonal wind reversal. The SEC latitudinal bifurcation exhibits significant seasonal variations, with the southernmost position (16.4 °S) occurring in April and northernmost position (~13.9 °S) occurring in December (Zhai et al. 2014). A southern shift of the bifurcation latitude during wintertime may increase the amount of low $\Delta^{14}\text{C}$ waters from the upwelling-affected SEC, while a northern shift of the bifurcation latitude may bring in more non-upwelling waters from the Coral Sea which has higher $\Delta^{14}\text{C}$. Secondly, the central and southern GBR regions are influenced by seasonal wind reversals (Figure 4.1). From April to November, southeast trade winds are prevalent which move surface waters towards the northwest (onshore) (Steinberg 2007), suppressing the poleward-flowing EAC. ^{14}C is usually depleted in riverine dissolved inorganic carbon compared to seawater because it originates from old terrestrial organic matter which release CO_2 due to respiration and photo-oxidation. Masthead Island is near the Fitzroy and Calliope River catchments, so large freshwater input can possibly lower the surface ocean ^{14}C values in big floods. Therefore, the weak northward surface current during wintertime may

transport lower $\Delta^{14}\text{C}$ water to Masthead Island. During Austral summer (December to March), the northwest monsoon is more dominant, and the southern GRB region is mainly fed by the EAC (Steinberg 2007). It should be noted that northwest monsoons can also induce wind-driven shelf edge upwelling (Andrews and Gentien 1982). The variable timing and extent of upwelling may partially account for the out of phase association between $\Delta^{14}\text{C}$ and SST records. Masthead Island is located ~60 km offshore (inner continental shelf), which is unlikely to be affected by short-lived upwelling events. However, major upwelling events which occur every few years (e.g., during ENSO events) can extend to the entire continental shelf and modify shelf waters (Furnas and Mitchell 1996), thus confounding the Masthead Island $\Delta^{14}\text{C}$ seasonality in some years. After 1995, the phasing between $\Delta^{14}\text{C}$ and SST records becomes more variable (Figure 4.3), probably reflecting the changes in subsurface dynamics. The convective overturning of higher $\Delta^{14}\text{C}$ values between subsurface waters and the overlying surface waters was demonstrated in some Pacific ^{14}C depth profiles, which show higher ^{14}C in the mixed layer than in the surface water (Key 1996, Key et al. 1996, Key et al. 2002, Kumamoto et al. 2013).

The relationship between seawater ^{14}C and ENSO is quite variable in the South Pacific. Druffel and Griffin (1993, 1995) found that some El Niño events resulted in the displacement of low- $\Delta^{14}\text{C}$ waters into the southern GBR which lowered $\Delta^{14}\text{C}$ values at Abraham Reef. However, in other locations, such as the Galapagos (Guilderson and Schrag 1998), corals record higher $\Delta^{14}\text{C}$ values during most El Niño events because of the suppression of upwelling and long retention time of ^{14}C in surface water. The association of the Masthead Island ^{14}C record with ENSO is similar to the Abraham Reef coral record during post-bomb periods (Figure 4.3). Masthead Island $\Delta^{14}\text{C}$ values decreased during most El Niño events such as 1972-1973, 1976-1977, 1991-1992, and 1997-1998 but increased during other El Niño events such as 1982-1983. This may

be because some strong ENSO events caused the cessation of equatorial upwelling (Guilderson and Schrag 1998, Guilderson et al. 1998), so seawater $\Delta^{14}\text{C}$ values were higher compared to normal years.

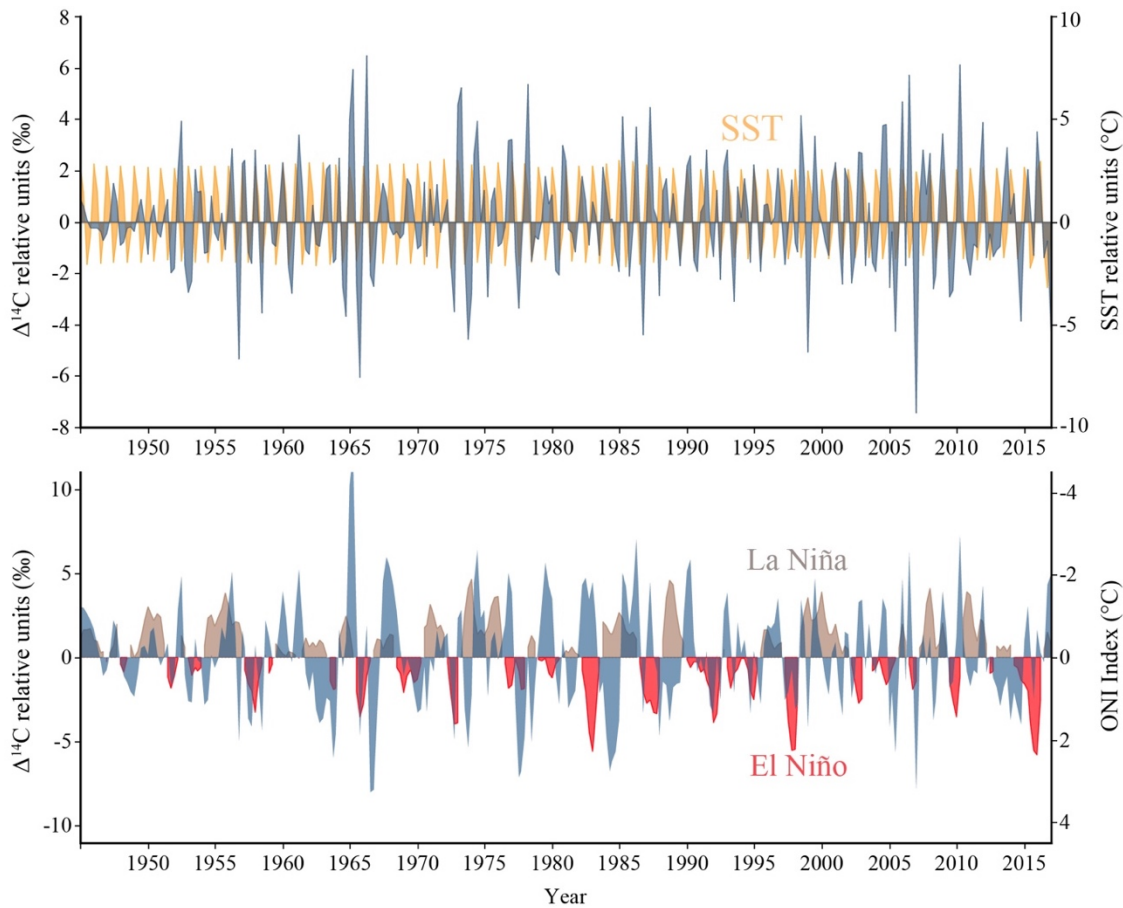


Figure 4.3 Comparison between southern GBR surface ocean $\Delta^{14}\text{C}$ record, SST record and ONI (ocean Niño index). Upper panel compares $\Delta^{14}\text{C}$ record with SST record after FIR high-pass filtering (2.5-year window, frequency ranging from 0.1-0.5). Lower panel compares $\Delta^{14}\text{C}$ record with ONI values after FIR high-pass filtering (20-year window, frequency ranging from 0.012-0.5). Blue colour represents filtered $\Delta^{14}\text{C}$ (relative units only), orange colour represents filtered SST (relative units only), red colour represents El Niño, grey colour represents La Niña.

4.4.3 Long-term oceanic ^{14}C uptake

Oceanic ^{14}C is controlled by air-sea exchange, lateral advection and shallow-to-deep ocean exchange. Oceanic uptake of bomb-derived ^{14}C increased sharply in the 1960s and early 1970s, continued during the 1980s, but slowed down throughout the 1990s and 2000s (Figures 4.2, 4.4). During the 1960s and early 1970s, post-bomb $\Delta^{14}\text{C}$ in the surface ocean was primarily affected by CO_2 gas exchange with the atmosphere due to the large air-sea $\Delta^{14}\text{C}$ gradient

(Figure 4.4a). Spatially variable $\Delta^{14}\text{C}$ values (Figure 4.2) indicate ^{14}C is more affected by ocean dynamics starting from the middle 1970s due to the weakening of air-sea $\Delta^{14}\text{C}$ gradients (Figure 4.4a).

The rise and the start of post-bomb peak plateau of Masthead Island $\Delta^{14}\text{C}$ are delayed by ~ 2 years compared to coral records from the equatorial and North Pacific (Figure 4.4b), which is in agreement with the delay between Northern and Southern Hemisphere $\Delta^{14}\text{C}$ values due to atmospheric troposphere mixing (Hua et al. 2013). Masthead Island $\Delta^{14}\text{C}$ peaks and levels off from 1975-1982 (Figures 4.2, 4.4), suggesting either the mixing with subsurface water is less intense during this time period or subsurface water is no longer severely depleted in ^{14}C , i.e., the vertical gradient in $\Delta^{14}\text{C}$ seawater has continued to decrease through time. After reaching the peak in 1982, Masthead Island $\Delta^{14}\text{C}$ values began decreasing at a rate of ~ 3.0 ‰ per year from 1982 to 2006 but slow to a rate of ~ 1.4 ‰ per year from 2006 to 2017 (Figure 4.2), revealing a change in the vertical inventories of the bomb ^{14}C in the GBR region (i.e., subsurface ocean starts to contain more young/high ^{14}C water) (Kumamoto et al. 2013).

After 1985, the air-sea ^{14}C gradient decreased but remained relatively constant among different locations (Figure 4.4b). The gradually emerging differences between Masthead Island, Guam and Kure Atoll coral records (Figure 4.4b) may therefore primarily reflect lateral advection and shallow to deep water exchange. Guam may be subject to increased inputs of lower ^{14}C waters due to equatorial upwelling, resulting in the Guam coral $\Delta^{14}\text{C}$ values decreasing more rapidly than Masthead Island during the mid-1990s (Figure 4.4b). The similarity between Masthead Island and Kure Atoll after the 1990s suggests the higher latitude regions had accumulated more bomb-derived ^{14}C , making the water less susceptible to dilution/modification from surrounding seawater with different ^{14}C signatures. In the 1990s, the Northern Hemisphere

atmospheric $\Delta^{14}\text{C}$ values became lower than those of Southern Hemisphere (Figure 4.4a, inset) (Hua et al. 2013), due to the greater release of anthropogenic CO_2 in the Northern Hemisphere. GBR seawater $\Delta^{14}\text{C}$ reached atmospheric level during the 2000s and started to overtake atmospheric $\Delta^{14}\text{CO}_2$ after 2010 (Figure 4.4). Even though the atmospheric ^{14}C has not been extended to 2018 (Hua et al. 2013, Turnbull et al. 2017), the downward trend of atmospheric ^{14}C does not cease because burning of ^{14}C free fossil fuels has continued and increased. Surface water $\Delta^{14}\text{C}$ samples from One Tree Island (30km offshore from Masthead Island) collected in November 2018 further confirmed that surface ocean $\Delta^{14}\text{C}$ is much higher than the atmosphere (Figure 4.4a). The air-sea $\Delta^{14}\text{CO}_2$ gradient reversed from positive to negative after 2010. The reversed gradient suggests that the ocean could start to return bomb-derived ^{14}C back to the atmosphere if the CO_2 gradient is favourable, and approach a significantly different state of equilibrium compared to the pre-industrial and pre-bomb eras.

4.4.4 Utilizing GBR coral ^{14}C records as a dating reference series

Bomb-derived ^{14}C recovered from hermatypic corals can be used to estimate the ages of other marine calcifying organisms (Fallon and Guilderson 2005; Andrews et al. 2016b; Andrews et al. 2018). Bomb ^{14}C dating of marine organisms can be done by projecting the measured ^{14}C values to the ^{14}C reference coral records using marker points (e.g., year of collection) (Fallon and Guilderson 2005; Andrews et al. 2018). Accurate estimation of the longevity and/or age of marine organisms is crucial to help manage exploited marine populations and comprehensively understand oceanographic/climate variability. The Masthead Island $\Delta^{14}\text{C}$ record provides a high-precision seawater ^{14}C history in the GBR regions covering pre-bomb era (1945) to the present (2017). The Masthead record in conjunction with the published records by Druffel and Griffin (1993, 1995, 1999) offer an opportunity to robustly date marine organisms collected in the GBR region and better understand the evolution of the GBR ecosystems.

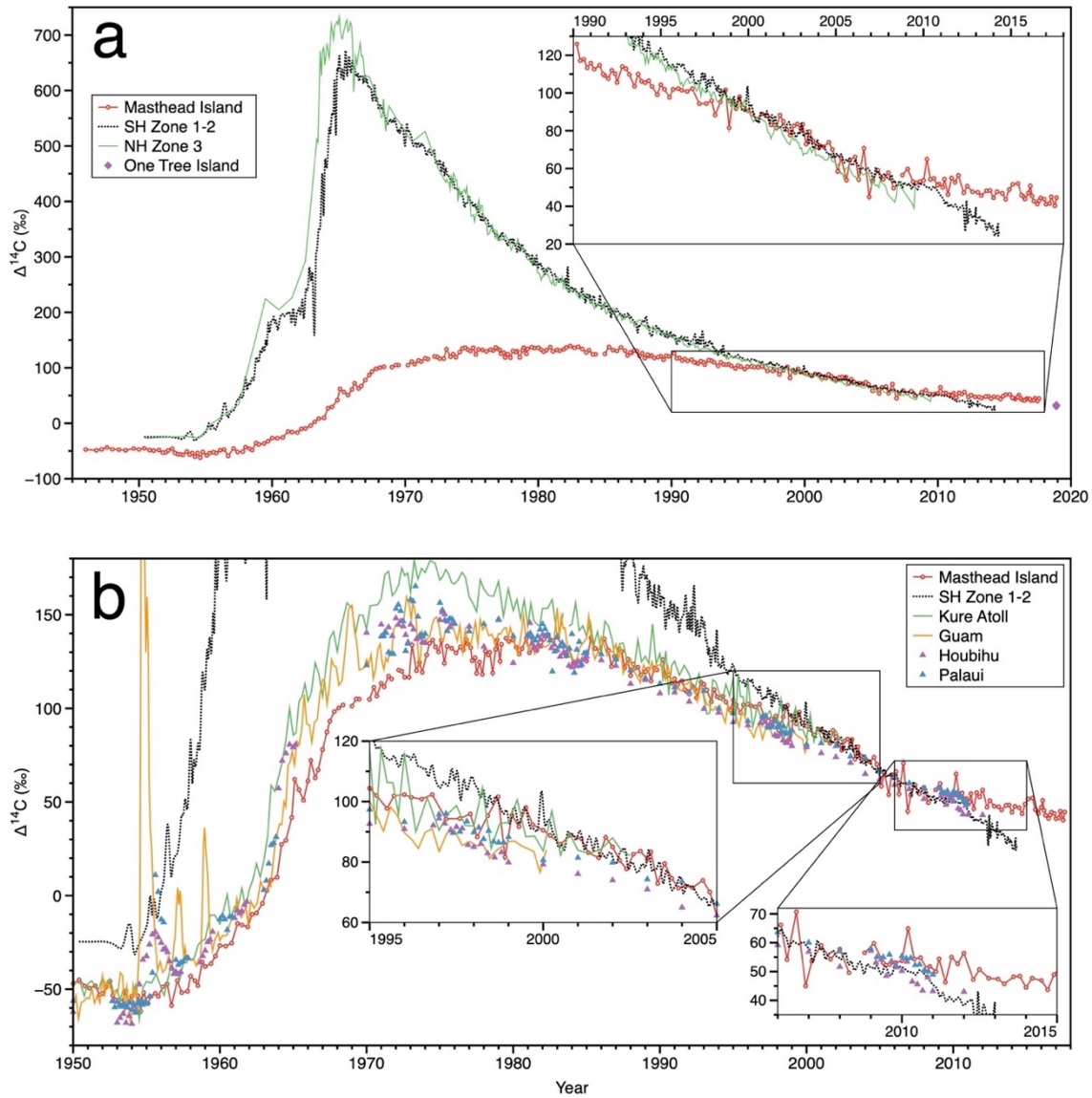


Figure 4.4 Comparison of $\Delta^{14}\text{C}$ records between Masthead Island (this study), atmospheric record (Hua et al. 2013) and four north Pacific coral sites (Guam (Andrews et al. 2016a), Kure Atoll (Andrews et al. 2016b), Houbihu and Palau (Ramos et al. 2019)). The insert in panel (a) shows the close-up comparisons between southern atmospheric ^{14}C and northern atmospheric ^{14}C after 1990, and between Masthead Island record with atmospheric record after 1990. The left insert in panel (b) shows Masthead Island and Kure Atoll converged with southern atmospheric ^{14}C around 2000 and were later on joined by Houbihu in 2004. The right insert in panel (b) shows Masthead Island and Palau ^{14}C are higher than atmospheric ^{14}C after 2010.

4.5 Conclusion

Oceanic uptake of bomb-derived ^{14}C can provide useful information on air-sea diffusion and seawater mixing dynamics. After the conclusion of bomb testing, the redistribution of bomb-derived ^{14}C has been robustly recorded by corals throughout the tropical oceans. The Masthead

Island coral record is in agreement with previously published coral records in the GBR and extends the record from the 1980s to 2017 confirming that the southern GBR is mainly influenced by the EAC. $\Delta^{14}\text{C}$ seasonality in the Masthead Island coral may result from changing influences of the SEC due to the seasonal shift of the bifurcation latitude and seasonal wind reversal. The extended $\Delta^{14}\text{C}$ time series through 2017 also suggests oceanic ^{14}C is no longer primarily controlled by air-sea exchange in the past two decades, instead, shallow-to-deep ocean exchange is playing a more important role. The air-sea diffusion may reach a new state of equilibrium as a result of the bomb-derived ^{14}C and continuous fossil fuel emissions. The Masthead $\Delta^{14}\text{C}$ record provides a continuous and validated high-resolution ^{14}C timeseries, making the age estimate of other marine organisms possible in the GBR region.

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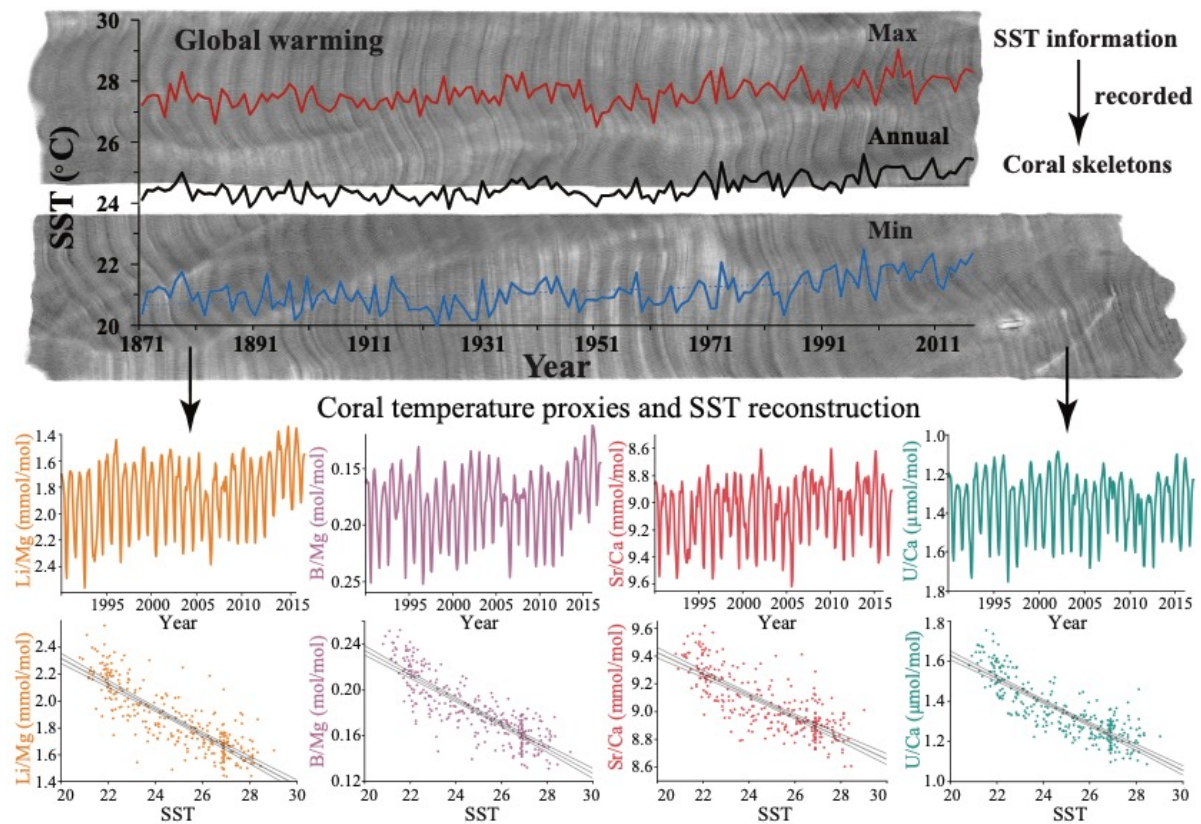
Chapter 5: Assessing multiproxy approaches (Sr/Ca, U/Ca, Li/Mg, and B/Mg) to reconstruct sea surface temperature from coral skeletons throughout the Great Barrier Reef

Chapter overview:

Chapter 3 and chapter 4 have demonstrated that coral $\Delta^{14}\text{C}$ is a reliable tracer for ocean circulation and climate variability such as El Niño-Southern Oscillation. Chapter 4 also reveals that air-sea $^{14}\text{CO}_2$ equilibrium has evolved to a new state which provides new insights for the oceanic uptake of anthropogenic CO_2 . The increasing amount of CO_2 has contributed to the rise of temperature and has adverse impacts on the global climate and ecosystems. For example, coral bleaching is associated with the increasing thermal stress as a result of global warming. Besides, deforestation, agriculture, urbanization, mining and other anthropogenic disturbances have contributed to soil erosion and enhanced the inputs/transport of terrestrial sediments and other contaminants into oceans. Chapter 5-7 therefore focus on the local scale reconstruction of anthropogenic environmental changes in the Central and Southern Great Barrier Reef (GBR) using multiple elemental ratios.

Chapter 5 has been published in *Science of The Total Environment*. Wu, Y., Fallon, S.J., Cantin, N.E. and Lough, J.M., 2021. Assessing multiproxy approaches (Sr/Ca, U/Ca, Li/Mg, and B/Mg) to reconstruct sea surface temperature from coral skeletons throughout the Great Barrier Reef. <https://doi.org/10.1016/j.scitotenv.2021.147393>. The content in this chapter is reproduced entirely in the exact same format of the published manuscript except that the references are merged into the thesis references. Supplemental information published along with the manuscript has been put at the end of this chapter. Author contribution has been stated after acknowledgement.

Graphical Abstract



Keywords:

Marine carbonate geochemistry; Paleoclimate records; Inter-colony variability

Highlights:

- Changes in sea surface temperature are important for understanding climate change
- Four seawater temperature proxies from *Porites* corals in Australia were assessed
- Li/Mg and B/Mg had better correlations with SST compared to Li/Ca and B/Ca
- U/Ca and Sr/Ca had better long-term reliability than Li/Mg and B/Mg
- Sea surface temperatures in this area are increasing

Abstract

Due to the increasing concerns of global warming and short instrumental records of sea surface temperature (SST), coral-based proxies, such as $\delta^{18}\text{O}$, Sr/Ca, U/Ca, and Li/Mg have been developed and applied to reconstruct SST in paleoclimate studies. However, these proxies are not universally applicable in different environments, because they are affected by coral physiology and various environmental factors. In this study, seven long-lived *Porites* corals were collected from the southern sector of the Great Barrier Reef (GBR) off the coast of Gladstone and the central sector of the GBR within the Whitsunday Islands in 2017 and 2018. Coral sites were selected to cover a wide latitudinal range with different annual temperature ranges. Century-long geochemical records (Li/Ca, B/Ca, Mg/Ca, Sr/Ca, and U/Ca) were generated using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) at weekly resolution. This study has tested the robustness of two traditional temperature proxies (Sr/Ca and U/Ca), a recently developed temperature proxy (Li/Mg), and an additional potential temperature proxy (B/Mg). U/Ca was found to be the most robust and stable temperature proxy for corals from the GBR over long-term timescales. Sr/Ca is a close second, however due to the lower response of Sr fractionation per 1 °C, it is more sensitive to analytical methods and less sensitive to annual SST changes than U/Ca. Li/Mg and B/Mg have clearer periodicity compared to Li/Ca and B/Ca. Both Li/Mg and B/Mg are strongly correlated with SST, which is due to the cancellation of temperature-independent commonality. Empirical calibrations established from this multi-proxy approach increase the certainty of temperature reconstruction when a single proxy does not perform well. These site- and colony-specific SST calibrations also provide an opportunity to revisit the universal multi-trace element calibration of sea surface temperatures (UMTECS) model, which does not require the knowledge of local SST for calibration.

5.1 Introduction

Continuous climate records on century timescales that precede the instrumental record are essential components to determine how climate change and global warming is affecting the tropical ecosystems (Abram et al., 2020; Chen et al., 1997; Gagan et al., 2000; Jiang et al., 2019; Lough, 2010; Lough et al., 2018; Sowers and Bender, 1995). Due to increasing concerns of global warming and short instrumental records of sea surface temperature (SST), natural archives such as corals have been developed and applied to reconstruct SST in tropical reef locations for paleoclimate and paleoenvironment studies (Beck et al., 1997; Urban et al., 2000). *Porites* coral colonies are long-lived solitary individuals that provide annual growth patterns that can be visualised through X-ray techniques, providing an opportunity to extend instrumental SST records by several hundred years (Abram et al., 2020; DeLong et al., 2014; DeLong et al., 2013).

Variations in elemental ratios (such as Li/Ca, B/Ca, Mg/Ca, Sr/Ca, U/Ca, and Li/Mg) and $\delta^{18}\text{O}$ preserved in coral skeletons were found to strongly correlate with SST leading to the application of these proxies to reconstruct past SST (Bryan and Marchitto, 2008; Fallon et al., 2003; Fallon et al., 1999; Fowell et al., 2016; Hathorne et al., 2013; Min et al., 1995; Montagna et al., 2014; Shen and Dunbar, 1995; Sinclair et al., 1998). Among the studies, Sr/Ca and $\delta^{18}\text{O}$ were usually considered as the most robust temperature proxy (Alibert and McCulloch, 1997; Beck et al., 1992; McCulloch et al., 1999; Smith et al., 1979). However, these SST proxies are not universally applicable in different environments. Empirical calibrations (proxies vs SST) can vary between different sites and between different coral colonies under similar seawater conditions (Fallon et al., 2003; Marshall and McCulloch, 2002; Sinclair, 2015). These observed variations can partially result from differences in analytical methods, calibration standards, sampling resolutions, SST datasets, and environmental conditions (Armid et al., 2011; Correge,

2006; Fallon et al., 2003; Ourbak et al., 2006; Quinn and Sampson, 2002; Sinclair et al., 1998). More importantly, physiological and physicochemical processes (“vital effects”) also affect trace element partitioning, raising the concern that these proxies are not purely temperature dependent and may be further regulated by vital effects from the coral host calcification rate. Such vital effects significantly reduce the universal application of these proxies and make colony specific calibration necessary. The most accurate way to overcome vital effects is by calibrating the available SST and geochemical data from the individual coral colony and then applying the calibration curve to the rest of the coral skeletal geochemical records where instrumental SST data is not available (Fowell et al., 2016; Sinclair, 2015). This approach has site limitations due to the lack of instrumental records in remote areas. It is therefore difficult to utilize fossil corals if there are no overlaps with modern corals. Recently, a few models have been developed to attempt to circumvent vital effects, such as Rayleigh-Based Multi-Element (RBME) coral temperature reconstruction (Gaetani et al., 2011), Sr-U thermometry (Alpert et al., 2017; DeCarlo et al., 2016), and universal multi-trace element calibration of sea surface temperatures (UMTECS) (D'Olive et al., 2018). These models are useful approaches to avoid in-situ calibrations, improve annual temperature calibrations, or obtain the calibration curves without using SST.

In this study, centennial-scale geochemical information of Li/Ca, B/Ca, Mg/Ca, Sr/Ca, U/Ca, Li/Mg, and B/Mg were extracted from seven long-lived *Porites* coral cores at high temporal resolution. Coral cores collected in this work have a wide latitudinal spread covering the Central and Southern GBR, which have different annual SST ranges (Max and Min temperature range). Power spectrum analysis was used to estimate the periodicity of different elemental ratios. Principal Component Analysis was performed to understand how different normalizations (e.g., Li/Ca vs Li/Mg) correlate with SST. In addition, universal multi-trace

element calibration of sea surface temperatures (UMTECS) by D'Olivo et al. (2018) was revisited and tested using the empirical calibrations established in this study. The main objective of this work was to assess the reliability of using Sr/Ca (traditional paleothermometer), U/Ca (traditional paleothermometer), Li/Mg (recently developed paleothermometer) and B/Mg (potential paleothermometer proposed in this study) to reconstruct SST in the Central and Southern GBR using LA-ICPMS. This multi-proxy approach can potentially improve the applicability of coral palaeothermometry over a single elemental ratio temperature reconstruction.

5.2 Methods

5.2.1 Study area and climate information

Gladstone Harbour, the world's fourth largest coal exporting terminal, is located in the Australian subtropics, ~520 km northeast of Brisbane. Gladstone Harbour is surrounded by Curtis Island to the north and Facing Island on the east and southeast, with the terrestrial freshwater inputs from the Fitzroy, Calliope, and Boyne Rivers (Figure 5.1). The Whitsunday Islands lies within the Australian tropics off the central coast of Queensland. The Whitsunday Island region is an important gateway for tourism in central GBR and is mainly influenced by Proserpine and O'Connell Rivers (Figure 5.1). Both the Gladstone and Whitsundays regions have wet summers and dry winters. Approximately 75% of the precipitation occurs during the Australian Monsoon season which is influenced by seasonal North Westerly winds which deliver moist tropical air masses promoting sustained rain and storms in the summer (December - April) (Lough 2007). The summer monsoons can also bring tropical cyclones into both regions. The winter half year (April to October) is usually associated with minimal precipitation. Along with strong seasonality, rainfall and river flows in north-eastern Queensland show high inter-annual variability linked to El Nino Southern Oscillation (ENSO) variability (Lough 2007). Despite some disparity in annual discharge from rivers across

latitudinal gradients, decadal variation in drought and flood cycles across the Queensland coastline reveal coherent patterns in monsoon activity on decadal time scales (Cantin et al., 2018, 2019).

Porites spp. coral cores were collected from five locations in the Southern GBR (Gladstone region) in May and August 2017 and from the Central GBR throughout the Whitsunday Islands in February 2018 (Figure 5.1, Table S5.1). South End Curtis Island (SEN01C; 23.75 °S 151.31°E) is in the north channel between Facing Island and Curtis Island within proximity to the Gladstone Harbour and the river mouth of Calliope River and Boyne River (Figure 5.1). Hummocky Island (HUM03A, HUM04B; 23.40°S 151.14°E) is located to the north of Curtis Island, ~30 km from the mouth of Fitzroy River. Both South End Curtis Island and Hummocky Island are inshore coastal reef locations. Masthead Island (MAS02A; 23.53°S 151.74°E) is located ~60 km northeast offshore from Gladstone Harbour in the Capricorn Bunkers group. In the Whitsunday Islands, Shaw Island (SHW82C; 20.48°S 149.07°E) is located ~40 km from the mouth of Proserpine and O'Connell Rivers and South Molle Island (SMI01C and SMI81A; 20.26°S 148.83°E) is located near the exit of Whitsunday passage.

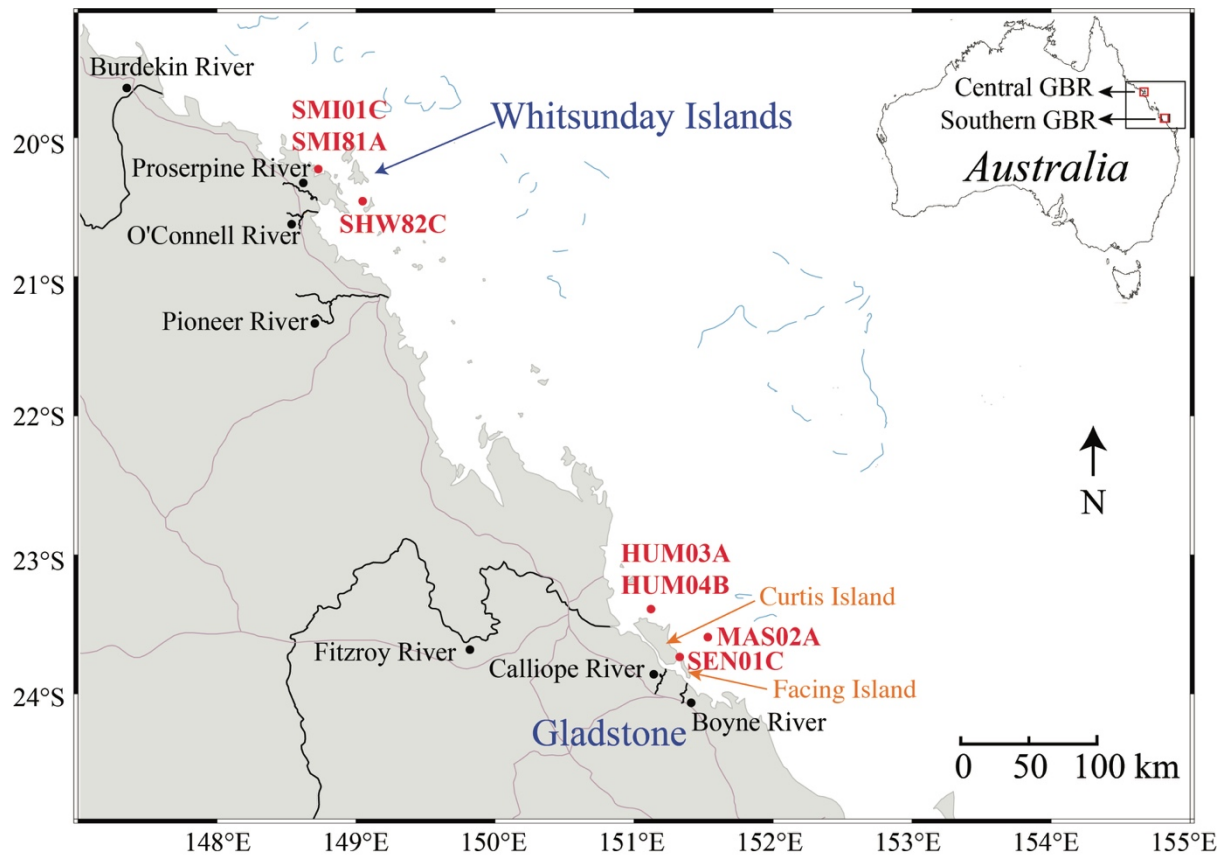


Figure 5.1 Sample locations (red circles) for the coral cores from the Southern GBR (Gladstone region) and from the Central GBR (Whitsunday Islands). HUM03A and HUM04B from Hummock Island were collected from different colonies; MAS02A was collected from Masthead Island; SEN01C was collected from South End Curtis Island; SMI01C and SMI81A from South Molle Island were collected from the same colony in 1984 and for this study in 2018; SHW82C was collected from Shaw Island. Note: Symbols for SMI01C and SMI81A overlap with each other, and symbols for HUM03A and HUM04B overlap with each other.

5.2.2 Sea surface temperature (SST)

In-situ monthly SST data were obtained from the Australian Institute of Marine Science (AIMS) temperature loggers located at the sampling sites or by averaging the overlapping data from nearby sites (Figure S5.1). In-situ data can be accessed via the AIMS website (<http://data.aims.gov.au/>). Overall, in-situ data at these locations covers the time period of the 1990s to present. For South Molle Island (SMI81A), logger data was obtained from Daydream Island. For Shaw Island (SHW82C), logger data was obtained from Seaforth Island and Pine Island. In-situ SST for the mid-shelf offshore site Masthead Island (MAS01E) was obtained by averaging data from 9 loggers (Boult Reef, Erskine Island, Heron Island, Lady Musgrave, Masthead Reef, North Reef, One Tree Island, Tryon Island, Wreck Island) within 30 km of

Masthead Island. In-situ SST for Hummocky Island (HUM02A and HUM03A) was obtained by averaging data from 7 loggers (Barren Island, Half tide Rocks, Halfway Island, Humpy Island, North Keppel Island, Peak Island, and Pelican Island) within 30 km of Hummocky Island. In-situ data was not available from Facing Island, so satellite-derived SST was used for the coral collected from South End Curtis Island (SEN01C).

A limitation of the in-situ logger SST is that the data record is not continuous and is short in length (Figure S5.1). To obtain a more complete dataset, NOAA's Optimum Interpolation Sea Surface Temperature (OISST) (Reynolds et al., 2007) and Hadley Centre Sea Ice and Sea Surface Temperature (HadISST) (Rayner et al., 2003) were examined and used in this work. The HadISST grid box for Gladstone and Whitsunday corals was centered on 23.5°S 151.5°E and 20.5°S 148.5°E, respectively. OISST has higher spatial resolution ($0.25^\circ \times 0.25^\circ$) so OISST datasets for the individual locations were obtained (Figure S5.1). A comparison of the in-situ SST, OISST and HadISST SST records over the time period 1990-2017 shows that both satellite-derived datasets were strongly correlated with in-situ SST (Figure S5.2) but the correlation between OISST and in-situ SST ($r^2 > 0.98, p < 0.01$) was higher than the correlation between HadISST and in-situ SST ($r^2 \sim 0.92-96, p < 0.01$). In comparison to the satellite-derived SST, the in-situ loggers recorded colder winter temperature in reefs closer to the continental coast (Figure S5.1a, b, c), similar to Fallon et al., (2003). However, the in-situ logger SST has a lower amplitude compared to the satellite SST for the mid-shelf MAS01E coral site (Figure S5.1d). Linear relationships between in-situ SST and OISST were used to construct the composite/adjusted SSTs (Fallon et al., 2003; Kawakubo et al., 2017) for the continuous period of 1990-2016. The adjusted OISSTs were then used to calculate the correlations between different elemental ratios and SST during this assessment period (1990-2016).

5.2.3 Sample preparation and LA-ICP-MS analysis

Coral cores were processed at the AIMS Coral Core archive by slicing into parallel 6.5 mm thick slices. The core slices were X-rayed and undertook gamma densitometry and luminescence analyses (Chalker and Barnes, 1990; Lough et al., 2002). Coral slices were cut along the maximum growth axis into sequential 95×25 mm pieces to fit into the laser sample holder for geochemical analysis at the Research School of Earth Sciences, the Australian National University. The sections were cut using a bandsaw from the back side of the skeleton, with the blade entering half the depth of the skeleton at which point the pieces were fractured by hand to ensure that each piece fits together continuously down core. Coral skeletons were cleaned 3 times using an ultrasonic probe with Milli-Q water and then oven-dried at 60 °C.

Laser ablation–inductively coupled plasma–mass spectrometry (LA–ICP–MS) was used to measure the abundance of ^7Li , ^{11}B , ^{24}Mg , ^{43}Ca , ^{86}Sr , and ^{238}U . This technique provides relatively fast and high spatial resolution analysis of seasonal to decadal changes in elements incorporated into the coral skeletal matrix (Alibert and Kinsley, 2008; Fallon et al., 1999; Kawakubo et al., 2017; Moyer et al., 2012; Sinclair et al., 1998). A 193 nm ArF Helex MkII excimer laser system was used to ablate the coral slices. A Varian 820 single collector ICPMS and a Thermo iCAP RQ ICPMS were used to measure the coral material sent from laser chamber. Analysis tracks were selected by following the main axis of coral growth (Alibert and McCulloch, 1997; DeLong et al., 2007; DeLong et al., 2013).

Before analysis, samples were cleaned twice by the laser using a slit 200 μm wide parallel to the growth axis and 600 μm wide perpendicular to the growth axis at a 10 Hz laser pulse repetition rate. This removed ~ 10 μm of coral materials from the surface (Prouty et al., 2010; Wyndham et al., 2004). This preablation process was shown to aid in increasing the

reproducibility of repeat runs in the same track (Fallon et al., 2002; Moyer et al., 2012; Prouty et al., 2010; Sinclair et al., 1998; Wyndham et al., 2004). Scan speed for preablation was set to 200 $\mu\text{m/s}$. For analysis, a rectangular slit 100 μm wide parallel to the growth axis and 500 μm wide perpendicular to the growth axis was used with a 5 Hz laser repetition rate and a scan speed of 100 $\mu\text{m/s}$. After data averaging, each data point corresponds to ~ 0.59 mm of coral extension. The NIST 614 and NIST 612 glass standards (Horn et al., 1997; Pearce et al., 1997) were used for the minor trace element (^7Li), and an inhouse developed coral standard from Davies Reef, Great Barrier Reef (GBR) was used for major coral elements (^{11}B , ^{24}Mg , ^{43}Ca , ^{86}Sr , and ^{238}U) (Fallon et al., 1999; Fallon et al., 2002). The entire sampling routine consisted of ~ 200 s of background with the laser off, ~ 120 s of analysis of the NIST 614, ~ 120 s of analysis of the NIST 612, ~ 120 s of analysis of the coral standard, the track along the coral, then a second analysis of the coral standard, the NIST 612, the NIST 614 and a further 200s of background.

Trace elemental concentrations were reported as ratios normalized to ^{43}Ca (element/Ca ratios). Raw counts were background subtracted, drift corrected and calibrated from standards using the *LAtools* Python package, which was developed for the reproducible reduction of LA-ICP-MS data (Branson et al., 2019). The analytical uncertainty of this LA-ICP-MS technique is listed in Table S5.2. By substituting the analytical uncertainty to the normal element/Ca vs SST calibration equations (Tables 5.1, S5.3), an SST uncertainty was estimated to be 0.5 $^{\circ}\text{C}$ for B/Ca, 0.7 $^{\circ}\text{C}$ for Mg/Ca, 2.1 $^{\circ}\text{C}$ for Sr/Ca, and 0.7 $^{\circ}\text{C}$ for U/Ca (Fallon et al., 2003; Sayani et al., 2019).

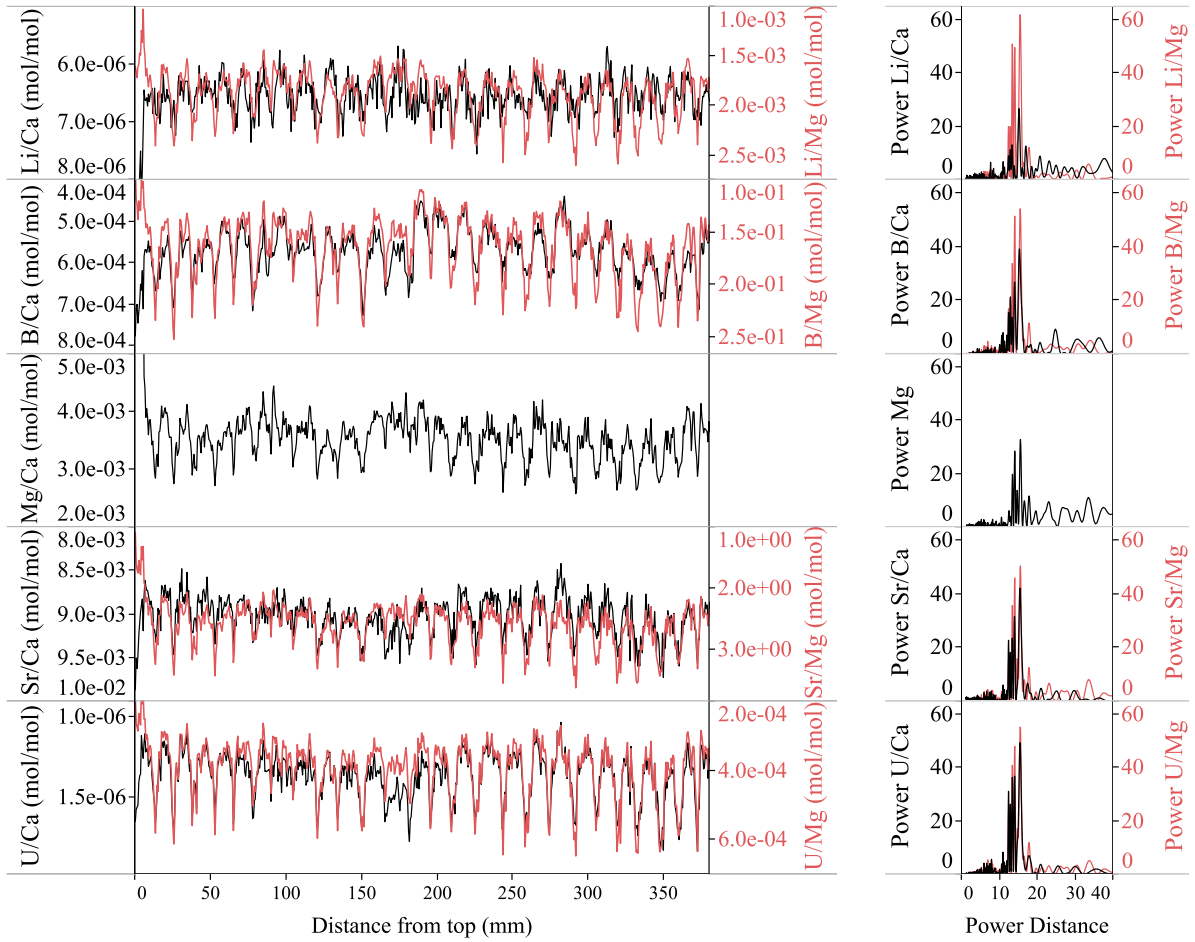


Figure 5.2 Results of elemental ratios vs distance (left panel) and power spectra analysis of Li/Ca, Li/Mg, B/Ca, B/Mg, Mg/Ca, Sr/Ca, Sr/Mg, U/Ca, and U/Mg (right panel) (using HUM03A as an example, similar results can be obtained for other corals). Black color is the traditional normalization to Ca, and red color is the normalization to Mg. All elemental ratios have clear cycles but the normalization to Mg significantly enhance the periodicity of Li/Ca and B/Ca. After translating distance to time, each power spectra document a 12-month (1 year) periodicity at $p < 0.01$ (see Figure S5.5).

5.2.4 Age models and statistical analyses

Coral elemental ratios need to be translated from length to time to make direct comparisons to the SST record. Preliminary age models were made by counting annual high-low density bands from the living tissue layer at the top of the core in relation to the collection year and then fine-tuned by geochemical records. U/Ca was used as the major temperature proxy to construct time series for all corals because of its long-term clear seasonal cycles (Figure S5.3).

Like other studies (Chen et al., 2019; D'Olivo et al., 2018; Fallon et al., 2003), clear sharp peaks (U/Ca maxima in this study) occurred during the winter with broad wide valleys (U/Ca minima) occurring in summer. Therefore, the relationship of elemental ratios vs SST was made by

aligning the maximum U/Ca values to the minimum SST values, and by aligning the minimum U/Ca values to the maximum SST values where appropriate. During some challenging years when U/Ca anomalies were evident, other elemental ratios (e.g., Sr/Ca, B/Ca, Mg/Ca, and Li/Mg) were utilized to assist the establishment of chronology. Coral growth was assumed to be linear between the winter minimums and summer maximums (D'Olive et al., 2018). Geochemical data between winter maximum and summer minimum were re-sampled by linear interpolation using Analyseries 2.0.8 (Paillard et al., 1996). Analyseries was also used to reduce the data resolution from weekly to monthly to facilitate the correlation analysis between elemental ratios and monthly SST records. To test how different elemental ratios tracked temperature, the root mean square error was calculated, defined as:

$$RMSE = \sqrt{\frac{1}{n} \sum_{i=1}^n (Predicted_i - Actual_i)^2}$$

where $Predicted_i$ is the i 'th coral-derived SST, $Actual_i$ is the i 'th instrumental SST record, and n is the total number of monthly data during the calibration period.

Classic power spectrum analysis was used to evidence periodicity of Li/Ca, Li/Mg, B/Ca, B/Mg, Mg/Ca, Sr/Ca, Sr/Mg, U/Ca, and U/Mg by documenting the average frequencies over each coral's analysed period. Power spectrum analysis was generated using PAST 3.2 (Hammer et al., 2001). Correlation analysis and Principal Component Analysis (PCA) (e.g., Chen et al., 2018; Feng et al., 2019; Pandolfi et al., 2003; Lough et al., 2020) were performed to better interpret the grouping of trace elements and their mutual correlations. Effective number of freedom (v_{eff}) and p values were adjusted to account for lag-1 autocorrelation when reporting the statistical significance of a correlation (Hu et al., 2017). PCA is a classic classification system based on linear classification. PCA uses linear fitting to reduce high-dimensional data (e.g., Li/Ca, Li/Mg, B/Ca, B/Mg, Mg/Ca, Sr/Ca, Sr/Mg, U/Ca, and U/Mg) which are originally

distributed in multiple dimensions, and projects these transformed data onto several new axes (PC loadings) to facilitate visualization and interpretation.

5.3. Results

5.3.1 Elemental ratios

A comparison of the Li/Ca, Li/Mg, B/Ca, B/Mg, Mg/Ca, Sr/Ca, and U/Ca ratios from different coral cores with SST is presented in Figure S5.3. Geochemical records at HUM03A, HUM04B, MAS02A, SEN01C, SMI01C, SMI81A, and SHW82C encompassed the time periods of 1898-2017, 1978-2017, 1906-2017, 1902-2017, 1860-1984, 1975-2017, and 1949-2017, respectively. Seasonal cycles were clear for all elemental ratios except for Li/Ca. These elemental ratios varied in conjunction with changes in sea surface temperature (Figure S5.3). Li/Ca, Li/Mg, B/Ca, B/Mg, Sr/Ca, and U/Ca were negatively correlated with SST, while Mg/Ca was positively correlated with SST. Some corals have anomalously high values of Li/Ca, B/Ca, or Mg/Ca at the core tops, which contains large quantities of organic material within the tissue layer thus accumulating the deposition of these elements. Besides, non-sinusoidal “cryptic” signals were also evident for some elemental ratios during certain time periods. For example, short-term (weekly to monthly) anomalies of U/Ca, Sr/Ca, and Mg/Ca ratios were recorded at HUM03A for years 2005, 2009, and 2010 (Figure S5.3a), while these elemental ratios displayed clear seasonal cycles in the same years at the adjacent coral core HUM04B (Figure S5.3b). To accommodate the in-situ SST availability and to avoid elemental ratio anomalies as a result of the tissue layer at the top of the core, the assessment/calibration period was selected to be 1990-2016. Over this common period, medium values of coral Li/Ca, Li/Mg, B/Ca, B/Mg, Mg/Ca, Sr/Ca, and U/Ca ranged from 5.70 to 7.54 $\mu\text{mol/mol}$, 1.63 to 1.86 mmol/mol , 0.49 to 0.61 mmol/mol , 0.11 to 0.17 mol/mol , 3.05 to 4.57 mmol/mol , 8.73 to 9.01 mmol/mol , and 1.10 to 1.44 $\mu\text{mol/mol}$, respectively (Figure S5.4).

5.3.2 Periodicity and correlation

Li, B, Sr, and U were normalized to Mg to explore the periodicity of Li/Mg, B/Mg, Sr/Mg, and U/Mg and their sensitivities to SST in comparison to Li/Ca, B/Ca, Sr/Ca, and U/Ca. Power spectrum analysis showed that the annual growth rate derived from different elemental ratios varied within a narrow range of 13-15 mm per year (Figure 5.2), which is comparable to the annual growth rate ($14.3 \text{ mm} \cdot \text{yr}^{-1}$) based on density bands. After the conversion from distance to time, each elemental ratio contained a dominant one-year periodicity (Figure S5.5). Power spectrum analysis also showed that the seasonal variations of Li/Mg and B/Mg were clearer than those of Li/Ca and B/Ca, but the seasonal variations of Sr/Ca and U/Ca did not show an improvement after normalizing to Mg (Figure 5.2). Correlation analysis showed that Sr/Ca and U/Ca as well as Mg/Ca and U/Ca were strongly correlated ($r > 0.8$, $p < 0.01$) at most sites (Table S5.4). For other elemental ratios in most corals, Li/Ca was weakly correlated (not statistically significant at most sites, Table S5.4) with B/Ca, Mg/Ca, Sr/Ca, and U/Ca, while B/Ca was highly correlated with Sr/Ca and U/Ca ($r > 0.6$, $p < 0.01$; Table S5.4).

5.3.3 Principal Component Analysis

Principal Component Analysis (PCA) was performed to classify the large datasets (Li/Ca, B/Ca, Mg/Ca, Sr/Ca, U/Ca, Li/Mg, B/Mg, Sr/Mg, and U/Mg) and identify the dominant factors that influence the data variability. For each coral core, two principal components (PC1 and PC2) explained ~90% of the total variance, showing that two independent processes control the partitioning of these elements (Li, B, Mg, Sr, and U). For better comparison and interpretation, loading plots were adjusted by rotating an angle of θ , which is the angle between SST data points and PC1 axis (Figure S5.6). The rotated PC1 (RPC1) is then considered to represent an SST dependent factor while rotated PC2 (RPC2) is an SST independent factor. Results showed that Sr/Ca and U/Ca were tightly clustered, and their variance were dominated by RPC1 while Li/Ca and B/Ca were more prone to be affected by both RPC1 and RPC2 (Figure 5.3). Similar

to the power spectrum analysis, Li/Mg, B/Mg, Sr/Mg, and U/Mg were placed in context with Li/Ca, B/Ca, Sr/Ca, and U/Ca for each coral core (Figure 5.3). Results showed that the normalization to Mg significantly improved Li and B's sensitivity to SST; that is, Li/Mg and B/Mg were more correlated with RPC1 than Li/Ca and B/Ca. However, normalization to Mg did not improve Sr and U's sensitivity to SST, instead, Sr/Mg and U/Mg were more affected by the secondary control (RPC2) (Figure 5.3).

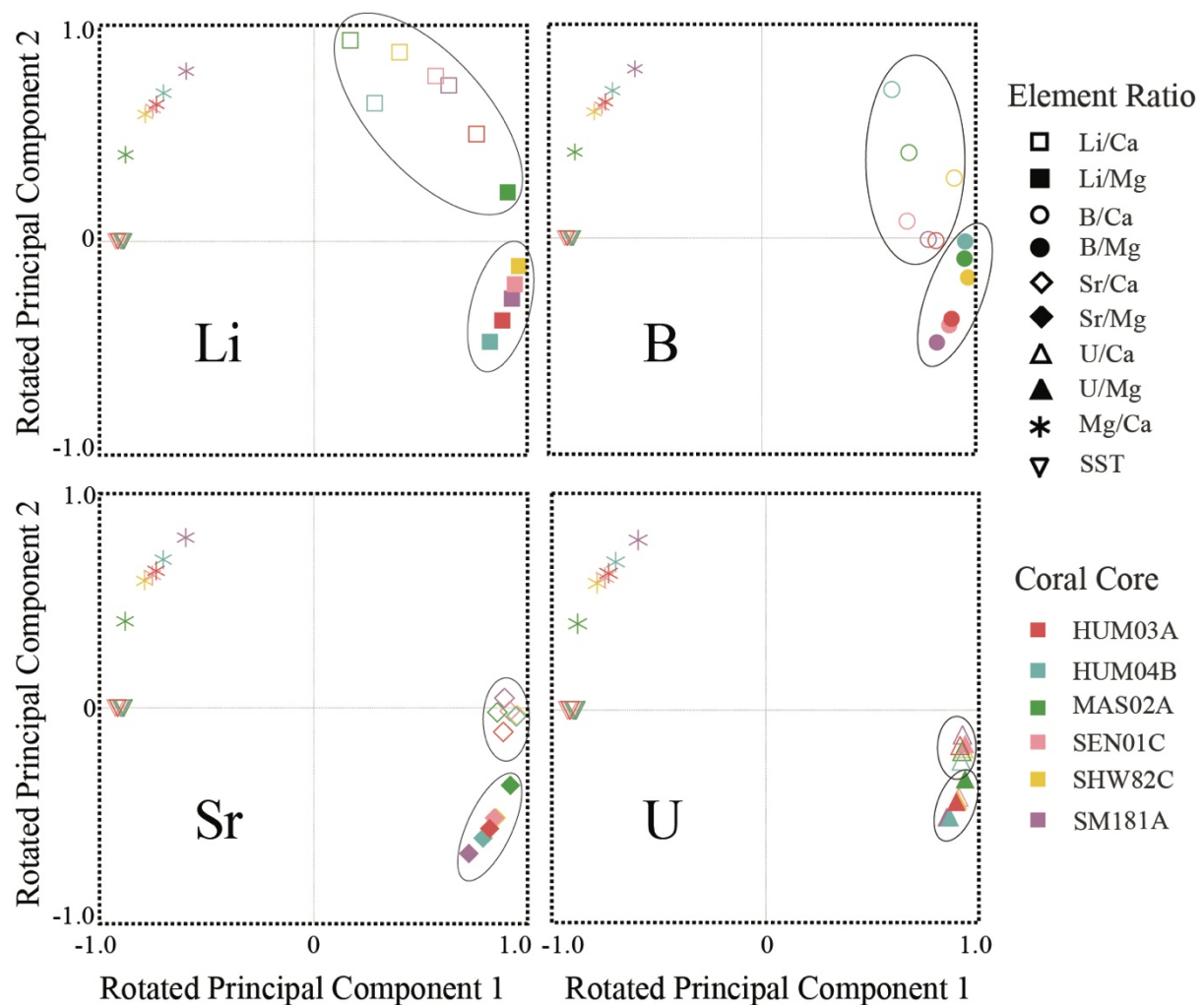


Figure 5.3 Rotated loadings of each element onto the first two principal components (PC) for HUM03A, HUM04B, MAS02C, SEN01C, SHW82C, and SMI81A. PC1 and PC2 are orthogonal (i.e., uncorrelated). Cumulative of PC1 and PC2 explain ~90% of the variance for each coral core. PC loadings vary from -1.0 to 1.0. The absolute value of PC loadings can be interpreted as the correlation between different elemental ratios and the respective principal components. For better comparison, the original PC1 and PC2 were rotated by multiplying a rotation matrix using SST as the reference (Figure S5.6). The rotated PC1 (RPC1) represents SST dependent factors while RPC2 represent non-SST factors. Open symbol represents the traditional normalization to Ca while closed symbol represents the normalization to Mg. Li/Mg and B/Mg can be better explained by RPC1 than Li/Ca and B/Ca. However, Sr/Mg and U/Mg deviate from their initial positions which are better correlated with RPC1. Note: this graph is for visualization only.

Table 5.1 Coefficients derived from elemental ratios (Sr/Ca (mmol/mol), U/Ca (μmol/mol), Li/Mg (mmol/mol) and B/Mg (mmol/mol)) vs SST ($p < 0.01$), root mean square error (RMSE) and long-term SST changes.

Coral ID		Assessment/calibration interval (1990-2016)						SST reconstruction				SST changes (°C) during respective coral record period		
		Slope	StdErr	Intercept	StdErr	r^2	% change per 1 °C at 25 °C	Test interval	RMSE	Calibration interval	RMSE	Trend	Coral- derived SST	HadISST
SMI81A	Sr/Ca	-0.042	0.002	9.798	0.061	0.48	0.48	1975-1989	1.54	1990-2016	1.57	Warming	1.7	0.4
SMI81A	U/Ca	-0.027	0.001	1.877	0.031	0.60	2.26	1975-1989	1.66	1990-2016	1.38	Warming*	0.4	0.4
SMI81A	Li/Mg	-0.053	0.002	3.134	0.049	0.70	2.93	1975-1989	1.46	1990-2016	1.25	Warming	1.3	0.4
SMI81A	B/Mg	-4.888	0.254	261.240	6.469	0.54	3.52	1975-1989	1.60	1990-2016	1.50	Warming	0.7	0.4
SHW82C	Sr/Ca	-0.047	0.002	9.991	0.045	0.69	0.53	1949-1989	2.01	1990-2016	1.24	Cooling*	-0.2	0.7
SHW82C	U/Ca	-0.027	0.001	1.790	0.029	0.62	2.38	1949-1989	2.10	1990-2016	1.33	Warming	0.6	0.7
SHW82C	Li/Mg	-0.064	0.002	3.288	0.050	0.77	3.78	1949-1989	2.55	1990-2016	1.14	Cooling	-3.3	0.7
SHW82C	B/Mg	-6.918	0.223	287.428	5.671	0.75	6.04	1949-1989	1.58	1990-2016	1.10	Warming	1.3	0.7
HUM03A	Sr/Ca	-0.044	0.002	10.097	0.058	0.52	0.49	1898-1989	1.82	1990-2016	1.46	Warming	2	0.8
HUM03A	U/Ca	-0.034	0.002	2.189	0.037	0.61	2.53	1898-1989	1.60	1990-2016	1.35	Warming	1.1	0.8
HUM03A	Li/Mg	-0.055	0.002	3.207	0.055	0.65	3.02	1898-1989	1.90	1990-2016	1.25	Warming	1.3	0.8
HUM03A	B/Mg	-6.780	0.306	328.486	7.411	0.60	4.26	1898-1989	1.68	1990-2016	1.42	Warming	1.5	0.8
HUM04B	Sr/Ca	-0.048	0.002	10.196	0.048	0.65	0.53	1978-1989	0.68	1990-2016	1.30	Warming	0.6	0.3
HUM04B	U/Ca	-0.039	0.002	2.404	0.040	0.63	2.68	1978-1989	0.73	1990-2016	1.31	Cooling*	-0.4	0.3
HUM04B	Li/Mg	-0.054	0.003	3.198	0.072	0.51	2.93	1978-1989	0.85	1990-2016	1.54	Cooling	-1.6	0.3
HUM04B	B/Mg	-7.412	0.289	340.931	7.011	0.67	4.76	1978-1989	0.75	1990-2016	1.19	Cooling*	-0.5	0.3
SEN01C	Sr/Ca	-0.061	0.002	10.502	0.058	0.66	0.68	1902-1989	1.71	1990-2016	1.31	Warming*	0.2	0.8
SEN01C	U/Ca	-0.044	0.001	2.410	0.035	0.74	3.41	1902-1989	1.54	1990-2016	1.12	Cooling*	-0.2	0.8
SEN01C	Li/Mg	-0.070	0.003	3.509	0.069	0.65	3.98	1902-1989	2.43	1990-2016	1.21	Cooling	-1.7	0.8
SEN01C	B/Mg	-7.992	0.334	370.465	8.038	0.64	4.68	1902-1989	2.34	1990-2016	1.23	Cooling	-2.2	0.8
MAS02A	Sr/Ca	-0.053	0.002	10.191	0.057	0.62	0.6	1906-1989	1.72	1990-2016	1.34	Warming	1.1	0.8
MAS02A	U/Ca	-0.042	0.002	2.387	0.040	0.68	3.17	1906-1989	1.78	1990-2016	1.19	Warming	1.2	0.8
MAS02A	Li/Mg	-0.059	0.003	3.242	0.075	0.53	3.32	1906-1989	2.20	1990-2016	1.56	Warming	2.2	0.8
MAS02A	B/Mg	-6.480	0.287	300.068	6.972	0.62	4.69	1906-1989	1.98	1990-2016	1.29	Warming	1.8	0.8

Note: Over the assessment interval (1990-2016), coefficients (slopes, intercepts and r^2 values) were derived from normal calibration equation ($\text{Element/Ca} = a + b \times \text{SST}$) to make comparison with literature values, where a (intercepts) and b (slopes) are constants of linear regression fitting. SST change was calculated from the respective coral record period. StdErr is short for standard error.

* Trends not significant at 95% confidence level.

5.3.4 SST calibrations using elemental ratios

Results from sections 3.2 and 3.3 showed that Sr/Ca, U/Ca, Li/Mg, and B/Mg were better correlated with annual SST variations. Therefore, linear regression analyses were performed to quantify the correlation between these elemental ratios and the respective composite SSTs (adjusted OISST by in-situ SST, see section 2.3) (Figure 5.4). It is noteworthy that some recent studies proposed exponential regression for Li/Mg (Cuny-Guirriec et al., 2019; Fowell et al., 2016; Hathorne et al., 2013; Montagna et al., 2014). A detailed discussion about the differences between linear and exponential regressions is beyond the scope of this study. The r^2 values obtained from linear and exponential regressions were quite close based on our results; therefore, further discussions were based on the more commonly computed linear regressions.

Although the Gladstone corals (SEN01C, HUM03A, and HUM04B) may be susceptible to highly variable environmental conditions due to port development and river runoff (Cantin et al., 2018), all four temperature-sensitive elemental ratios at these sites performed well and do not seem to be affected by the hydrological and anthropogenic stress as revealed by the linear regression results (Table 5.1, Figure 5.4). r^2 of SST to U/Ca, Sr/Ca, Li/Mg, and B/Mg at SEN01C (Mid Harbour Zone) were 0.74 ($p < 0.01$), 0.66 ($p < 0.01$), 0.65 ($p < 0.01$), and 0.64 ($p < 0.01$), respectively. For HUM03A, Li/Mg had the strongest relationship with SST ($r^2 = 0.65$, $p < 0.01$) followed by U/Ca ($r^2 = 0.61$, $p < 0.01$), B/Mg ($r^2 = 0.60$, $p < 0.01$), and Sr/Ca ($r^2 = 0.52$, $p < 0.01$). For HUM04B, B/Mg had the best relationship with SST ($r^2 = 0.67$, $p < 0.01$), followed by Sr/Ca ($r^2 = 0.65$, $p < 0.01$), U/Ca ($r^2 = 0.63$, $p < 0.01$), and Li/Mg ($r^2 = 0.51$, $p < 0.01$). For MAS02A, the regression performance followed the order of U/Ca ($r^2 = 0.68$, $p < 0.01$) > Sr/Ca ($r^2 = 0.62$, $p < 0.01$) = B/Mg ($r^2 = 0.62$, $p < 0.01$) > Li/Mg ($r^2 = 0.53$, $p < 0.01$). For SHW82C, Li/Mg has the strongest relationship with SST ($r^2 = 0.77$, $p < 0.01$), followed closely by B/Mg ($r^2 = 0.75$, $p < 0.01$), and then Sr/Ca ($r^2 = 0.69$, $p < 0.01$) and U/Ca ($r^2 = 0.62$,

$p < 0.01$). Elemental ratios at SMI81A had slightly poorer relationship with SST, with r^2 of Li/Mg, U/Ca, B/Mg and Sr/Ca being 0.70 ($p < 0.01$), 0.60 ($p < 0.01$), 0.54 ($p < 0.01$), and 0.48 ($p < 0.01$), respectively.

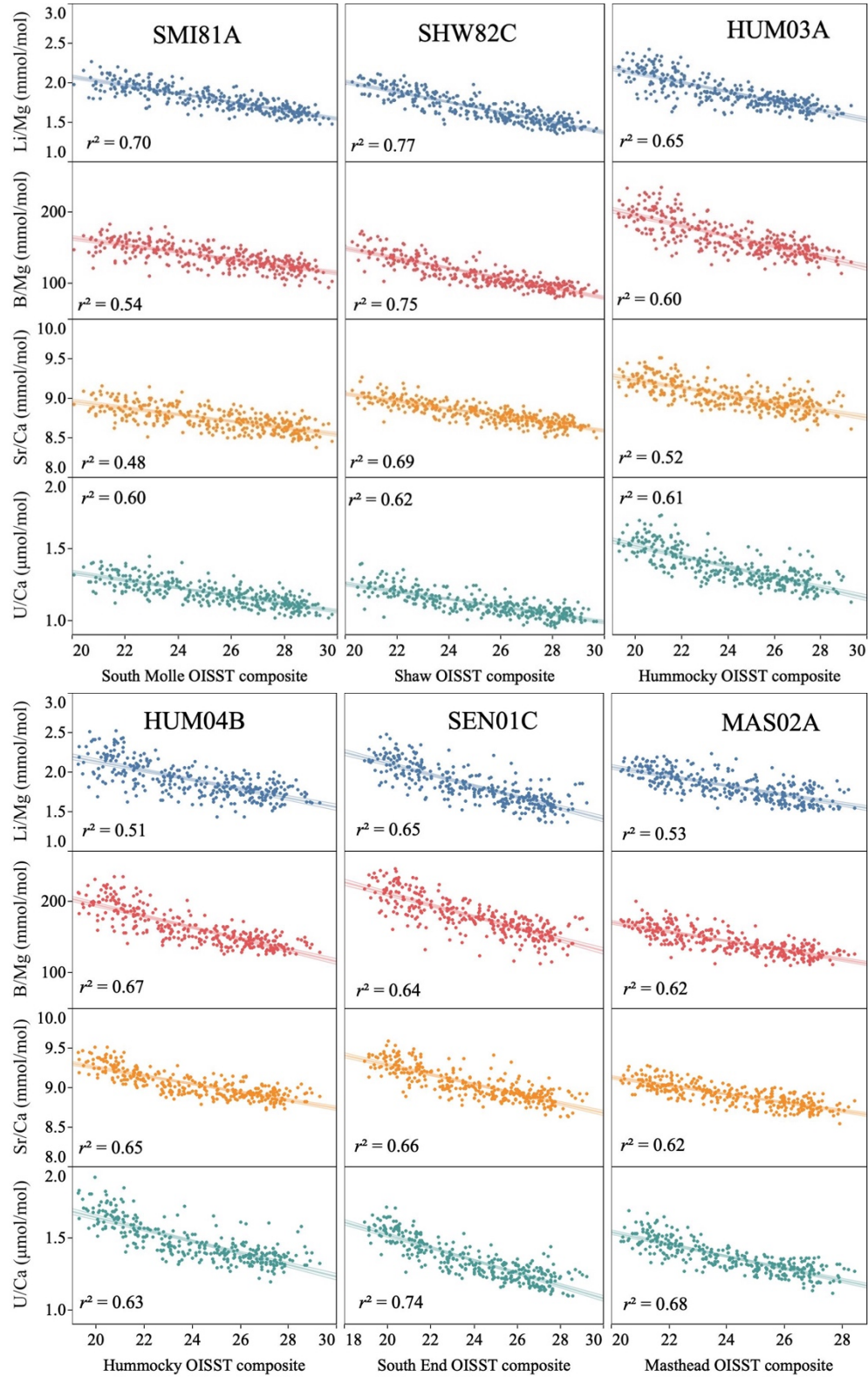


Figure 5.4 Scatter plots of elemental ratios (Li/Mg (blue), B/Mg (red), Sr/Ca (orange) and U/Ca (green)) for coral cores collected from Whitsunday Islands and Gladstone Harbour over a common assessment/calibration period (1990-2016). Linear regression is plotted with line and confidence band at $p < 0.05$. Detailed coefficients for the regression can be found in Table 5.1.

5.4. Discussion

5.4.1 Elemental ratio variability and temperature dependence

5.4.1.1 Sr/Ca

To date Sr/Ca has been considered the most robust paleothermometer for tropical corals (Beck et al., 1992; Corregge, 2006; DeLong et al., 2013; Gagan et al., 2012; McCulloch et al., 1994; Pfeiffer et al., 2009; Quinn and Sampson, 2002; Schrag, 1999). Sr^{2+} is similar to Ca^{2+} in chemistry; therefore, Sr^{2+} can substitute for Ca^{2+} in the coral lattice. Sr partitioning between aragonite and seawater has been suggested to be negatively correlated with SST; that is, a smaller amount of Sr relative to Ca incorporated during aragonite formation with increasing temperature (Alibert and McCulloch, 1997; Corregge, 2006; Gaetani and Cohen, 2006).

r^2 values from the Sr/Ca-SST relationship ranged from 0.48 ($p < 0.01$) at SMI81A to 0.69 ($p < 0.01$) at SHW82C (Table 5.1), which is lower than many literature relationships (e.g., Chen et al., 2019; D'Olive et al., 2018). In this study, Sr/Ca does not outperform other temperature proxies during the calibration period of 1990-2016, with two of six corals (SMI81A and HUM03A) recording the least evident periodicity and Sr/Ca-SST relationship. The % change of Sr/Ca per 1 °C (0.55% on average) is much lower than that of the other proxies (~3-4%) (Table 5.1); therefore, the larger analytical error related to LA-ICPMS may limit its usefulness. Even though the slopes and intercepts from Sr/Ca-SST regressions (Table 5.1) fall broadly into the range of literature values (Chen et al., 2019; Fallon et al., 2003; Sinclair, 2005), these values are statistically different, revealing the site-specific changes in the partitioning of Sr in different corals (Chen et al., 2019; Fallon et al., 2003; Fowell et al., 2016). An offset from different

calibration curves means that a particular Sr/Ca value would yield different calibrated SST values, thus inhibiting a universal calibration of SST using Sr/Ca ratios in corals. The difference in Sr incorporation at different sites can be attributed to variable seawater pH, seawater Sr/Ca, coral physiology (such as extension rate, calcification rate) and stress events (Devilliers et al., 1994; Ferrier-Pages et al., 2002; Fowell et al., 2016; Kuffner et al., 2012; Marshall and McCulloch, 2002; Tanaka et al., 2015). Further examination of the calibration curves shows that the site-specific calibration coefficients (slopes and intercepts) are linearly correlated (Figure 5.5a). This relationship has also been noticed in other studies (D'Olivo et al., 2018; Deng et al., 2014; Marshall and McCulloch, 2002) and it has been further explored in the universal multi-trace element calibration of sea surface temperatures model (see section 4.2).

5.4.1.2 U/Ca

U/Ca has been suggested to be a relatively robust SST proxy, especially for massive *Porites* corals (Felis et al., 2009; Min et al., 1995; Ourbak et al., 2006; Quinn and Sampson, 2002; Shen and Dunbar, 1995). In this study, U/Ca ratios from all sites are strongly correlated with SST, Sr/Ca, and Mg/Ca (Figure 5.4, Table S5.4), and such covariation is consistent with past studies (Cardinal et al., 2001; DeCarlo et al., 2015; Felis et al., 2009; Quinn and Sampson, 2002; Sinclair, 2005).

Factors controlling U incorporation into coral skeletons remain inconclusive (Sinclair et al., 1998; Wei et al., 2000; Fallon et al., 2003). A few studies show that U/Ca not only correlates with SST, but also correlates with pH and carbonate ion concentration ($[\text{CO}_3^{2-}]$) (DeCarlo et al., 2015; Inoue et al., 2011; Raddatz et al., 2014). Seasonal signals of U/Ca in corals, therefore, may not directly reflect ambient seawater temperature, but may be dominated by other seasonal variations in environmental factors influencing coral biomineralization. Uranium was found to

substitute for CO_3^{2-} as a carbonate ion complex rather than for Ca^{2+} (Reeder et al., 2000). Earlier work suggested that the anionic $[\text{UO}_2(\text{CO}_3)_3]^{4-}$ complex was dominant in seawater (Djogic et al., 1986; Dong and Brooks, 2006; Kalin et al., 2005); however, recent experimental data has shifted the consensus to cation-balanced complexes (such as $\text{CaUO}_2(\text{CO}_3)_3^{2-}$ and/or $\text{MgUO}_2(\text{CO}_3)_3^{2-}$) due to the overwhelmingly higher concentrations of Mg^{2+} and Ca^{2+} in seawater (Endrizzi and Rao, 2014). Since the U-carbonate ion complex varies in conjunction with $[\text{CO}_3^{2-}]$ and/or pH, the covariation of U/Ca with SST could be an indirect reflection of U/Ca with $[\text{CO}_3^{2-}]$. A recent abiogenic aragonite precipitation experiment showed that U/Ca aragonite was inversely correlated with $[\text{CO}_3^{2-}]$ but independent of pH and temperature (DeCarlo et al., 2015). Therefore, U probably substitutes into the coral skeleton as an anion but ends up occupying the cation site. However, in all cores used in this study across a wide latitudinal gradient, annual U/Ca cycling is perfectly in phase with seasonal maximum and minimum cycles in SST (Figures 5.2, S5.3), and such covariance would require that $[\text{CO}_3^{2-}]$ and/or pH variations synchronously with temperature in both amplitude and frequency.

5.4.1.3 Mg/Ca

Coral Mg/Ca has been found to be a good SST proxy in some locations (e.g., Mitsuguchi et al., 1996; Wei et al., 2000). However, the incorporation pathways of Mg into coral skeletons are not fully established. Mg^{2+} may directly substitute for Ca^{2+} in calcite (Politi et al., 2010), while this may not be true in aragonite (Finch and Allison, 2008). The relatively small ionic radius of Mg^{2+} may severely distort the aragonite lattice. Therefore, Mg^{2+} is more likely to be located in disordered sites and/or defect sites, consistent with the finding that Mg is rich in organics or amorphous calcium carbonate (ACC) (Case et al., 2010; Sinclair et al., 2006). The other possibility for Mg^{2+} incorporation may be surface adsorption or loose binding in the coral lattice (Case et al., 2010).

This study shows that Mg/Ca broadly increases with SST (Table S5.4), but the relationship is weak at most sites ($r^2 \sim 0.2-0.5$, $p < 0.01$; Table S5.3). Many studies have also noted that biological effects (e.g., skeletal growth rates, microstructural entrapments, defect sites), environmental variations (e.g., carbonate ion concentrations and maybe salinity), and Rayleigh fractionation can affect Mg/Ca incorporation (Armid et al., 2011; Case et al., 2010; Cross and Cross, 1984; Inoue et al., 2007; Meibom et al., 2004; Mitsuguchi et al., 2003; Reynaud et al., 2007; Sinclair et al., 2006). Therefore, the biological and environmental factors (independent of SST) may be superimposed to the linear trend between Mg/Ca and SST thus limiting the use of Mg/Ca as an accurate SST proxy for *Porites* corals in the GBR.

5.4.1.4 Li/Mg

Li^+ is a conservative monovalent cation in seawater with a long residence time (Huh et al., 1998). Li incorporation into the coral skeleton was found to be temperature dependent, but also influenced by calcification rate (Hathorne et al., 2013; Rollion-Bard and Blamart, 2015). From inorganic aragonite experiments, Li^+ was assumed to be incorporated through heterovalent substitution due to the difference in charge between Li^+ and Ca^{2+} (Marriott et al., 2004; Okumura and Kitano, 1986). However, this process may be complicated considering the small ionic size of Li^+ . Li^+ may also be trapped into defect sites similar to Mg^{2+} (Amiel et al., 1973; Watanabe et al., 2001). At most sites in this work, the annual periodicity of Li/Ca is weak (Figure S5.3), and Li/Ca was found to be poorly correlated with SST (Figure 5.3, Table S5.4). This suggests that Li/Ca alone cannot be applied as an accurate temperature proxy unless the biological effects can be minimised (Hathorne et al., 2013).

In contrast to Li/Ca and Mg/Ca, Li/Mg ratios have consistent, stable seasonal cycles at all coral sites (Figures 5.2, S5.3), and a strong relationship ($r^2 > 0.6$ on average, $p < 0.01$; Figure 5.4) was found between Li/Mg and temperature, consistent with previous studies (Bryan and

Marchitto, 2008; Case et al., 2010; D'Olivo et al., 2018; Fowell et al., 2016; Hathorne et al., 2013; Montagna et al., 2014; Marchitto et al., 2018; Raddatz et al., 2013; Zinke et al., 2019). The higher correlation between Li/Mg and SST lies in the elimination of vital effects and the amplification of the opposite temperature controls on Li/Ca and Mg/Ca (Fowell et al., 2016). Li/Mg is not influenced by Rayleigh fractionation because the partition coefficients (K_d) for both Li and Mg are $\ll 1$ (Gaetani and Cohen, 2006; Gaetani et al., 2011; Marriott et al., 2004) and Li^+ has a similar ionic size with Mg^{2+} (Bryan and Marchitto, 2008). Since coral calcification strongly discriminates the uptake of Mg and Li, Mg/Ca and Li/Ca ratios are assumed to remain “constant” in the extracellular calcifying fluid during the precipitation process, thus purely reflecting other environmental impacts on Li/Mg (Case et al., 2010). This hypothesis is supported by our power spectrum and PCA results (Figures 5.2, 5.3), showing that dividing Li/Ca by Mg/Ca smooths the data and increases the temperature dependence by cancelling out some temperature-independent commonality. The Li/Mg-SST relationship seems universal because Li/Mg is less affected by colony-specific or species-specific offsets over a wide temperature range (Figure S5.7a); however, the colony-specific offsets are still evident over a narrow temperature range (Figure S5.7b), suggesting that Li/Mg also requires site-specific calibrations like other temperature proxies (Fowell et al., 2016).

5.4.1.5 B/Mg

Boron is a conservative element in seawater (Lee et al., 2010). Clear B/Ca seasonality associated with SST variations have been found in a few locations (Fallon et al., 1999, 2003). Moderate relationships ($r^2 \sim 0.27\text{-}0.63$, $p < 0.01$, Table S5.3) between B/Ca and SST were found in this study, and the relationships were site specific. SHW82C has the highest r^2 (0.63, $p < 0.01$) while the r^2 in other corals is much lower (0.35-0.44, $p < 0.01$), with the lowest r^2 (0.27, $p < 0.01$) observed in HUM04A (Table S5.3). Several studies have shown that B incorporates into coral aragonite as an anion, with the primary form suggested to be $\text{B}(\text{OH})_4^-$

(Hemming and Hanson, 1992; Hemming et al., 1995; Holcomb et al., 2016; Mavromatis et al., 2015). B/Ca incorporation into aragonite is not only affected by temperature, but also by other factors such as carbonate chemistry and growth rate (Holcomb et al., 2016; Mavromatis et al., 2015; Sinclair et al., 1998; Wara et al., 2003). Temperature may play an indirect role by manipulating the parent calcifying solution and B speciation (Holcomb et al., 2016); therefore, B/Ca ratios serve more like an indicator for carbonate chemistry than ambient seawater temperature.

Inspired by Li/Mg, B/Ca ratios were normalized to Mg/Ca to eliminate biological and other environmentally controlled changes in B/Ca, while preserving the temperature sensitivity. Even though B/Ca was suggested to be a function of $[\text{CO}_3^{2-}]$ and pH instead of temperature in the calcifying fluid (DeCarlo et al., 2018), the results for the use of B/Mg as thermometer than either B/Ca or Mg/Ca alone were quite encouraging with an improvement of the periodicity and the correlation with SST (Figures 5.2, 5.3). This suggests that normalising B/Ca to Mg/Ca may cancel out the nonlinearity of the Mg/Ca vs SST or B/Ca vs SST relationship. Like Li/Mg, the ratio of B/Mg in the calcifying fluid should remain relatively constant as aragonite precipitates because both B and Mg are not preferentially incorporated ($K_d \ll 1$). Besides, the ratio of B/Mg has amplified the opposing temperature controls on B/Ca and Mg/Ca, resulting in a better correlation between B/Mg and SST. However, whether B/Mg can be applied as a widely used paleothermometer needs to be confirmed from more coral studies in other locations.

U/Ca and B/Ca are both sensitive to $[\text{CO}_3^{2-}]$ (DeCarlo et al., 2015, 2018), but the ratio of U/Mg did not improve the temperature sensitivity of U/Ca like B/Mg (Figure 5.3, Table S5.4). The K_d between U and $[\text{CO}_3^{2-}]$ (~ 0.3 ; DeCarlo et al., 2015) is much higher than that of B/ $[\text{CO}_3^{2-}]$

(~0.04; Holcomb et al., 2016), suggesting that U is more affected by Rayleigh fractionation. Besides, a strong anticorrelation between U/Ca and Mg/Ca has been found in this work (Table S5.4) and in others' work (Fallon et al., 2003; Sinclair, 2005; Sinclair et al., 2006). Mg was found to be rich in the centers of calcification (opaque regions) while U is rich in light material (translucent regions), suggesting that the partitioning of U competes with partitioning of Mg at different phases and this behavior may be regulated by biogeochemical processes (Sinclair et al., 2006). Therefore, the normalization of U/Ca to Mg/Ca has amplified the vital effects instead of eliminating them.

5.4.2 Universal SST reconstruction model

As noted above, elemental ratios vs SST calibrations tend to remain colony-specific but the slopes and intercepts from different calibration equations are linearly correlated (Figure 5.5a). Based on these regressions, D'Olivo et al. (2018) developed an “universal multi-trace element calibration scheme” (UMTECS) to reconstruct the sea surface temperature. The calibration is considered as universal, because it doesn't require prior knowledge of the SST record for a specific coral location. This model requires a few regression lines to define coefficients for calculation and requires two temperature proxies (D'Olivo et al., 2018). In this work, several coral cores were examined spanning a relatively wide latitude and different SST range, and four good candidates for SST reconstructions have been proposed, making this dataset ideal to revisit the UMTECS model. The original UMTECS was slightly modified to clarify some assumptions and make the derivations more straightforward. Briefly, the model-derived regression line requires the determination of a ‘geometric centroid’ and the ‘elemental ratio value at SST=0 °C’. The basic principle from this binary proxy calibrations can be visualized in the geometric model (Figure 5.5).

5.4.2.1 Geometric centroid

It has been noted that calibration offsets are universal for different temperature proxies (e.g., Sr/Ca, U/Ca) (Alpert et al., 2016; Fallon et al., 1999; Quinn and Sampson, 2002; Sinclair et al., 1998). However, the intercepts and slopes from different calibrations are not remarkably different, instead, they are linearly correlated (Figure 5.5a) which suggests the presence of geometric centroid for an elemental ratio vs SST plane (D’Olivo et al., 2018). The presence of a geometric centroid means all site-specific calibration lines will pass through a common area and can be proved by the following solvable equations. Using Sr/Ca vs SST as an example, a reconstruction equation (an inversion of the normal calibration equation) can be written as:

$$SST = Sr/Ca \times Slope_i + Intercept_i \quad (1)$$

where ‘i’ represents slopes and intercepts calculated from different corals.

Rearranging equation (1) to make it look like the following way:

$$Intercept_i = - Sr/Ca \times Slope_i + SST \quad (2)$$

$Intercept_i$ and $Slope_i$ obtained from Sr/Ca vs SST linear regression are themselves linearly correlated, yielding a new regression line:

$$Intercept_i = a \times Slope_i + b \quad (3)$$

where a and b are the slope and intercept from the regression of [$Slope_i$, $Intercept_i$]

If a unique coordinate ($Sr/Ca_{centroid}$, $SST_{centroid}$) does exist, it should fit equation (3), by looking like

$$Intercept_i = -Sr/Ca_{centroid} \times Slope_i + SST_{centroid} \quad (4)$$

Combining equations (3) and (4), resulting in

$$Sr/Ca_{centroid} = -a, \text{ and } SST_{centroid} = b$$

The above derivation is slightly different from D’Olivo et al. (2018). They used slope as the subject in equation (2), while intercept was used here for simplicity and for easier calculation.

There are only negligible differences by choosing the different subjects in the linear regression. Based on the above derivation, centroid coordination (Metal/Ca_{centroid}, SST_{centroid}) for four elemental ratios are listed in Table S5.6.

5.4.2.2 Elemental ratio at SST=0 °C

The determination of an elemental ratio at SST=0°C is illustrated in Figure 5.5b (blue plane). First, intercepts (i.e., SST=0 °C) derived from different elemental ratio vs SST calibrations (e.g., Sr/Ca vs SST and U/Ca vs SST) are linearly correlated (Figure S5.8), yielding

$$\text{Sr/Ca}_{\text{Intercept}} = c \times \text{U/Ca}_{\text{Intercept}} + d \quad (5)$$

Second, the two elemental ratios are themselves correlated (i.e., Sr/Ca is linearly correlated with U/Ca) (Table S5.4), yielding

$$\text{Sr/Ca} = e \times \text{U/Ca} + f \quad (6)$$

Therefore, (0, Sr/Ca_{Intercept}) or (0, U/Ca_{Intercept}) can be obtained by solving equations (5) and (6):

$$\text{U/Ca}_{\text{Intercept}} = (f - d)/(c - e) \quad (7)$$

$$\text{Sr/Ca}_{\text{Intercept}} = e \times (f - d)/(c - e) + f \text{ or } c \times (f - d)/(c - e) + d \quad (8)$$

D'Olivo et al. (2018) used a slightly different way to obtain the (0, Sr/Ca_{Intercept}). They assumed Sr/Ca vs Li/Mg (Sr/Ca vs U/Ca in our example) regression line would pass (Sr/Ca_{centroid}, Li/Mg_{centroid}) so they substitute this coordinate into equation (6). In both their study and this study, estimated SST_{centroid} for different elemental ratios are not identical (Table S5.6). Therefore, our derivation avoided the step of substituting (Sr/Ca_{centroid}, Li/Mg_{centroid}) into equation (6). However, the uncertainties from their approach could be small because their determined SST_{centroid} values were only slightly different.

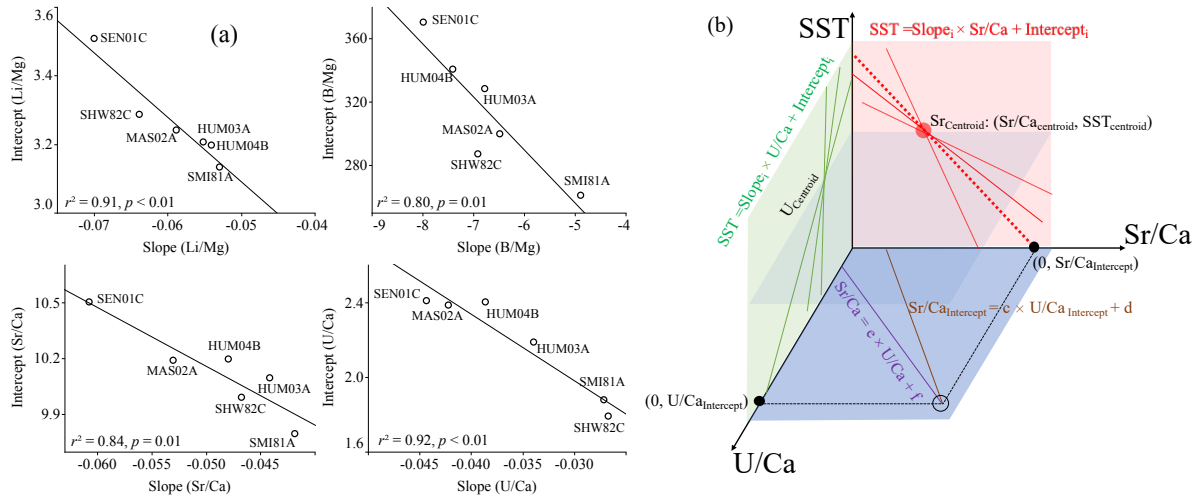


Figure 5.5 (a) Slopes and intercepts generated from the linear regressions between elemental ratios (Sr/Ca, U/Ca, Li/Mg, B/Mg) and SST; (b) Mathematic demonstration of the universal calibration of SST based on multi-trace elements. Panel (a) shows that slopes and intercepts from different calibrations are linearly correlated, thus proving the presence of geometric centroid for different temperature-dependent elemental ratios. Panel (b) presents three main assumptions for this model: (1) SST is linearly correlated with two temperature proxies (e.g., Sr/Ca, U/Ca) (pink and green plane); (2) Sr/Ca and U/Ca are linearly correlated (blue plane, purple line); and (3) intercepts obtained from colony-specific elemental ratios vs SST calibrations are linearly related (blue plane, brown line). Using Sr/Ca vs SST system (pink plane) as an example, the model-derived regression line (pink dashed line) passes through $(Sr/Ca_{\text{centroid}}, SST_{\text{Sr-centroid}})$ and $(0, Sr/Ca_{\text{Intercept}})$. The other combinations include Sr/Ca + Li/Mg, Sr/Ca + B/Mg, U/Ca + Sr/Ca, U/Ca + Li/Mg, U/Ca + B/Mg, Li/Mg + Sr/Ca, Li/Mg + U/Ca, Li/Mg + B/Mg, B/Mg + Sr/Ca, B/Mg + U/Ca, and B/Mg + Li/Mg.

5.4.2.3 Model output

Based on the above derivations, coefficient (slope, intercept) for a reconstruction line for Sr/Ca vs SST can be simply calculated as:

$$\text{Slope}_{\text{Sr/Ca}} = \text{SST}_{\text{centroid}} / (\text{Sr/Ca}_{\text{centroid}} - \text{Intercept}_{\text{Sr/Ca}}) \quad (9)$$

$$\text{Intercept}_{\text{Sr/Ca}} = \text{SST}_{\text{centroid}} \times \text{Intercept}_{\text{Sr/Ca}} / (\text{Intercept}_{\text{Sr/Ca}} - U/Ca_{\text{centroid}}) \quad (10)$$

Due to various combinations of elemental ratios, 12 UMTECS-derived coefficients (slopes, intercepts) for each coral core were generated. To test the effectiveness and the reproducibility of the model, UMTECS-derived SST reconstructions were compared with empirical SST reconstructions at different coral sites with selected combinations (Figure 5.6), showing some encouraging results. For example, UMTECS reconstruction lines can be very close to empirical calibration lines (Figure 5.6a), with the average SST residues (ΔSST) < 0.5 °C (Figure 5.6b).

However, some UMTECS reconstruction lines deviate significantly from the empirical reconstruction lines, which can result in the overestimation or underestimation of SST. This suggests that UMTECS reconstructions do not always reproduce colony-specific reconstructions. To quantify these offsets, MAS02A was used as example to compare the empirical Sr/Ca reconstruction with UMTECS-derived reconstructions using Sr/Ca-U/Ca, Sr/Ca-B/Mg, and Sr/Ca-Li/Mg combinations (panel MAS02A in Figure 5.6). By substituting the average concentration of Sr/Ca (8.91 mmol/mol) into the calibration lines, the resulting SST are 24.2 °C, 24.5 °C, 24.8 °C, and 22.0 °C for the Sr/Ca empirical calibration, Sr/Ca-U/Ca, Sr/Ca-B/Mg, and Sr/Ca-Li/Mg, respectively. Similar offsets can be observed in other corals using different proxy combinations based on our datasets (Figure S5.9). Overall, Li/Mg-Sr/Ca, Sr/Ca-U/Ca, and U/Ca-B/Mg were found to outperform the other combinations. As expected, UMTECS-derived slopes and intercepts are linearly correlated with the empirical slope and intercept, because they are forced to pass through a common geometric centroid (Figure S5.9b). Therefore, model outputs can be constrained by the range of empirical slopes and intercepts from site-specific calibrations. Seawater temperature ranges from ~19 °C to ~30 °C in the Central and Southern GBR. Any reconstructed SST that is far beyond this normal range is not optimal for coral growth and those model results can be ruled out. Despite some uncertainties, UMTECS can still be effective and reproducible in a few cases, so it has the potential to be applied in reconstructing paleoclimate records (such as for fossil corals) (D'Olivo et al., 2018). The simplified derivation and calculation also make this model more applicable to be tested in other regions especially when multi-element analyses are performed. A more comprehensive understanding of (1) centroid coordinates, (2) Sr/Ca vs U/Ca correlation and (3) [Sr/Ca vs SST]_{intercept} vs [U/Ca vs SST]_{intercept} correlation can potentially reduce the model uncertainty.

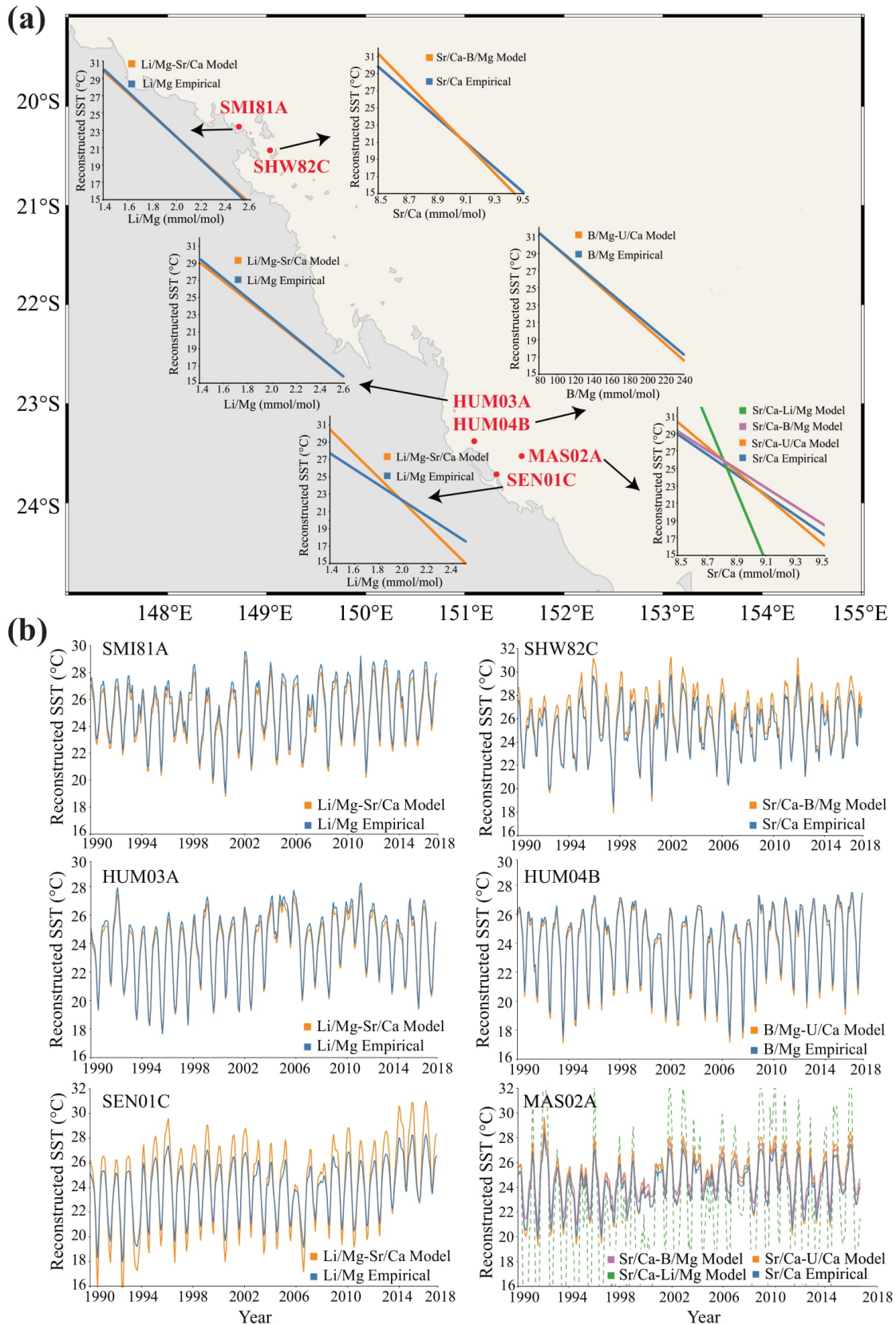


Figure 5.6 Comparison between UMTECS reconstructions and empirical SST reconstructions. Test of UMTECS using different combinations of Sr/Ca, U/Ca, Li/Mg, and B/Mg is presented using MAS02A as an example. Panel (a) compares the UMTECS-derived calibration lines with empirical calibration lines at each coral site; panel (b) compares the reconstructed SST from UMTECS model and from site-specific calibrations.

5.4.3 Long-term trend and reconstruction

Since centennial-scale geochemical archives were generated, long-term SST reconstruction was made using four elemental ratios for each coral core. HadISST was used for the reconstruction assessment due to the length of the time series. SST prior to 1990 was reconstructed using the respective proxy vs SST calibration equations determined from the calibration period (1990-2016) (Tables 5.1, S5.3). This approach tests the reliability of the proxy vs SST calibration during a period other than the calibration interval.

SST in the Whitsundays and in the vicinity of Gladstone Harbour have significantly warmed since the late 19th century (Figure S5.10; Lough et al., 2018). Three quarters of the geochemical records from the Central GBR and the Southern GBR reveal a consistent warming trend (Table 5.1, Figure 5.7). Long-term SST changes derived from U/Ca ratios are closest to instrumental values, followed by Sr/Ca (Table 5.1). In contrast to Sr/Ca and U/Ca, Li/Mg and B/Mg derived SST are less stable over the long-term timescale. For example, the discrepancies between Li/Mg (or B/Mg) derived SST and instrumental SST in SEN01C strengthened prior to 1970 (Figure 5.7). This can be attributed to the anomalously higher Mg/Ca values (Figure S5.3d). For other corals, Li/Ca or B/Ca are accountable for the misfit (e.g., HUM04B, Figure S5.3b). For a century-scale reconstruction, the average SST residuals (Δ SST) between HadISST and coral-derived SST ranged from 1.2°C to 1.7°C. The root mean square error (RMSE) during the calibration period were generally lower than 1.5 (Table 5.1) but slightly higher than those in other studies (e.g., D'Olivo et al., 2018). The higher RMSE values determined in this work may be due to the longer calibration period we used (uncertainties in HadISST) and/or larger analytical uncertainties related to LA-ICPMS method. RMSE were consistently higher in the test period (prior to 1990) for different elemental ratios (Table 5.1), so were the SST residuals (Δ SST) (Figure 5.7). The larger uncertainties between coral-derived SST and HadISST in the

test period (prior to 1990) suggest that the calibration coefficients generated from calibration period are not conservative spanning the entire record. However, due to the limitation of observational coverage, instrumental dataset (e.g., HadISST) also has large uncertainties and is more reliable from 1950 onwards (D'Olivo et al., 2019; Deser et al., 2010; Lough et al., 2018).

Coral-derived SST also displayed evident interannual and decadal variations that may not truly represent oceanographic variability (Figure 5.7) (Alpert et al., 2016; DeLong et al., 2014; Kawakubo et al., 2017). These interannual shifts do not occur randomly for a single elemental ratio, instead, they can be mirrored by other geochemical records. This is most evident for Sr/Ca and U/Ca records which show concurrent fluctuations in most cases (Figure 5.7). Such variations may be due to vital effects during coral calcification (Alpert et al., 2016; DeLong et al., 2014; Kawakubo et al., 2017). The LA-ICPMS method can be quite sensitive to the selection of sampling transect due to its high spatial resolution analysis (Alibert and Kinsley, 2008; Fallon et al., 1999; Kawakubo et al., 2017; Kawakubo et al., 2014; Sinclair et al., 1998). Even though the analysis transects were carefully selected (Figure S5.11), a better or more reproducible geochemical records may be obtained by putting more efforts on selecting the optimal sampling transects and running replicate transects on adjacent growth paths (DeLong et al., 2007; DeLong et al., 2013; Kawakubo et al., 2017).

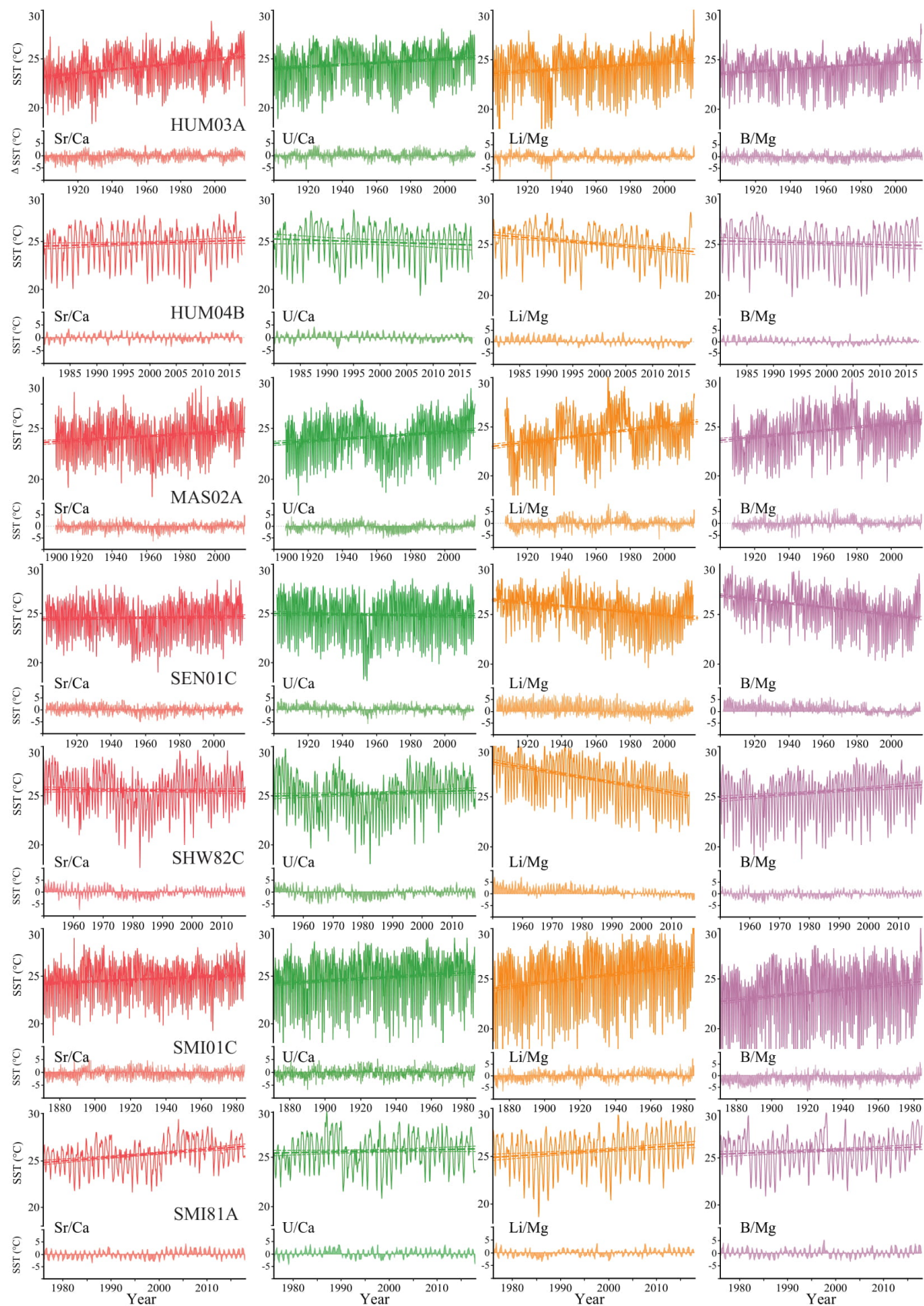


Figure 5.7 Comparison between monthly HadISST and reconstructed SST for each coral core using four elemental ratios (Sr/Ca, U/Ca, Li/Mg, and B/Mg). SST residues (Δ SST) were calculated as the discrepancy between coral-derived SST and HadISST. Linear regression is plotted with line and confidence band at $p < 0.05$.

5.4.4 Summary of the Sr/Ca, U/Ca, Li/Mg, and B/Mg paleothermometer

Coral Li/Ca, B/Ca, and Mg/Ca ratios alone have complicated relationship with seawater temperature (e.g., Hathorne et al., 2013; DeCarlo et al., 2018). However, results for the use of Li/Mg and B/Mg as thermometer were very encouraging with a significant improvement of their correlation with SST (Figures 5.2, 5.3, Table S5.4). Li/Ca, B/Ca, and Mg/Ca are similarly influenced by calcification processes, and their partition coefficient (K_d) are all $\ll 1$ (Montagna et al., 2014; Holcomb et al., 2016). The ratio of Li/Mg or B/Mg has effectively minimised the impacts of Rayleigh fractionation and preserved the temperature sensitivities. Over a short calibration/assessment period 1990-2016, the performance of Li/Mg and B/Mg was similar or even better than U/Ca and Sr/Ca, however, Li anomalies and Mg anomalies occurred more frequently over the longer time series, which prevents the use of Li/Mg or B/Mg for long-term paleoclimate reconstruction.

Compared to other proxies in this work, Sr/Ca has a slightly weaker correlation with SST during the calibration period 1990-2016 due to its lower % change per 1 °C (higher sensitivity to analytical methods). However, PCA results showed that Sr/Ca at different coral sites clustered neatly and Sr/Ca is mainly controlled by temperature dependent factors (PC1; Figure 5.3). Besides, the long-term reconstruction shows that Sr/Ca is relatively stable and consistent with instrumental records, with five of six coral records suggesting warming trend in the past century. These results reaffirm that Sr/Ca is a robust temperature proxy for *Porites* corals.

Seasonal U/Ca variability may be regulated by the $[\text{CO}_3^{2-}]$ which is indirectly controlled by temperature; however, U/Ca has recorded stable and clear seasonal changes in SST spanning the entire record period. The U/Ca reconstructed SST has relatively low RMSE in both calibration and test periods and reveals the most reasonable long-term SST changes at most

sites (Table 5.1). Similar to Sr/Ca, a relative tight cluster of U/Ca has been noticed and U/Ca is strongly correlated with PC1 (Figure 5.3). However, PCA results also showed that U/Ca is controlled by the temperature independent factor (PC2). These observations are consistent with the assumption that Sr/Ca and U/Ca are both affected by Rayleigh fractionation, but Sr partitioning is temperature-dependent and insensitive to carbonate ion concentrations (DeCarlo et al., 2016). Overall, our results showed that Sr/Ca and U/Ca are more reliable than Li/Mg and U/Mg when applied in longer time-series.

5.5 Conclusion

SST reconstructed from long coral records are quite valuable, offering us a window to look back in time. In this study, two traditional temperature proxies (Sr/Ca, U/Ca), a recently developed temperature proxy (Li/Mg) and a potential temperature proxy (B/Mg) were investigated using corals from the Central and Southern GBR. In contrast to Li/Ca, B/Ca, and Mg/Ca, Li/Mg and B/Mg demonstrate a stronger correlation with temperature. Power spectrum analysis shows that Li/Mg has the strongest annual periodicity, closely followed by U/Ca, B/Mg, and Sr/Ca. During the calibration period, r^2 values of the linear regressions are comparable for four elemental ratios. Over the long-term reconstruction, U/Ca and Sr/Ca are more reliable and have lower uncertainties compared to Li/Mg and B/Mg. Although the U/Ca or B/Mg discussed in this study may not be directly temperature-dependent, we still endorse using them as paleothermometer or using them as cross-validation for other ‘more established’ temperature proxies. The multiproxy approach from SMI01C, SMI81A, HUM03A, and MAS02A consistently revealed a long-term warming trend thus increasing our confidence in using these coral cores for paleo environmental reconstructions. Future work can focus on improving the universally applicable temperature model such as UMTECS and build up a world-wide calibration framework by embedding the emerging site-specific calibrations.

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CRedit authorship contribution statement

Yang Wu: Conceptualization, Formal analysis, Investigation, Writing –original draft, Writing – review & editing, Visualization. Stewart J. Fallon: Resources, Writing – review & editing, Supervision, Funding acquisition. Neal E. Cantin: Resources, Writing – review & editing, Funding acquisition. Janice M. Lough: Resources, Writing – review & editing, Funding acquisition.

5.6 Supplementary Information

Table S5.1 Geographic locations of *Porites* spp. coral cores examined in this work.

Site	Core ID	Latitude (°S)	Longitude (°E)	Record period
South End Curtis Island	SEN01C	23.7547	151.31693	1902-2016
Hummocky Island	HUM03A	23.40348	151.14716	1898-2017
Hummocky Island	HUM04B	23.40239	151.146	1978-2017
Masthead Island	MAS02A	23.53196	151.74033	1906-2017
South Molle Island	SMI01C	20.25878	148.8283	1860-1984
South Molle Island	SMI81A	20.25878	148.8283	1975-2017
Shaw Island	SHW82C	20.4796	149.0691	1949-2017

Table S5.2 Average (Avg) values and standard deviation (Std) for three standards (Davies Reef, NIST614, NIST612) used in this study.

Standard	Elemental Ratio (mol/mol)									
	Li/Ca		B/Ca		Mg/Ca		Sr/Ca		U/Ca	
	Avg	Std	Avg	Std	Avg	Std	Avg	Std	Avg	Std
Davies	n/a*	n/a	5.7E-04	1.8E-05	4.4E-03	1.5E-04	8.9E-03	1.7E-04	1.1E-06	4.9E-08
NIST612	2.7E-03	9.6E-05	1.5E-03	4.3E-05	1.3E-03	6.4E-05	4.2E-04	6.3E-05	7.4E-05	3.5E-06
NIST614	1.1E-04	4.5E-06	6.5E-05	1.0E-05	6.6E-04	3.4E-05	2.5E-04	4.7E-05	1.6E-06	7.0E-08

* Not available in Davies Reef coral standard

Table S5.3 Coefficients derived from robust linear regressions between element ratios (Li/Ca (mol/mol), Li/Mg (mmol/mol), B/Ca (mol/mol), Mg/Ca (mol/mol), Sr/Ca (mmol/mol), U/Ca (μmol/mol), and B/Mg (mmol/mol)) and SST at different coral sites over a common assessment period 1990–2016. StdErr is short for standard error.

Coral ID	Elemental Ratio	N	Slope	StdErr	t-value	p-value	Intercept	StdErr	t-value	p-value	r ²
SMI81A	Li/Ca	324	-0.078	0.007	-11.52	<0.01	8.779	0.172	50.91	<0.01	0.29
SMI81A	Li/Mg	324	-0.053	0.002	-27.34	<0.01	3.134	0.049	63.49	<0.01	0.70
SMI81A	B/Ca	324	-0.009	0.001	-15.79	<0.01	0.753	0.015	50.72	<0.01	0.44
SMI81A	B/Mg	324	-4.888	0.254	-19.25	<0.01	261.240	6.469	40.38	<0.01	0.54
SMI81A	Mg/Ca	324	0.068	0.006	12.20	<0.01	2.107	0.141	14.92	<0.01	0.32
SMI81A	Sr/Ca	324	-0.042	0.002	-17.40	<0.01	9.798	0.061	160.02	<0.01	0.48
SMI81A	U/Ca	324	-0.027	0.001	-22.07	<0.01	1.877	0.031	60.01	<0.01	0.60
SHW82C	Li/Ca	324	-0.061	0.008	-7.15	<0.01	9.098	0.215	42.26	<0.01	0.14
SHW82C	Li/Mg	324	-0.064	0.002	-32.18	<0.01	3.288	0.050	65.23	<0.01	0.77
SHW82C	B/Ca	324	-0.015	0.001	-23.03	<0.01	0.895	0.017	52.77	<0.01	0.63
SHW82C	B/Mg	324	-6.918	0.223	-30.97	<0.01	287.428	5.671	50.68	<0.01	0.75
SHW82C	Mg/Ca	324	0.132	0.007	18.66	<0.01	1.239	0.179	6.92	<0.01	0.52
SHW82C	Sr/Ca	324	-0.047	0.002	-26.45	<0.01	9.991	0.045	222.85	<0.01	0.69
SHW82C	U/Ca	324	-0.027	0.001	-23.02	<0.01	1.790	0.029	60.75	<0.01	0.62
HUM03A	Li/Ca	324	-0.054	0.003	-16.46	<0.01	7.842	0.080	98.08	<0.01	0.46
HUM03A	Li/Mg	324	-0.055	0.002	-24.46	<0.01	3.207	0.055	58.68	<0.01	0.65
HUM03A	B/Ca	324	-0.011	0.001	-15.82	<0.01	0.845	0.017	48.72	<0.01	0.44
HUM03A	B/Mg	324	-6.780	0.306	-22.17	<0.01	328.486	7.411	44.32	<0.01	0.60
HUM03A	Mg/Ca	324	0.070	0.004	15.81	<0.01	1.821	0.108	16.93	<0.01	0.44
HUM03A	Sr/Ca	324	-0.044	0.002	-18.53	<0.01	10.097	0.058	174.90	<0.01	0.52
HUM03A	U/Ca	324	-0.034	0.002	-22.52	<0.01	2.189	0.037	59.93	<0.01	0.61
HUM04B	Li/Ca	324	-0.017	0.004	-4.24	<0.01	6.121	0.100	61.41	<0.01	0.05
HUM04B	Li/Mg	324	-0.054	0.003	-18.22	<0.01	3.198	0.072	44.49	<0.01	0.51
HUM04B	B/Ca	324	-0.010	0.001	-10.89	<0.01	0.721	0.021	33.55	<0.01	0.27
HUM04B	B/Mg	324	-7.412	0.289	-25.62	<0.01	340.931	7.011	48.63	<0.01	0.67
HUM04B	Mg/Ca	324	0.072	0.005	14.00	<0.01	1.297	0.125	10.34	<0.01	0.38
HUM04B	Sr/Ca	324	-0.048	0.002	-24.35	<0.01	10.196	0.048	213.61	<0.01	0.65
HUM04B	U/Ca	324	-0.039	0.002	-23.32	<0.01	2.404	0.040	59.94	<0.01	0.63
SEN01C	Li/Ca	324	-0.062	0.007	-9.38	<0.01	7.699	0.158	48.66	<0.01	0.21
SEN01C	Li/Mg	324	-0.070	0.003	-24.43	<0.01	3.509	0.069	50.82	<0.01	0.65
SEN01C	B/Ca	324	-0.010	0.001	-14.73	<0.01	0.834	0.016	53.61	<0.01	0.40
SEN01C	B/Mg	324	-7.992	0.334	-23.96	<0.01	370.465	8.038	46.09	<0.01	0.64
SEN01C	Mg/Ca	324	0.095	0.006	14.96	<0.01	1.157	0.154	7.53	<0.01	0.41
SEN01C	Sr/Ca	324	-0.061	0.002	-25.11	<0.01	10.502	0.058	180.21	<0.01	0.66
SEN01C	U/Ca	324	-0.044	0.001	-30.13	<0.01	2.410	0.035	67.95	<0.01	0.74
MAS02A	Li/Ca	324	-0.027	0.011	-2.52	0.01	6.936	0.256	27.06	<0.01	0.02
MAS02A	Li/Mg	324	-0.059	0.003	-19.01	<0.01	3.242	0.075	43.13	<0.01	0.53
MAS02A	B/Ca	324	-0.009	0.001	-13.13	<0.01	0.700	0.016	44.41	<0.01	0.35
MAS02A	B/Mg	324	-6.480	0.287	-22.58	<0.01	300.068	6.972	43.04	<0.01	0.62
MAS02A	Mg/Ca	324	0.096	0.006	16.50	<0.01	1.168	0.141	8.31	<0.01	0.46
MAS02A	Sr/Ca	324	-0.053	0.002	-22.55	<0.01	10.191	0.057	178.35	<0.01	0.62
MAS02A	U/Ca	324	-0.042	0.002	-25.86	<0.01	2.387	0.040	60.18	<0.01	0.68

Table S5.4 Correlations (Spearman's r ; Pearson's r (p value)) between all elemental ratios and SST at different coral sites over a common assessment period 1990-2016. The listed p values were adjusted to account for first-order autocorrelation.

		Li/Ca	B/Ca	Mg/Ca	Sr/Ca	U/Ca	Li/Mg	B/Mg	Sr/Mg	U/Mg	SST
SMI81A	Li/Ca	1.00; 1.00 (<0.01)									
		0.45; 0.40 (<0.01)	1.00; 1.00 (<0.01)								
SMI81A	B/Ca	0.05; 0.17 (0.23)	-0.44; -0.43 (<0.01)	1.00; 1.00 (<0.01)							
		0.57; 0.55 (<0.01)	0.62; 0.62 (<0.01)	-0.49; -0.47 (<0.01)	1.00; 1.00 (<0.01)						
SMI81A	Mg/Ca	0.49; 0.46 (<0.01)	0.63; 0.64 (<0.01)	-0.63; -0.61 (<0.01)	0.85; 0.86 (<0.01)	1.00; 1.00 (<0.01)					
		0.52; 0.46 (<0.01)	0.64; 0.62 (<0.01)	-0.8; -0.79 (<0.01)	0.76; 0.76 (<0.01)	0.84; 0.83 (<0.01)	1.00; 1.00 (<0.01)				
SMI81A	Li/Mg	0.23; 0.14 (0.32)	0.82; 0.82 (<0.01)	-0.86; -0.86 (<0.01)	0.67; 0.65 (<0.01)	0.76; 0.75 (<0.01)	0.86; 0.86 (<0.01)	1.00; 1.00 (<0.01)			
		0.06; -0.01 (0.94)	0.52; 0.5 (<0.01)	-0.98; -0.98 (<0.01)	0.63; 0.63 (<0.01)	0.73; 0.73 (<0.01)	0.86; 0.88 (<0.01)	0.90; 0.90 (<0.01)	1.00; 1.00 (<0.01)		
SMI81A	B/Mg	0.23; 0.18 (0.18)	0.6; 0.58 (<0.01)	-0.9; -0.89 (<0.01)	0.74; 0.75 (<0.01)	0.9; 0.9 (<0.01)	0.91; 0.92 (<0.01)	0.90; 0.90 (<0.01)	0.95; 0.95 (<0.01)	1.00; 1.00 (<0.01)	
		-0.58; -0.55 (<0.01)	-0.67; -0.67 (<0.01)	0.56; 0.54 (<0.01)	-0.69; -0.69 (<0.01)	-0.78; -0.77 (<0.01)	-0.82; -0.82 (<0.01)	-0.72; -0.72 (<0.01)	-0.64; -0.63 (<0.01)	-0.74; -0.74 (<0.01)	1.00; 1.00 (<0.01)
SMI81A	Sr/Mg	0.06; -0.01 (0.94)	0.52; 0.5 (<0.01)	-0.98; -0.98 (<0.01)	0.63; 0.63 (<0.01)	0.73; 0.73 (<0.01)	0.86; 0.88 (<0.01)	0.90; 0.90 (<0.01)	1.00; 1.00 (<0.01)		
		0.23; 0.18 (0.18)	0.6; 0.58 (<0.01)	-0.9; -0.89 (<0.01)	0.74; 0.75 (<0.01)	0.9; 0.9 (<0.01)	0.91; 0.92 (<0.01)	0.90; 0.90 (<0.01)	0.95; 0.95 (<0.01)	1.00; 1.00 (<0.01)	
SMI81A	U/Mg	-0.58; -0.55 (<0.01)	-0.67; -0.67 (<0.01)	0.56; 0.54 (<0.01)	-0.69; -0.69 (<0.01)	-0.78; -0.77 (<0.01)	-0.82; -0.82 (<0.01)	-0.72; -0.72 (<0.01)	-0.64; -0.63 (<0.01)	-0.74; -0.74 (<0.01)	1.00; 1.00 (<0.01)
		-0.58; -0.55 (<0.01)	-0.67; -0.67 (<0.01)	0.56; 0.54 (<0.01)	-0.69; -0.69 (<0.01)	-0.78; -0.77 (<0.01)	-0.82; -0.82 (<0.01)	-0.72; -0.72 (<0.01)	-0.64; -0.63 (<0.01)	-0.74; -0.74 (<0.01)	1.00; 1.00 (<0.01)
SMI81A	SST	-0.55 (<0.01)	-0.67 (<0.01)	0.54 (<0.01)	-0.69 (<0.01)	-0.77 (<0.01)	-0.82 (<0.01)	-0.72 (<0.01)	-0.63 (<0.01)	-0.74 (<0.01)	1.00 (<0.01)
		-0.55 (<0.01)	-0.67 (<0.01)	0.54 (<0.01)	-0.69 (<0.01)	-0.77 (<0.01)	-0.82 (<0.01)	-0.72 (<0.01)	-0.63 (<0.01)	-0.74 (<0.01)	1.00 (<0.01)
SHW82C	Li/Ca	Li/Ca 1.00; 1.00 (<0.01)									
		0.56; 0.53 (<0.01)	1.00; 1.00 (<0.01)								
SHW82C	B/Ca	0.11; 0.17 (0.19)	-0.49; -0.51 (<0.01)	1.00; 1.00 (<0.01)							
		0.37; 0.32 (0.01)	0.84; 0.84 (<0.01)	-0.71; -0.73 (<0.01)	1.00; 1.00 (<0.01)						
SHW82C	Mg/Ca	0.22; 0.18 (0.15)	0.77; 0.8 (<0.01)	-0.77; -0.78 (<0.01)	0.89; 0.91 (<0.01)	1.00; 1.00 (<0.01)					
		0.4; 0.35 (<0.01)	0.75; 0.76 (<0.01)	-0.85; -0.86 (<0.01)	0.86; 0.87 (<0.01)	0.83; 0.84 (<0.01)	1.00; 1.00 (<0.01)				
SHW82C	Li/Mg	0.26; 0.2 (0.12)	0.86; 0.87 (<0.01)	-0.85; -0.86 (<0.01)	0.9; 0.91 (<0.01)	0.89; 0.91 (<0.01)	0.93; 0.93 (<0.01)	1.00; 1.00 (<0.01)			
		-0.05; -0.08 (0.53)	0.55; 0.59 (<0.01)	-0.99; -0.98 (<0.01)	0.78; 0.81 (<0.01)	0.81; 0.84 (<0.01)	0.88; 0.9 (<0.01)	0.89; 0.91 (<0.01)	1.00; 1.00 (<0.01)		
SHW82C	B/Mg	0.03; 0.00 (0.94)	0.64; 0.68 (<0.01)	-0.96; -0.94 (<0.01)	0.83; 0.86 (<0.01)	0.92; 0.93 (<0.01)	0.89; 0.91 (<0.01)	0.92; 0.95 (<0.01)	0.97; 0.98 (<0.01)	1.00; 1.00 (<0.01)	
		-0.36; -0.34 (0.01)	-0.8; -0.8 (<0.01)	0.7; 0.71 (<0.01)	-0.83; -0.82 (<0.01)	-0.79; -0.79 (<0.01)	-0.85; -0.85 (<0.01)	-0.87; -0.86 (<0.01)	-0.74; -0.76 (<0.01)	-0.78; -0.79 (<0.01)	1.00; 1.00 (<0.01)
SHW82C	Sr/Mg	-0.05; -0.08 (0.53)	0.55; 0.59 (<0.01)	-0.99; -0.98 (<0.01)	0.78; 0.81 (<0.01)	0.81; 0.84 (<0.01)	0.88; 0.9 (<0.01)	0.89; 0.91 (<0.01)	1.00; 1.00 (<0.01)		
		0.03; 0.00 (0.94)	0.64; 0.68 (<0.01)	-0.96; -0.94 (<0.01)	0.83; 0.86 (<0.01)	0.92; 0.93 (<0.01)	0.89; 0.91 (<0.01)	0.92; 0.95 (<0.01)	0.97; 0.98 (<0.01)	1.00; 1.00 (<0.01)	
SHW82C	U/Mg	-0.36; -0.34 (0.01)	-0.8; -0.8 (<0.01)	0.7; 0.71 (<0.01)	-0.83; -0.82 (<0.01)	-0.79; -0.79 (<0.01)	-0.85; -0.85 (<0.01)	-0.87; -0.86 (<0.01)	-0.74; -0.76 (<0.01)	-0.78; -0.79 (<0.01)	1.00; 1.00 (<0.01)
		-0.36; -0.34 (0.01)	-0.8; -0.8 (<0.01)	0.7; 0.71 (<0.01)	-0.83; -0.82 (<0.01)	-0.79; -0.79 (<0.01)	-0.85; -0.85 (<0.01)	-0.87; -0.86 (<0.01)	-0.74; -0.76 (<0.01)	-0.78; -0.79 (<0.01)	1.00; 1.00 (<0.01)
SHW82C	SST	-0.34 (0.01)	-0.8 (<0.01)	0.71 (<0.01)	-0.82 (<0.01)	-0.79 (<0.01)	-0.85 (<0.01)	-0.86 (<0.01)	-0.76 (<0.01)	-0.79 (<0.01)	1.00 (<0.01)
		-0.34 (0.01)	-0.8 (<0.01)	0.71 (<0.01)	-0.82 (<0.01)	-0.79 (<0.01)	-0.85 (<0.01)	-0.86 (<0.01)	-0.76 (<0.01)	-0.79 (<0.01)	1.00 (<0.01)
HUM03A	Li/Ca	Li/Ca 1.00; 1.00									

		(<0.01)										
		0.46;	1.00;									
HUM03A	B/Ca	0.45	1.00									
		(<0.01)	(<0.01)									
		-0.32;	1.00;									
HUM03A	Mg/Ca	-0.33	-0.54	1.00								
		(<0.01)	(<0.01)	(<0.01)								
		0.5;	0.74;	-0.58;	1.00;							
HUM03A	Sr/Ca	0.49	0.75	-0.63	1.00							
		(<0.01)	(<0.01)	(<0.01)	(<0.01)							
		0.54;	0.71;	-0.63;	0.94;	1.00;						
HUM03A	U/Ca	0.52	0.73	-0.7	0.95	1.00						
		(<0.01)	(<0.01)	(<0.01)	(<0.01)	(<0.01)						
		0.62;	0.6;	-0.93;	0.65;	0.71;	1.00;					
HUM03A	Li/Mg	0.61	0.61	-0.94	0.71	0.78	1.00					
		(<0.01)	(<0.01)	(<0.01)	(<0.01)	(<0.01)	(<0.01)					
		0.46;	0.87;	-0.85;	0.76;	0.77;	0.87;	1.00;				
HUM03A	B/Mg	0.45	0.87	-0.88	0.8	0.83	0.9	1.00				
		(<0.01)	(<0.01)	(<0.01)	(<0.01)	(<0.01)	(<0.01)	(<0.01)				
		0.38;	0.6;	-0.98;	0.7;	0.74;	0.94;	0.9;	1.00;			
HUM03A	Sr/Mg	0.39	0.62	-0.98	0.76	0.81	0.96	0.92	1.00			
		(<0.01)	(<0.01)	(<0.01)	(<0.01)	(<0.01)	(<0.01)	(<0.01)	(<0.01)			
		0.47;	0.69;	-0.88;	0.85;	0.92;	0.89;	0.89;	0.94;	1.00;		
HUM03A	U/Mg	0.46	0.69	-0.91	0.86	0.93	0.93	0.93	0.97	1.00		
		(<0.01)	(<0.01)	(<0.01)	(<0.01)	(<0.01)	(<0.01)	(<0.01)	(<0.01)	(<0.01)		
		-0.69;	-0.69;	0.68;	-0.72;	-0.77;	-0.81;	-0.79;	-0.74;	-0.8;	1.00;	
HUM03A	SST	-0.68	-0.69	0.7	-0.74	-0.78	-0.82	-0.79	-0.75	-0.79	1.00	
		(<0.01)	(<0.01)	(<0.01)	(<0.01)	(<0.01)	(<0.01)	(<0.01)	(<0.01)	(<0.01)	(<0.01)	
		Li/Ca	B/Ca	Mg/Ca	Sr/Ca	U/Ca	Li/Mg	B/Mg	Sr/Mg	U/Mg	SST	
		1.00;										
HUM04B	Li/Ca	1.00										
		(<0.01)										
		0.37;	1.00;									
HUM04B	B/Ca	0.37	1.00									
		(<0.01)	(<0.01)									
		0.15;	0.06;	1.00;								
HUM04B	Mg/Ca	0.19	0.06	1.00								
		(0.08)	(0.68)	(<0.01)								
		0.23;	0.5;	-0.65;	1.00;							
HUM04B	Sr/Ca	0.22	0.53	-0.66	1.00							
		(0.03)	(<0.01)	(<0.01)	(<0.01)							
		0.1;	0.34;	-0.77;	0.88;	1.00;						
HUM04B	U/Ca	0.07	0.38	-0.76	0.92	1.00						
		(0.51)	(<0.01)	(<0.01)	(<0.01)	(<0.01)						
		0.18;	0.07;	-0.94;	0.72;	0.8;	1.00;					
HUM04B	Li/Mg	0.15	0.09	-0.93	0.75	0.8	1.00					
		(0.16)	(0.54)	(<0.01)	(<0.01)	(<0.01)	(<0.01)					
		0.16;	0.68;	-0.65;	0.82;	0.79;	0.71;	1.00;				
HUM04B	B/Mg	0.12	0.67	-0.69	0.87	0.83	0.76	1.00				
		(0.26)	(<0.01)	(<0.01)	(<0.01)	(<0.01)	(<0.01)	(<0.01)				
		-0.1;	0.02;	-0.99;	0.72;	0.82;	0.95;	0.7;	1.00;			
HUM04B	Sr/Mg	-0.13	0.05	-0.98	0.76	0.83	0.96	0.77	1.00			
		(0.22)	(0.72)	(<0.01)	(<0.01)	(<0.01)	(<0.01)	(<0.01)	(<0.01)			
		-0.05;	0.12;	-0.95;	0.79;	0.92;	0.92;	0.75;	0.97;	1.00;		
HUM04B	U/Mg	-0.07	0.17	-0.93	0.84	0.93	0.93	0.82	0.98	1.00		
		(0.50)	(0.21)	(<0.01)	(<0.01)	(<0.01)	(<0.01)	(<0.01)	(<0.01)	(<0.01)		
		-0.17;	-0.51;	0.62;	-0.78;	-0.79;	-0.68;	-0.83;	-0.67;	-0.73;	1.00;	
HUM04B	SST	-0.19	-0.54	0.62	-0.8	-0.79	-0.7	-0.83	-0.69	-0.75	1.00	
		(0.08)	(<0.01)	(<0.01)	(<0.01)	(<0.01)	(<0.01)	(<0.01)	(<0.01)	(<0.01)	(<0.01)	
		Li/Ca	B/Ca	Mg/Ca	Sr/Ca	U/Ca	Li/Mg	B/Mg	Sr/Mg	U/Mg	SST	
		1.00;										
SEN01C	Li/Ca	1.00										
		(<0.01)										
		0.35;	1.00;									
SEN01C	B/Ca	0.29	1.00									
		(0.04)	(<0.01)									
		0.52;	0.52;	1.00;								
SEN01C	Mg/Ca	-0.01	-0.39	1.00								
		(0.95)	(<0.01)	(<0.01)								

SEN01C	Sr/Ca	-0.11; 0.52 (<0.01)	-0.44; 0.45 (<0.01)	-0.71; -0.69 (<0.01)	1.00; 1.00 (<0.01)							
SEN01C	U/Ca	0.39; 0.36 (<0.01)	0.68; 0.64 (<0.01)	0.85; -0.74 (<0.01)	-0.75; 0.87 (<0.01)	1.00; 1.00 (<0.01)						
SEN01C	Li/Mg	0.49; 0.46 (<0.01)	0.54; 0.48 (<0.01)	0.84; -0.88 (<0.01)	-0.9; 0.86 (<0.01)	0.82; 0.84 (<0.01)	1.00; 1.00 (<0.01)					
SEN01C	B/Mg	0.23; 0.15 (0.29)	0.76; 0.73 (<0.01)	0.73; -0.9 (<0.01)	-0.9; 0.74 (<0.01)	0.85; 0.86 (<0.01)	0.88; 0.88 (<0.01)	1.00; 1.00 (<0.01)				
SEN01C	Sr/Mg	0.18; 0.13 (0.34)	0.47; 0.43 (<0.01)	0.79; -0.97 (<0.01)	-0.99; 0.81 (<0.01)	0.8; 0.83 (<0.01)	0.93; 0.93 (<0.01)	0.91; 0.93 (<0.01)	1.00; 1.00 (<0.01)			
SEN01C	U/Mg	0.26; 0.2 (0.13)	0.59; 0.54 (<0.01)	0.83; -0.91 (<0.01)	-0.94; 0.84 (<0.01)	0.93; 0.94 (<0.01)	0.92; 0.92 (<0.01)	0.94; 0.94 (<0.01)	0.96; 0.97 (<0.01)	1.00; 1.00 (<0.01)		
SEN01C	SST	-0.49; -0.47 (<0.01)	-0.68; -0.67 (<0.01)	-0.78; 0.67 (<0.01)	0.71; -0.79 (<0.01)	-0.84; -0.85 (<0.01)	-0.82; -0.82 (<0.01)	-0.82; -0.75 (<0.01)	-0.75; -0.82 (<0.01)	-0.82; 1.00 (<0.01)	1.00; 1.00 (<0.01)	
		Li/Ca 1.00; 1.00 (<0.01)	B/Ca 1.00; 1.00 (<0.01)	Mg/Ca 1.00; -0.4 1.00 (<0.01)	Sr/Ca 1.00; 1.00 (<0.01)	U/Ca 1.00; 0.84 1.00 (<0.01)	Li/Mg 1.00; 0.76 1.00 (<0.01)	B/Mg 1.00; 0.82 1.00 (<0.01)	Sr/Mg 1.00; 0.8 1.00 (<0.01)	U/Mg 1.00; 0.98 1.00 (<0.01)	SST 1.00; 1.00 (<0.01)	
MAS02A	Li/Ca	0.3; 0.31 (<0.01)	1.00; 1.00 (<0.01)									
MAS02A	B/Ca	0.12; 0.19 (0.08)	-0.44; -0.4 (<0.01)	1.00; 1.00 (<0.01)								
MAS02A	Mg/Ca	0.14; 0.09 (0.41)	0.63; 0.6 (<0.01)	-0.67; -0.66 (<0.01)	1.00; 1.00 (<0.01)							
MAS02A	Sr/Ca	0.1; 0.01 (0.93)	0.54; 0.47 (<0.01)	-0.83; -0.83 (<0.01)	0.84; 0.84 (<0.01)	1.00; 1.00 (<0.01)						
MAS02A	Li/Mg	0.47; 0.46 (<0.01)	0.58; 0.55 (<0.01)	-0.78; -0.78 (<0.01)	0.67; 0.65 (<0.01)	0.77; 0.76 (<0.01)	1.00; 1.00 (<0.01)					
MAS02A	B/Mg	0.07; 0.01 (0.93)	0.78; 0.75 (<0.01)	-0.9; -0.9 (<0.01)	0.77; 0.75 (<0.01)	0.83; 0.82 (<0.01)	0.82; 0.82 (<0.01)	1.00; 1.00 (<0.01)				
MAS02A	Sr/Mg	-0.08; -0.15 (0.17)	0.49; 0.44 (<0.01)	-0.99; -0.99 (<0.01)	0.76; 0.75 (<0.01)	0.87; 0.88 (<0.01)	0.79; 0.8 (<0.01)	0.92; 0.92 (<0.01)	1.00; 1.00 (<0.01)			
MAS02A	U/Mg	-0.01; -0.1 (0.37)	0.51; 0.44 (<0.01)	-0.96; -0.95 (<0.01)	0.78; 0.78 (<0.01)	0.95; 0.95 (<0.01)	0.81; 0.8 (<0.01)	0.9; 0.89 (<0.01)	0.98; 0.98 (<0.01)	1.00; 1.00 (<0.01)		
MAS02A	SST	-0.17; -0.12 (0.30)	-0.63; -0.6 (<0.01)	0.71; 0.72 (<0.01)	-0.78; -0.78 (<0.01)	-0.83; -0.83 (<0.01)	-0.73; -0.73 (<0.01)	-0.8; -0.8 (<0.01)	-0.76; -0.76 (<0.01)	-0.8; -0.8 (<0.01)	1.00; 1.00 (<0.01)	

Table S5.5 Factor loadings on rotated principal components (PC) for nine elemental ratios (Li/Ca, B/Ca, Mg/Ca, Sr/Ca, U/Ca, Li/Mg, B/Mg, Sr/Mg, and U/Mg) for each coral core.

Coral ID	Elemental Ratio	PC1	PC2	Coral ID	Elemental Ratio	PC1	PC2
HUM03A	Li/Ca	0.10	0.90	SHW82C	Li/Ca	-0.06	0.96
HUM03A	B/Ca	0.53	0.62	SHW82C	B/Ca	0.67	0.67
HUM03A	Mg/Ca	-0.96	-0.16	SHW82C	Mg/Ca	-0.97	0.15
HUM03A	Sr/Ca	0.65	0.61	SHW82C	Sr/Ca	0.85	0.41
HUM03A	U/Ca	0.70	0.59	SHW82C	U/Ca	0.90	0.27
HUM03A	Li/Mg	0.84	0.44	SHW82C	Li/Mg	0.90	0.35
HUM03A	B/Mg	0.86	0.44	SHW82C	B/Mg	0.94	0.29
HUM03A	Sr/Mg	0.95	0.27	SHW82C	Sr/Mg	0.99	-0.05
HUM03A	U/Mg	0.90	0.41	SHW82C	U/Mg	0.99	0.05
HUM03A	SST	-0.58	-0.70	SHW82C	SST	-0.80	-0.43
HUM04B	Li/Ca	-0.09	0.70	SM181A	Li/Ca	-0.21	0.94
HUM04B	B/Ca	0.16	0.91	SM181A	B/Ca	0.47	0.62
HUM04B	Mg/Ca	-0.95	0.23	SM181A	Mg/Ca	-0.99	-0.01
HUM04B	Sr/Ca	0.83	0.45	SM181A	Sr/Ca	0.49	0.74
HUM04B	U/Ca	0.90	0.27	SM181A	U/Ca	0.64	0.67
HUM04B	Li/Mg	0.94	0.02	SM181A	Li/Mg	0.76	0.58
HUM04B	B/Mg	0.83	0.48	SM181A	B/Mg	0.88	0.37
HUM04B	Sr/Mg	0.99	-0.11	SM181A	Sr/Mg	0.97	0.18
HUM04B	U/Mg	0.99	0.02	SM181A	U/Mg	0.90	0.39
HUM04B	SST	-0.77	-0.46	SM181A	SST	-0.53	-0.72
MAS02A	Li/Ca	-0.15	0.94	SEN01C	Li/Ca	-0.03	0.95
MAS02A	B/Ca	0.52	0.61	SEN01C	B/Ca	0.49	0.48
MAS02A	Mg/Ca	-0.96	0.09	SEN01C	Mg/Ca	-0.97	0.03
MAS02A	Sr/Ca	0.81	0.26	SEN01C	Sr/Ca	0.73	0.55
MAS02A	U/Ca	0.93	0.12	SEN01C	U/Ca	0.96	0.23
MAS02A	Li/Mg	0.78	0.51	SEN01C	Li/Mg	0.86	0.42
MAS02A	B/Mg	0.93	0.22	SEN01C	B/Mg	0.95	0.22
MAS02A	Sr/Mg	0.98	-0.04	SEN01C	Sr/Mg	0.98	0.11
MAS02A	U/Mg	0.99	0.01	SEN01C	U/Mg	0.83	0.45
MAS02A	SST	-0.84	-0.29	SEN01C	SST	-0.73	-0.57

Note: Extraction Method: Principal Component Analysis; Rotation Method: Varimax with Kaiser Normalization. Cumulative of PC1 and PC2 from nine elemental ratios explain ~ 90% of the variance for each coral core. SST is included for normalization and for better visualization (see Figure 5.3 in the main text and Figure S5.6).

Table S5.6 Coordination of centroid for Sr/Ca, U/Ca, Li/Mg, and B/Mg. Centroid for each elemental ratio was calculated by using equations (1)-(4). B/Mg centroid was calculated by excluding the data point from SHW82C.

	Sr/Ca (mmol/mol)	U/Ca (μ mol/mol)	Li/Mg (mmol/mol)	B/Mg (mmol/mol)
¹ SST _{centroid}	25.86	35.61	23.69	32.66
¹ Metal Ratio _{centroid}	8.82	0.70	1.88	66.24
² SST _{centroid}	31.46	35.57	18.80	33.51
² Metal Ratio _{centroid}	8.59	0.91	2.15	88.74

¹ Calculated from equation: SST=Slope $\times$ Elemental Ratios + Intercept, and use intercept as subject;

¹ Calculated from equation: Elemental Ratios=Slope $\times$ SST + Intercept, and use intercept as subject.

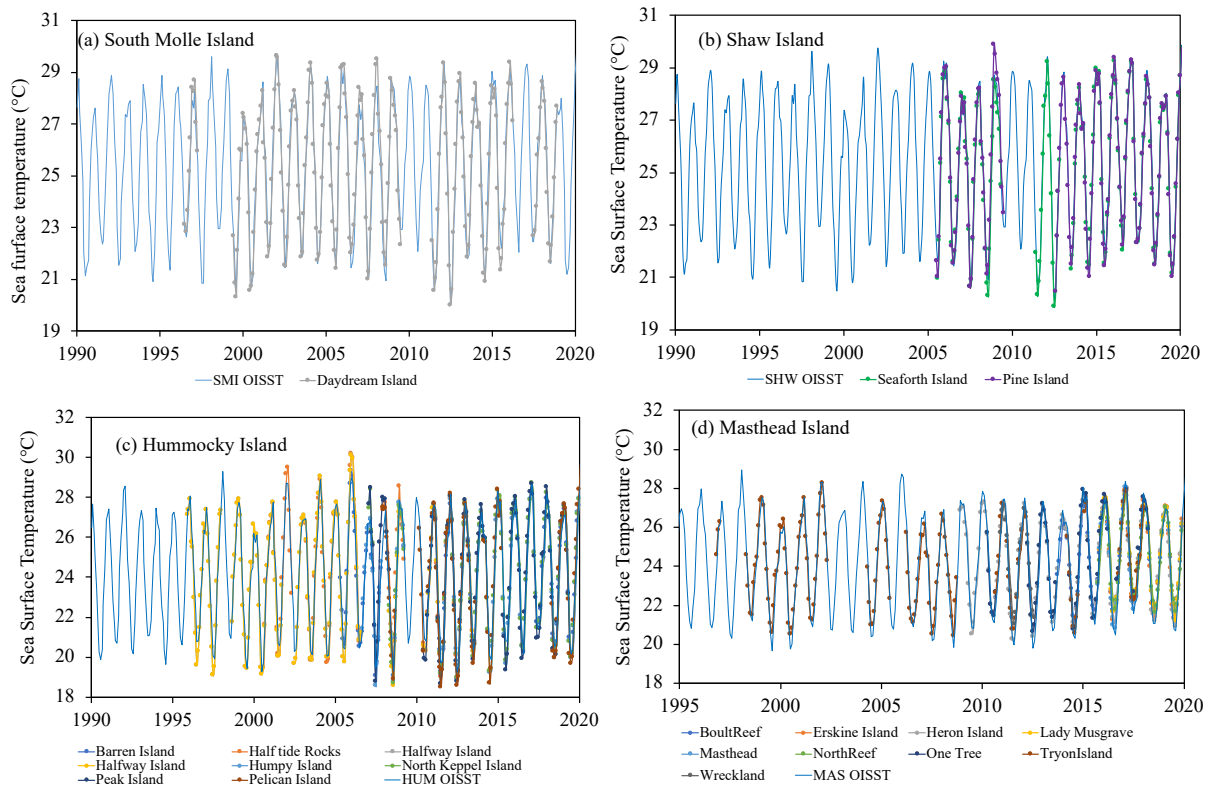


Figure S5.1 Comparison between OISST and in-situ data from coral sampling sites. If the in-situ data were too short in length or missing, nearby logger data (mostly <30km) were obtained and averaged. (a) In-situ SST from Daydream Island loggers, and South Molle Island (SMI) OISST centred on 20.375°S 148.875°E. (b) In-situ SST from Seaforth Island and Pine Island loggers, and Shaw Island (SHW) OISST centred on 20.375°S 148.875°E. (c) In-situ SST from Barren Island, Half tide Rocks, Halfway Island, Humpy Island, North Keppel Island, Peak Island, and Pelican Island loggers, and Hummocky Island (HUM) OISST centred on 23.375°S 151.125°E. (d) In-situ SST from Boulton Reef, Erskine Island, Heron Island, Lady Musgrave, Masthead Reef, North Reef, One Tree Island, Tryon Island and Wreck Island loggers, and Masthead Island (MAS) OISST centred on 23.625°S 151.625°E. All data are in monthly resolution (12 points per year).

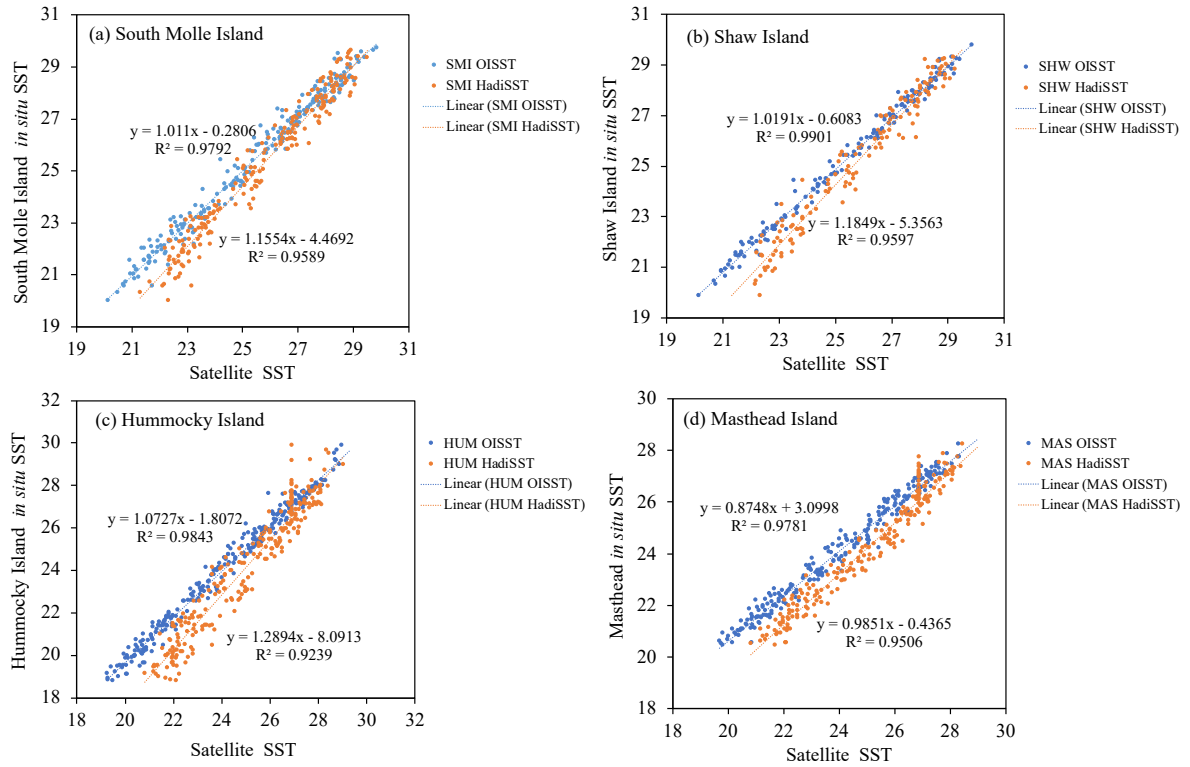


Figure S5.2 Linear regression between in-situ SST and satellite-derived SST. (a) In-situ SST from South Molle Island vs. HadISST (20.5°S 148.5°E) and OISST (20.375°S 148.875°E). (b) In-situ SST from Shaw Island vs. HadISST (20.5°S 148.5°E) and OISST (20.375°S 148.875°E). (c) In-situ SST from Hummocky Island vs. HadISST (23.5°S 151.5°E) and OISST (23.375°S 151.125°E). (d) In-situ SST from Masthead Island vs. HadISST (23.5°S 151.5°E) and OISST (23.625°S 151.625°E).

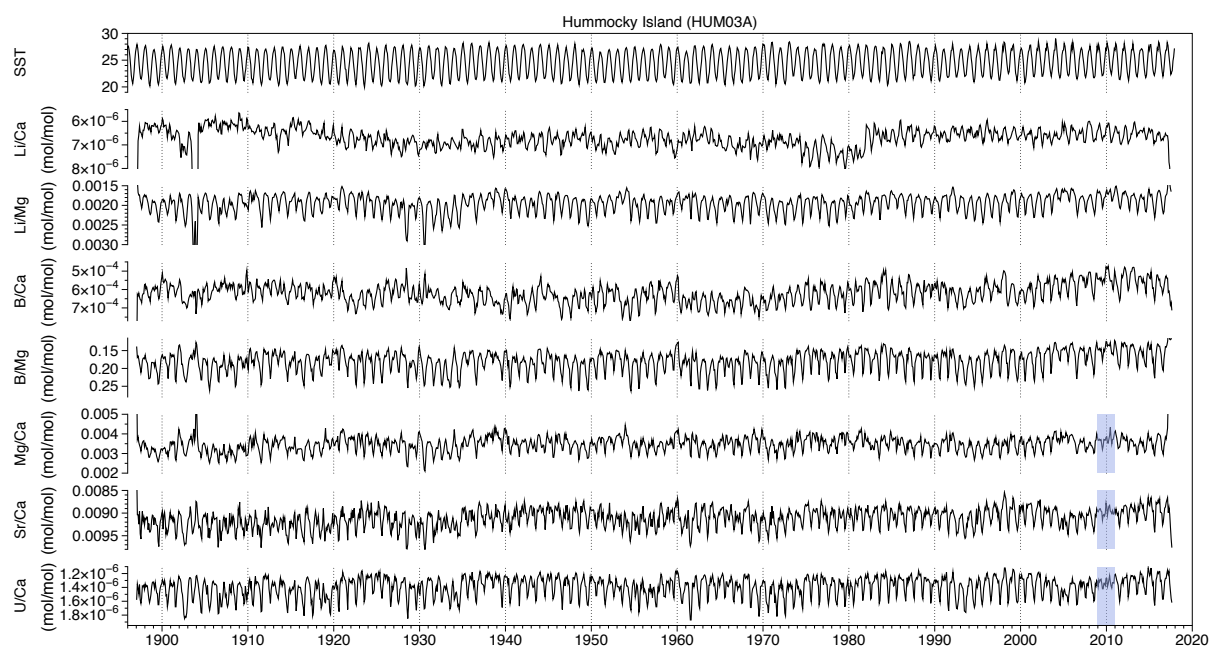


Figure S5.3a Time series of SST, Li/Ca, Li/Mg, B/Ca, B/Mg, Mg/Ca, Sr/Ca, and U/Ca at HUM03A. The blue shadings highlight the short-term anomalies of Mg/Ca, Sr/Ca, and U/Ca at HUM03A which are not reproducible at the adjacent coral core HUM04B. The calibration period and verification (reconstruction) period are 1990-2016 and 1898 to 1990, respectively (see main text for more details).

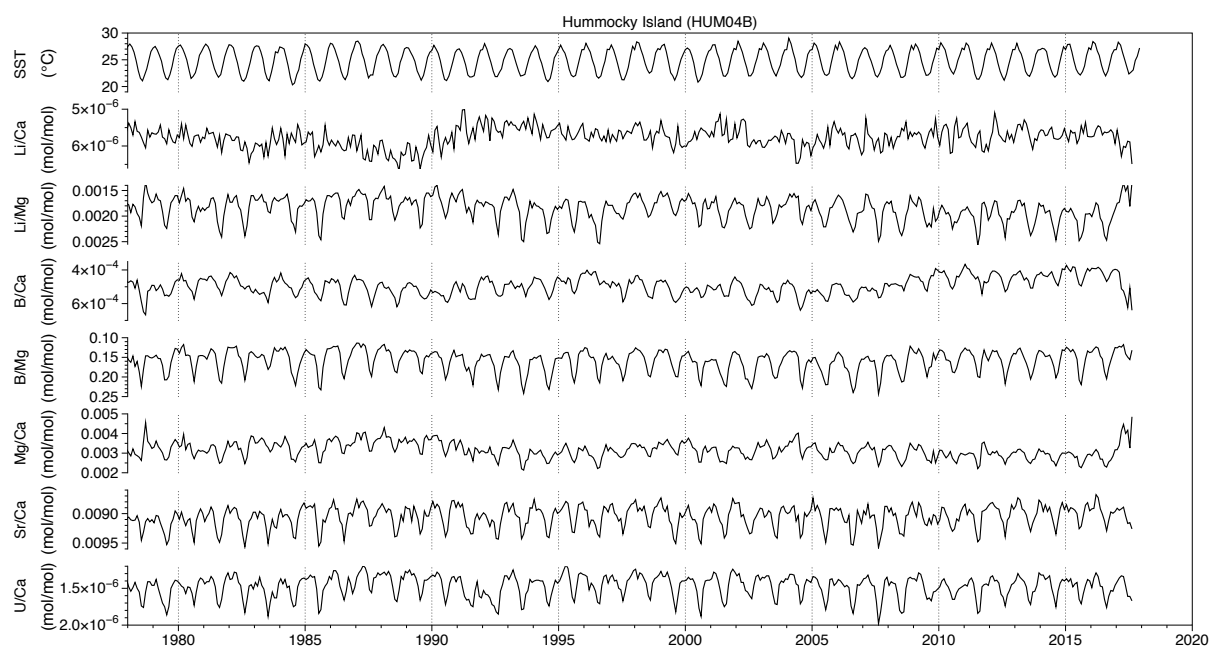


Figure S5.3b Time series of SST, Li/Ca, Li/Mg, B/Ca, B/Mg, Mg/Ca, Sr/Ca, and U/Ca at HUM04B. The calibration period and verification (reconstruction) period are 1990-2016 and 1978 to 1990, respectively (see main text for more details).

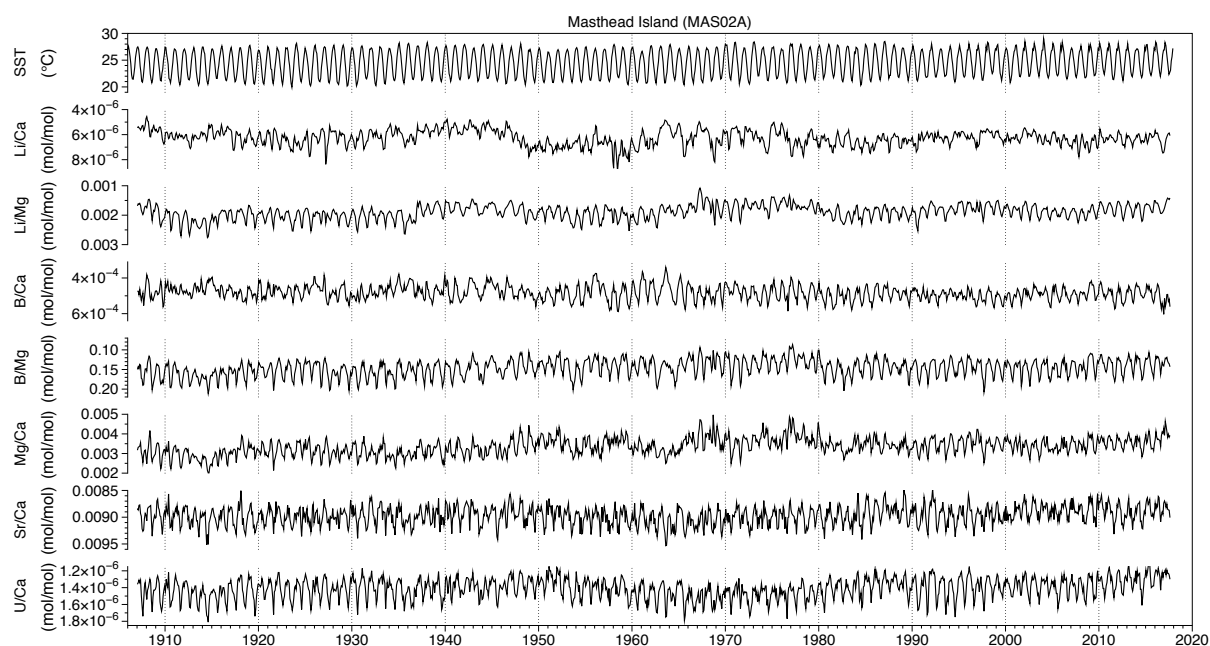


Figure S5.3c Time series of SST, Li/Ca, Li/Mg, B/Ca, B/Mg, Mg/Ca, Sr/Ca, and U/Ca at MAS02A. The calibration period and verification (reconstruction) period are 1990-2016 and 1906 to 1990, respectively (see main text for more details).

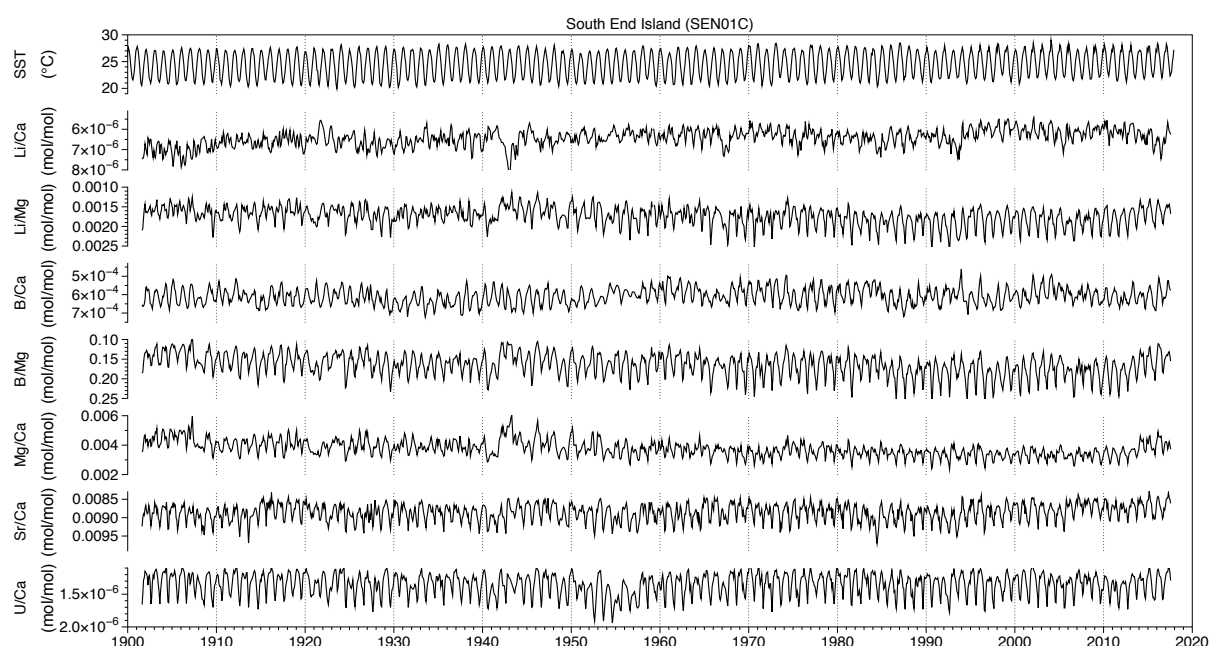


Figure S5.3d Time series of SST, Li/Ca, Li/Mg, B/Ca, B/Mg, Mg/Ca, Sr/Ca, and U/Ca at SEN01C. The calibration period and verification (reconstruction) period are 1990-2016 and 1902 to 1990, respectively (see main text for more details).

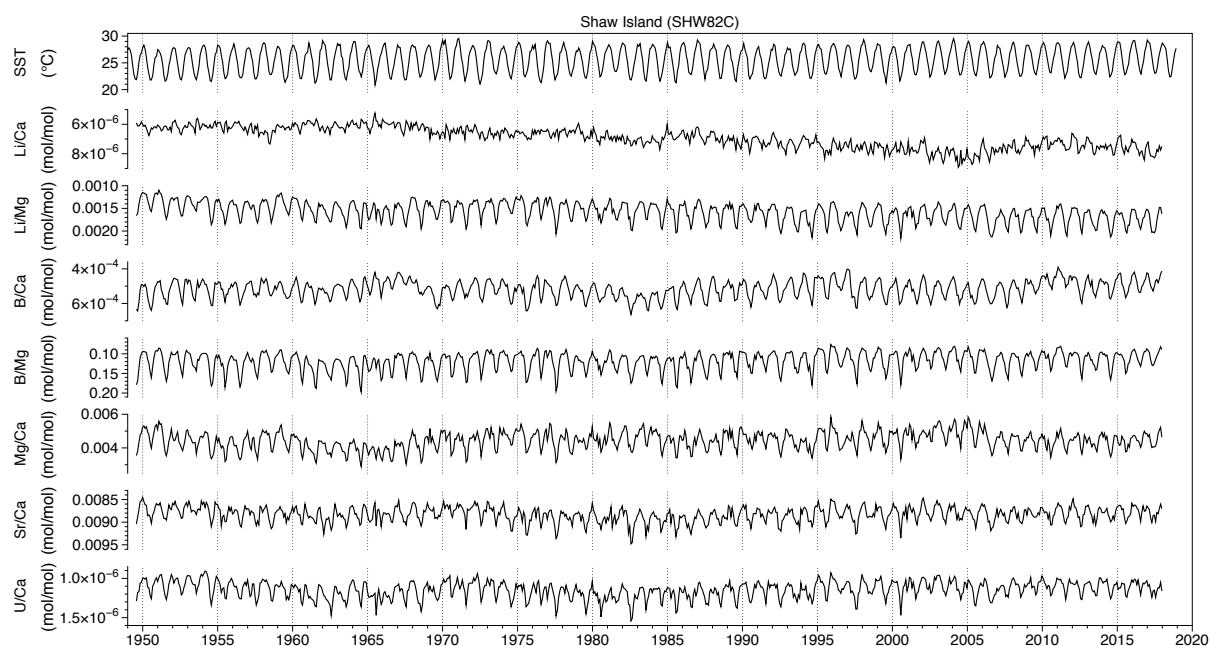


Figure S5.3e Time series of SST, Li/Ca, Li/Mg, B/Ca, B/Mg, Mg/Ca, Sr/Ca, and U/Ca at SHW82C. The calibration period and verification (reconstruction) period are 1990-2016 and 1949 to 1990, respectively (see main text for more details).

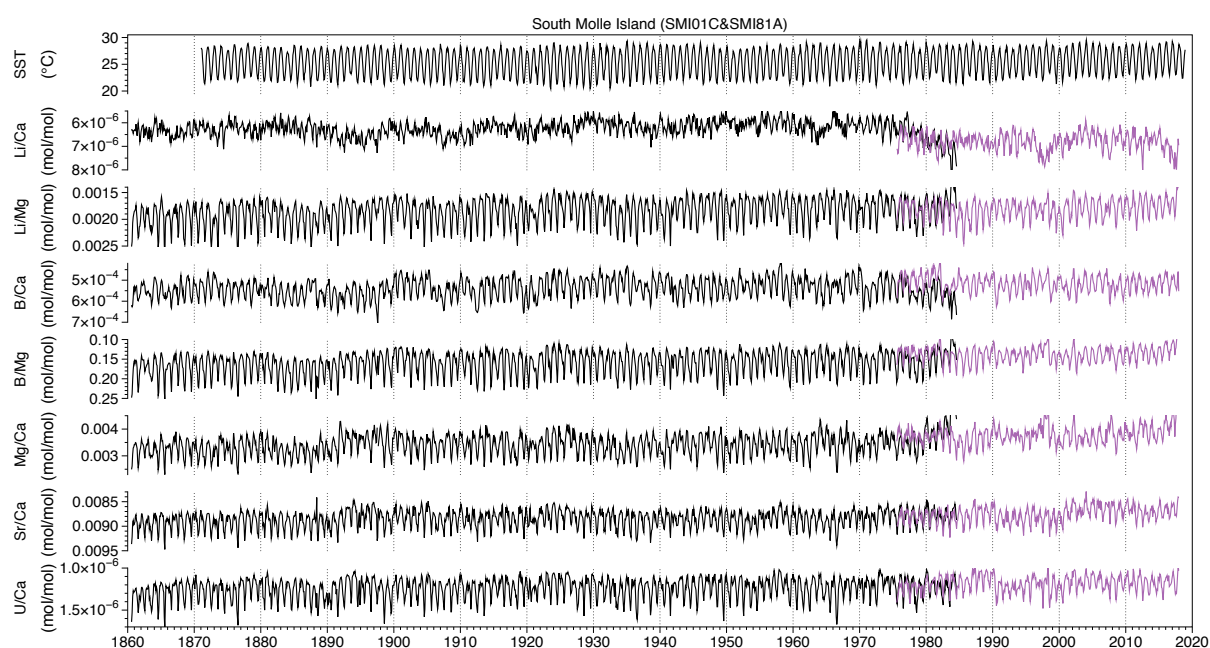


Figure S5.3f Time series of SST, Li/Ca, Li/Mg, B/Ca, B/Mg, Mg/Ca, Sr/Ca, and U/Ca at SMI01C (black) and SMI81A (purple). The calibration period and verification (reconstruction) period are 1990-2016 and 1860 to 1990, respectively (see main text for more details).

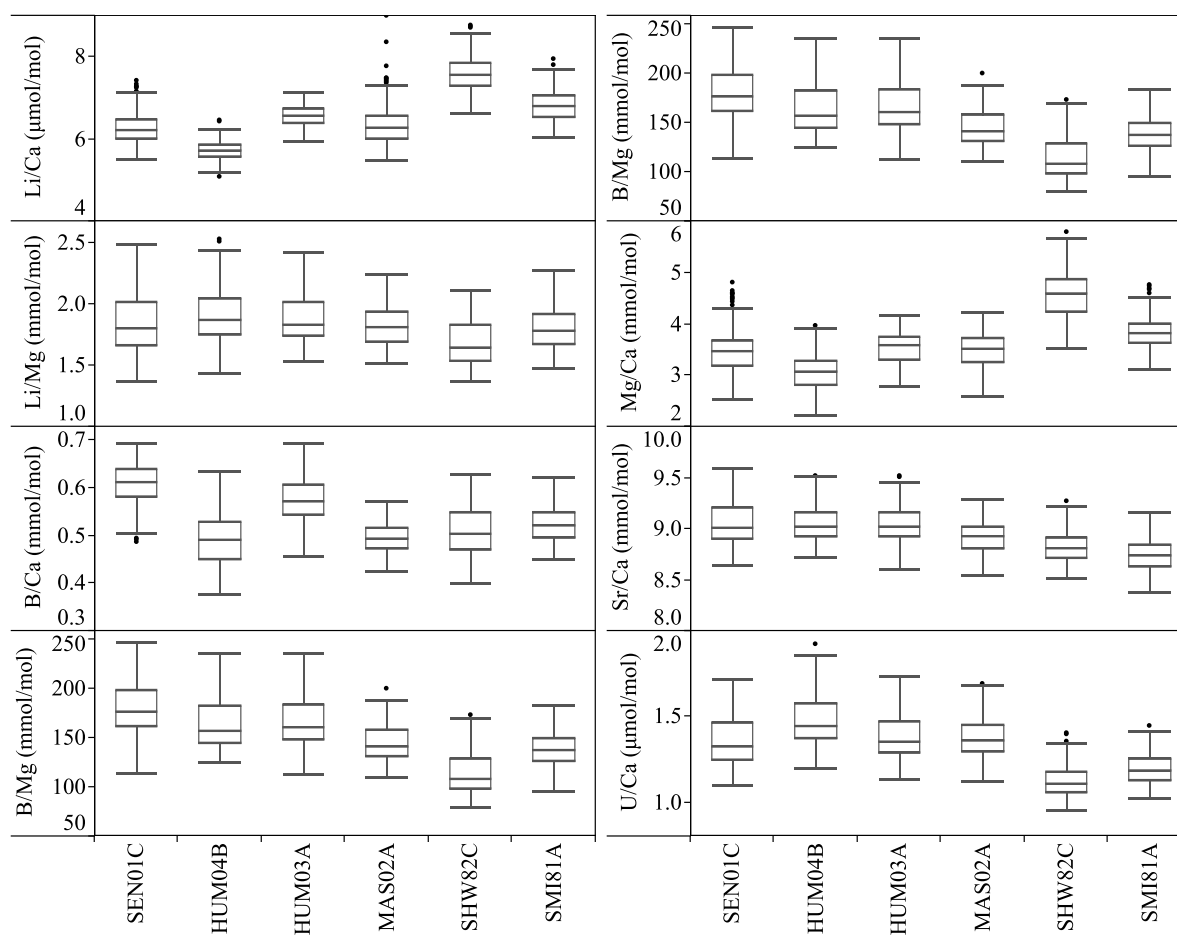


Figure S5.4 Comparison of Li/Ca, Li/Mg, B/Ca, B/Mg, Mg/Ca, Sr/Ca, and U/Ca ratios. For consistent comparison over a common period, only data for 1990-2016 are plotted. From the top to bottom, this box and whisper plot presents the five-number summary of upper whisker, upper hinge, medium, lower hinge, and lower whisker. Note: Whiskers extend to data within 1.5 times the interquartile range (IQR).

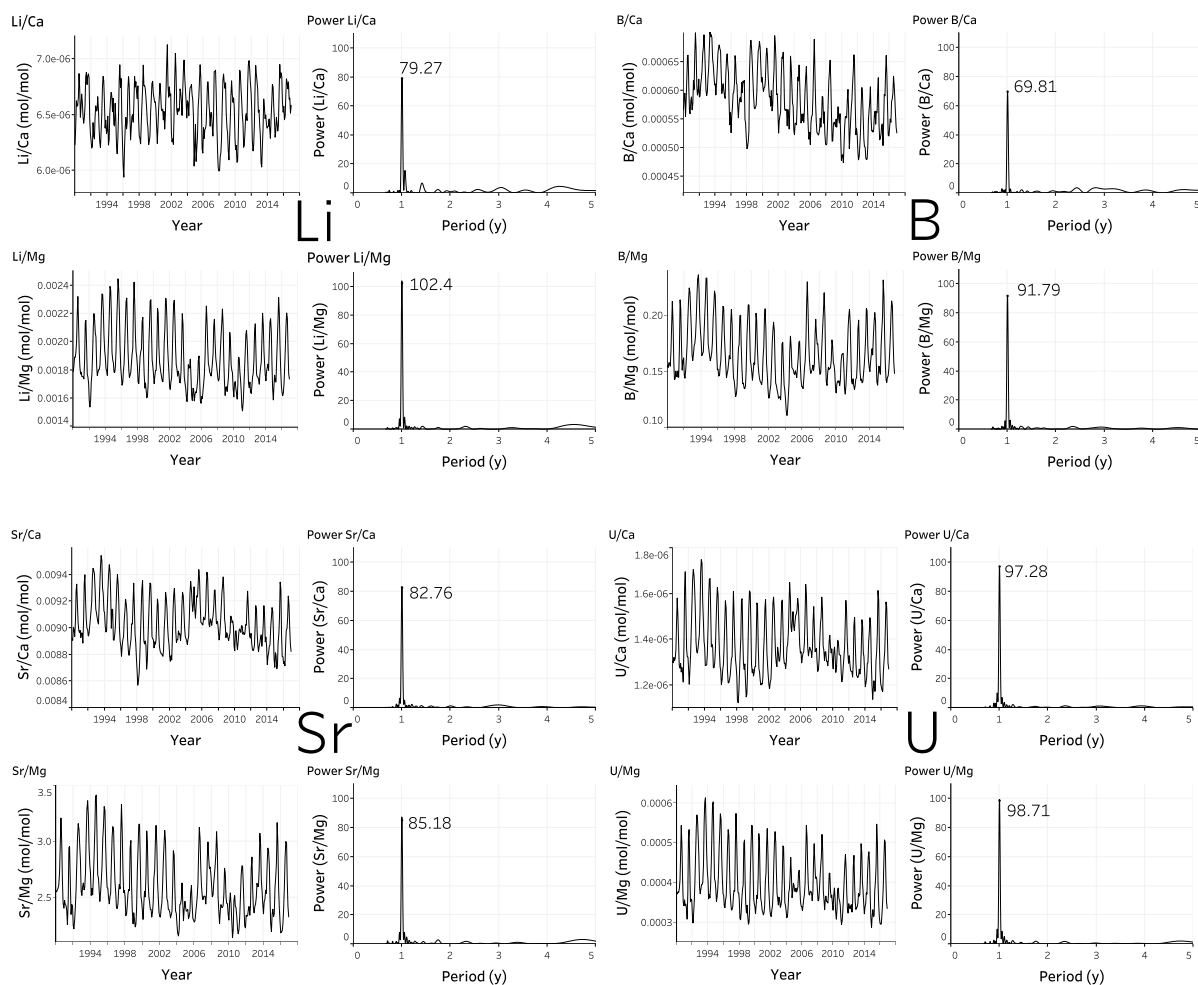


Figure S5.5 Time series of elemental ratios and the respective power spectra analysis of Li/Ca, Li/Mg, B/Ca, B/Mg, Sr/Ca, Sr/Mg, U/Ca, and U/Mg using HUM03A as an example. Each power spectra document a 12-month (1 year) periodicity at $p < 0.01$. For a better illustration, in the case of power spectra, frequency was converted into period (1/frequency).

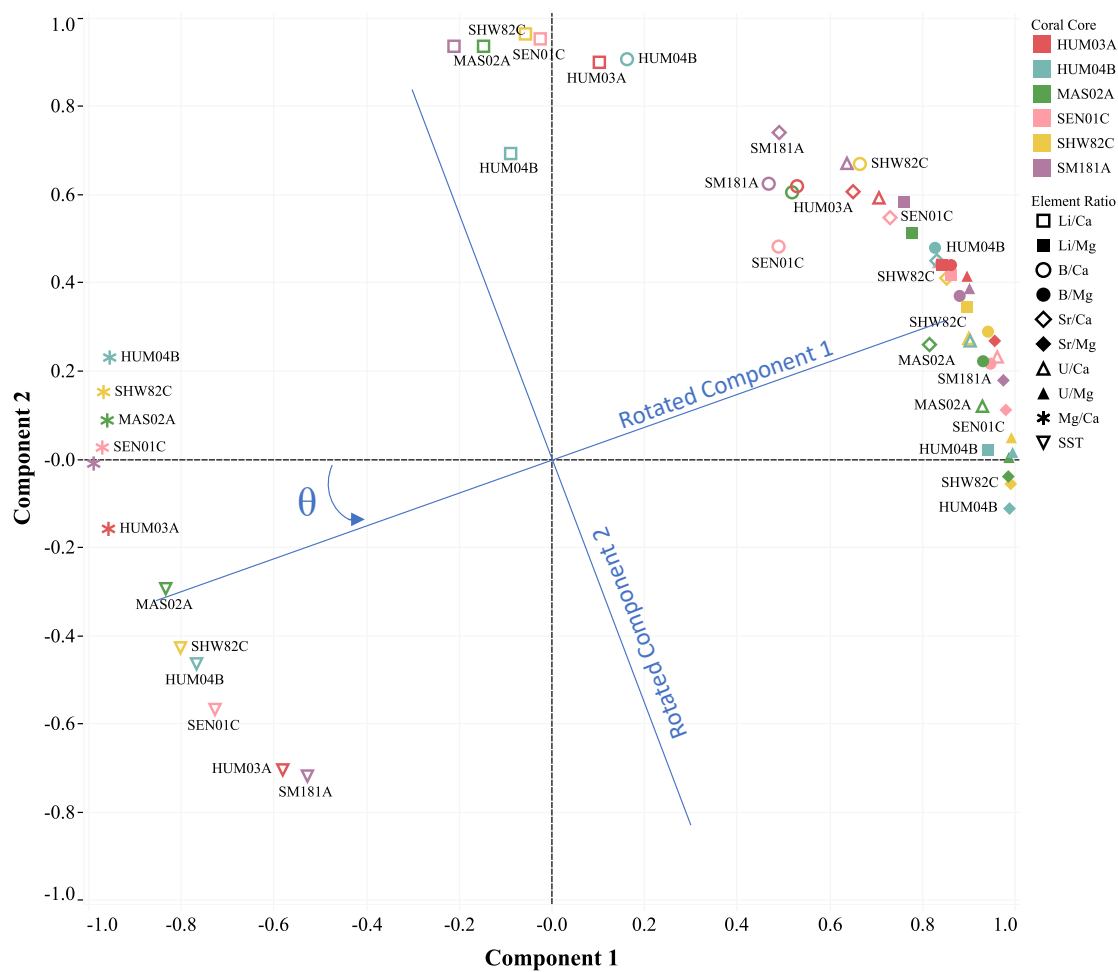


Figure S5.6 The loadings of each element onto the first two PCs from the PCA analysis. Cumulative of PC1 and PC2 explain ~90% of the variance for each coral core. Including of SST in this plot is for better visualization. Note: this graph is for visualization only, each principal component generated from individual corals are not identical. Blue lines show how to rotate the coordinates to make SST “purely” represented by PC2.

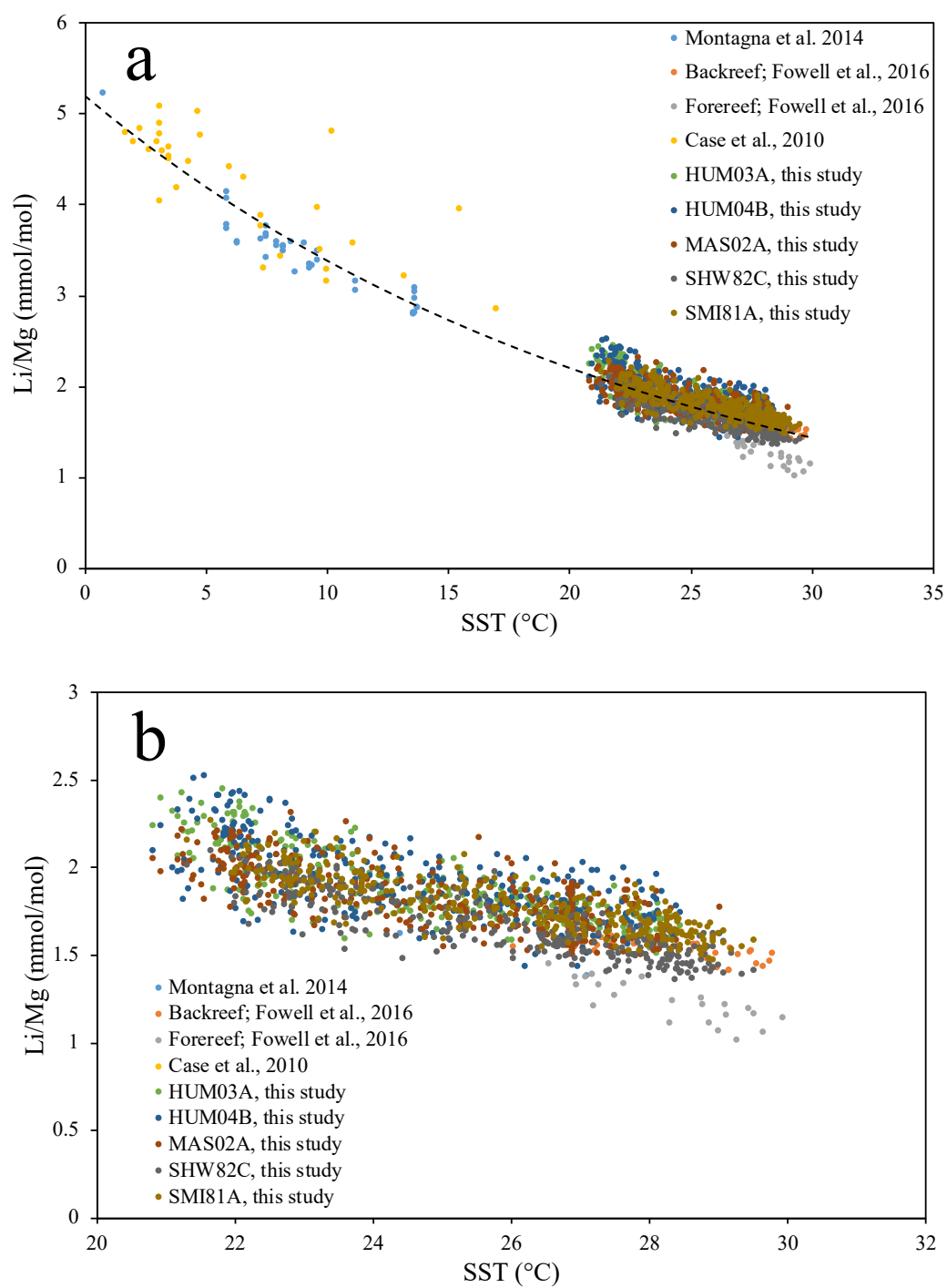


Figure S5.7 Scatter plots of Li/Mg and SST from different coral species over a wide range of seawater temperature (a) and from *Porites* corals only over a narrow range of seawater temperature (b).

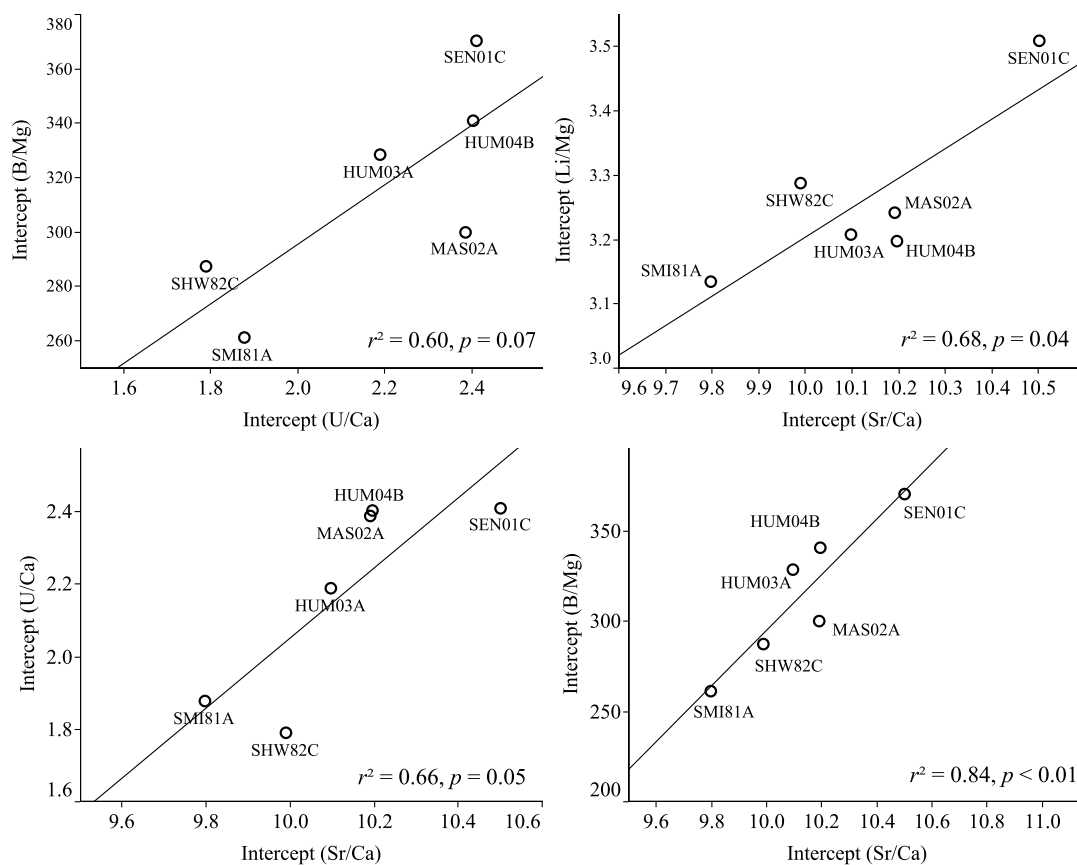


Figure S5.8 Relationships between the individual intercepts from colony-specific elemental ratios vs SST calibrations.

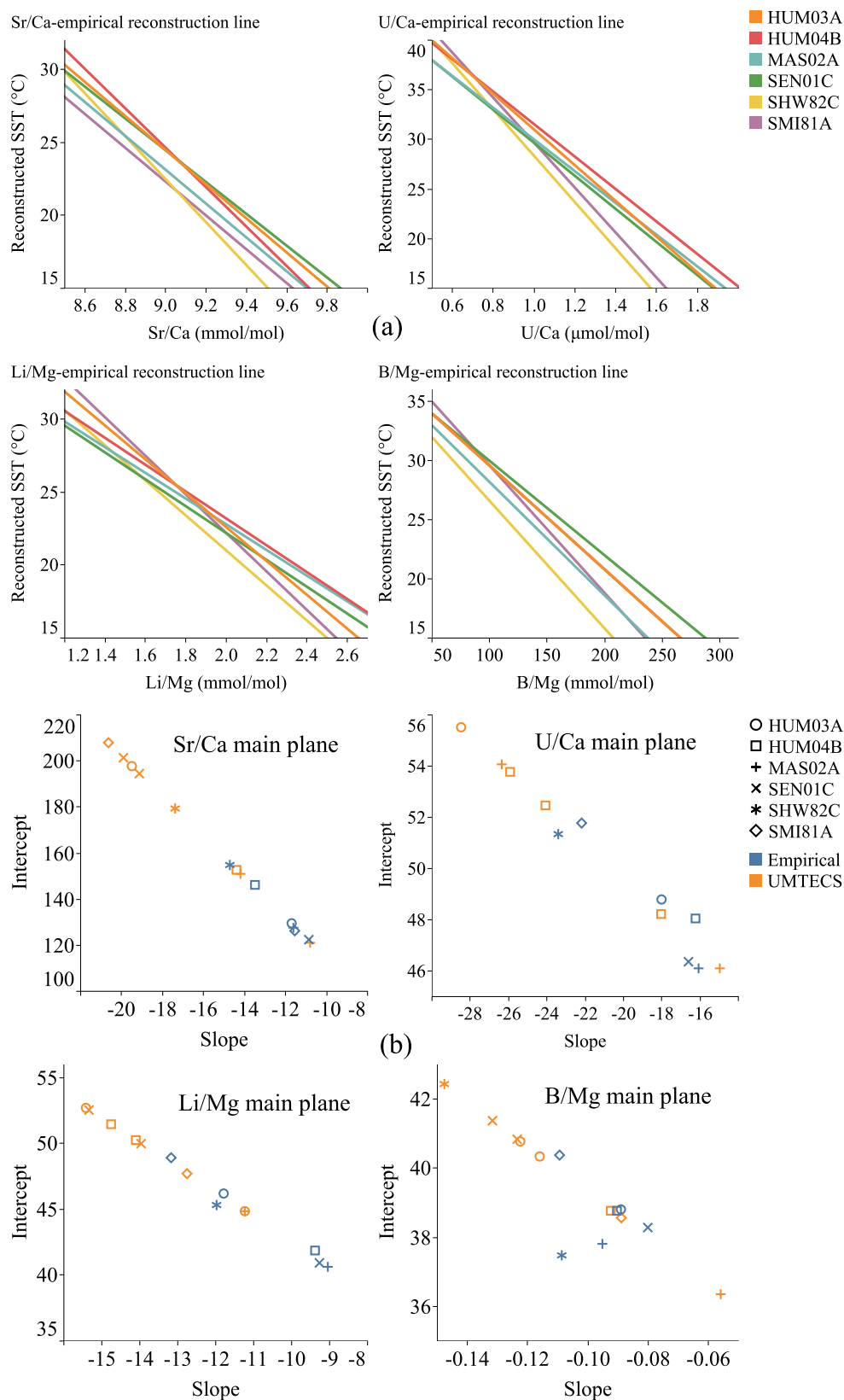


Figure S5.9 (a) SST reconstruction lines generated from the linear regressions between elemental ratios (Sr/Ca, U/Ca, Li/Mg, and B/Mg) and SST; (b) Coefficients (slopes and intercepts) generated from UMTECS model using different combinations of Sr/Ca, U/Ca, Li/Mg, and B/Mg for each coral core.

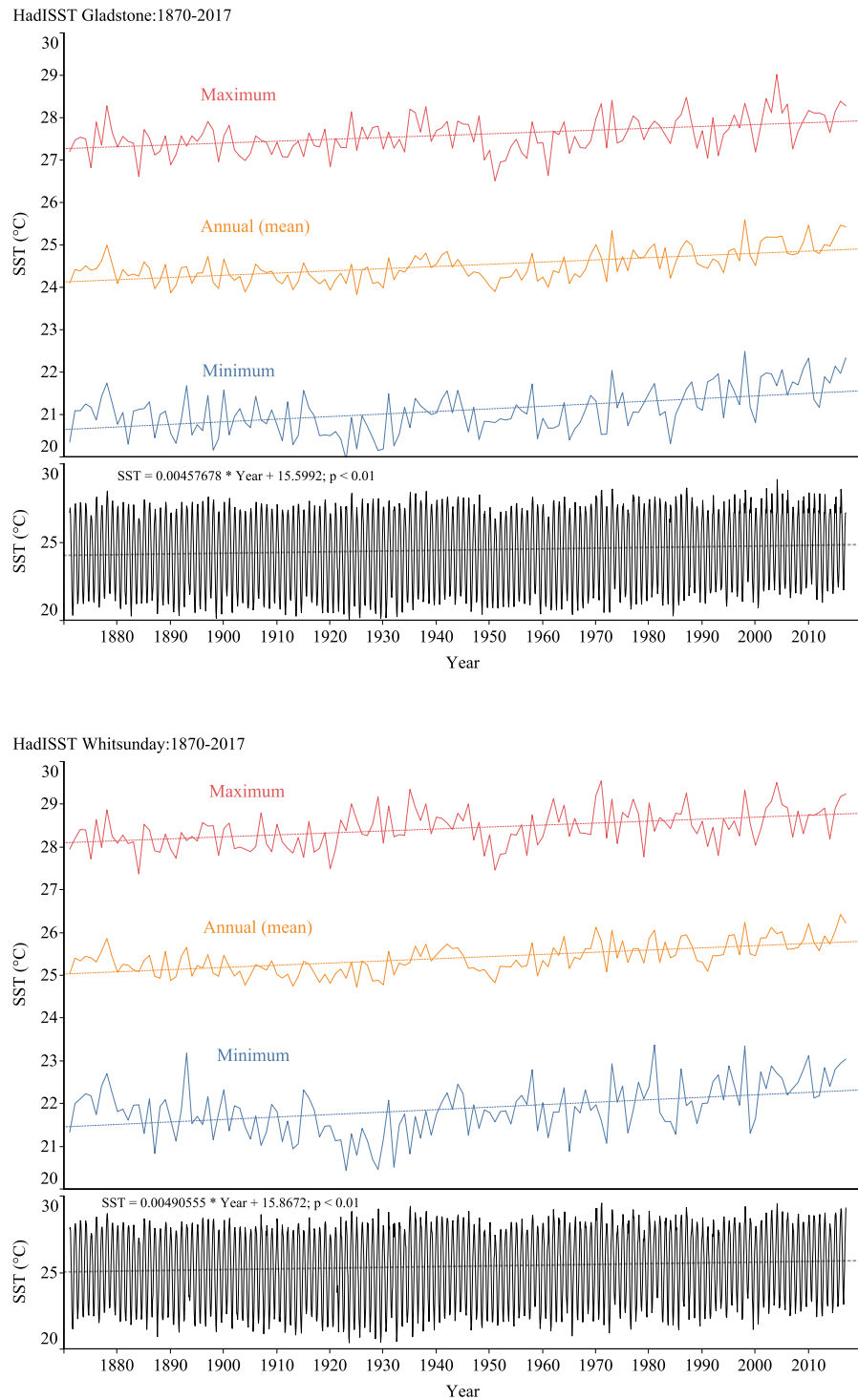


Figure S5.10 Maximum, annual, and minimum SST with linear trend lines in Gladstone (upper) and Whitsunday (lower) from 1870 to 2017.

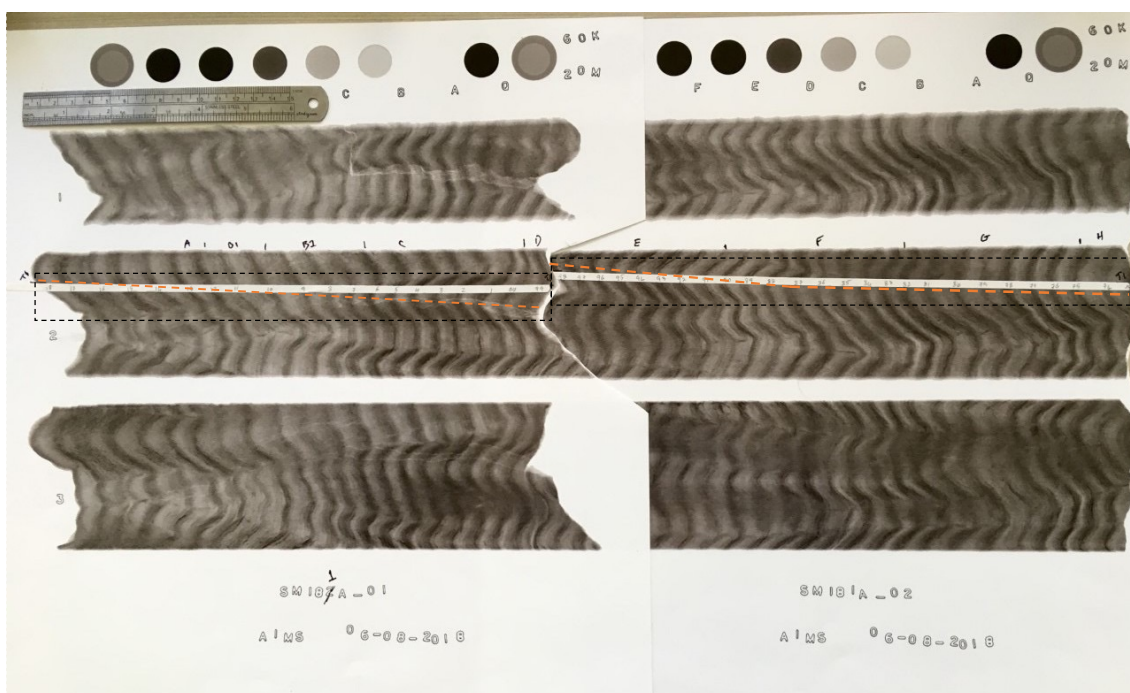


Figure S5.11 X-radiography images of SMI81A with subsampling transects marked with orange dashed lines. The X-ray image shows the location of the maximum vertical growth axis and the transect location for X-ray based gamma densitometry for annual density banding patterns, which we used to guide the geochemistry. The density analysis was centred on the dated annual banding patterns, each annual high-density band was dated in relation to the collection date at the top of the core, working continuously down core to provide the full chronology. The location of each subsection was marked in relation to the annual chronology with known years within each geochemistry slide section indicated by the Letter Scheme.

Chapter 6: Coral records of spatio-temporal environmental changes in the Gladstone Harbour

Chapter overview:

Australia is an isolated island continent, relying heavily on the import and export of commodities via commercial marine shipping. As Queensland's largest multi-commodity port, Gladstone Harbour has undergone dramatic port development in the past decades. This large-scale industrial development has benefited the local economy but it has also triggered adverse effects on the coastal environment. For example, dredging has disturbed the coastal sediment deposits and re-suspended many toxic aqueous metals and colloids. In addition, the construction of Alumina plants has introduced excessive aluminium (Al) to the ecosystem. Due to the lack of continuous seawater quality monitoring this chapter used laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) to develop century long geochemical records using corals from Gladstone Harbour. Five sites adjacent to Gladstone Harbour were analyzed (offshore control: MAS01E, inshore control: HUM02A and HUM03A, mid-harbour: SEN01C, harbour fringes: SAB05A and outer harbour: SEA10A and SEA11A). Distinct geochemical patterns have been recorded in the coral skeletons (e.g., elevated Al/Ca, Mn/Ca, Ti/Ca ratios from the local industrial developments and anthropogenic activities, elevated Ba/Ca, Y/Ca, La/Ca, Ce/Ca ratios due to dredging and/or river runoff). Principal Component Analysis confirmed the co-variance of several trace elements, suggesting that they were derived from the same source or have coherent geochemical signatures. This chapter shows that *Porites* corals adjacent to the Gladstone Harbour can be used as effective long-term recorders of environmental changes resulted from natural and anthropogenic influences. Results from this work can also offer guidance for the Australian governments to develop proper regulations to maintain a sustainable coastal development in the Gladstone region.

6.1 Introduction

The Great Barrier Reef (GBR) is the world's largest coral reef ecosystem and is well-known for its outstanding biodiversity and serves as an integral part for marine ecosystems. Over the past decades, the intensive anthropogenic activities (e.g., mining) and land use (e.g., agriculture) along the GBR has significantly modified the coastal river catchments and increased the input of land-based runoff of sediments, nutrients and other contaminants into the ocean. These anthropogenic pressures have posed many threats to reef communities and made the entire ecosystem at risk (Wooldridge and Done, 2009). In order to conserve the reef's biodiversity and predict how corals respond to changing water quality, it is critical to develop environmental proxies to extend our understanding of seawater conditions far beyond instrumental records (De'ath and Fabricius, 2010; De'ath et al., 2012; Saha et al., 2016).

Elemental compositions in the skeletons of *Porites* corals can be utilized to record the changes of marine environments. For example, Ba/Ca can not only indicate oceanic upwelling (Shen et al., 1992), but also serve as good indicator of coastal river runoff resulted from European settlement in eastern Queensland (McCulloch et al., 2003). In addition, dredging and dumping activities, which can directly remove or bury coral communities or indirectly increase turbidity and sedimentation, can also be reflected by coral geochemistry. For example, higher concentrations of Pb, Cu, and Zn were observed in corals from Townsville Harbour compared with offshore Orpheus Island (Esslemont, 2000) and were attributed to harbour dredging. Y/Ho ratio and other rare earth elements such as La and Ce have the potential to serve as effective proxies for dredging-induced marine contamination (Nguyen et al., 2013; Saha et al., 2016). Mining activities and oil pollution have been recorded in corals as well. For instance, elevated trace metals (Y, La, Ce, Mn, Zn, and Pb) were recorded in coral skeletons as a result of gold mining activities on Misima Island in Papua New Guinea (PNG) (Fallon et al., 2002). Likewise, higher metal concentrations were observed in a coral from Marinduque Island, Philippines due

to input from copper mine tailings (David, 2003). V/Ca can be a good proxy for oil pollution as petroleum is enriched in Vanadium (V) (Nguyen et al., 2013).

Gladstone Harbour is an important coal exporting terminal, and the Gladstone region has experienced significant industrial development and port expansion over the past century (Figure 6.1). Major industries include storage facilities for coal export, import of petroleum products, alumina refineries, aluminium smelters, electricity power station and Liquid Natural Gas (LNG) processing plants. The port expansion of Gladstone Harbour occurred during 5 major eras. (1) 1900-1930: small handling of shipping vessels and small dredging activities in 1918 and 1923; (2) 1930-1960: the first land reclamation in the 1930s, foreshore reclamation for the expansion of industry (e.g., petroleum products) and the maintenance dredging in the early 1950s; (3) 1960-1980: significant increase in coal exports from 1961-65 and the manufacturing of alumina starting from mid-1960s; (4) 1980-2000: industrial expansion related to the opening of aluminium smelter at Boyne Island in 1982, the first major dredging operations in 1981-82 and the subsequent annual maintenance dredging since 1993 and (5) 2000-2017: another major dredging operation in 2011-13 to optimise the shipping channels, and substantial increase in industrial activities associated with export and shipping.

To evaluate the contamination status in the Gladstone Harbour, this work examined the concentrations of 15 trace elements (Al, Ti, V, Mn, Fe, Ni, Cu, Zn, As, Y, Sn, La, Ce, Ba, Pb) in following coral sites: Seal Rocks (SEA10A, SEA11A), Sable Chief (SAB05A), South End (SEN01C), Hummocky Island (HUM02A, HUM03A), and Masthead Island (MAS01E). Results indicate natural (e.g., floods, storms) and anthropogenic processes (e.g., industrial activities associated with port developments) play a dominant role in controlling the elemental variabilities in corals. These contaminants were mainly delivered to the coastal seawater associated with river runoff, but other point sources of contaminants also exist. This work also

calculated distribution coefficients (K_d) to better understand the uptake and incorporation mechanisms of trace elements into coral skeletons.

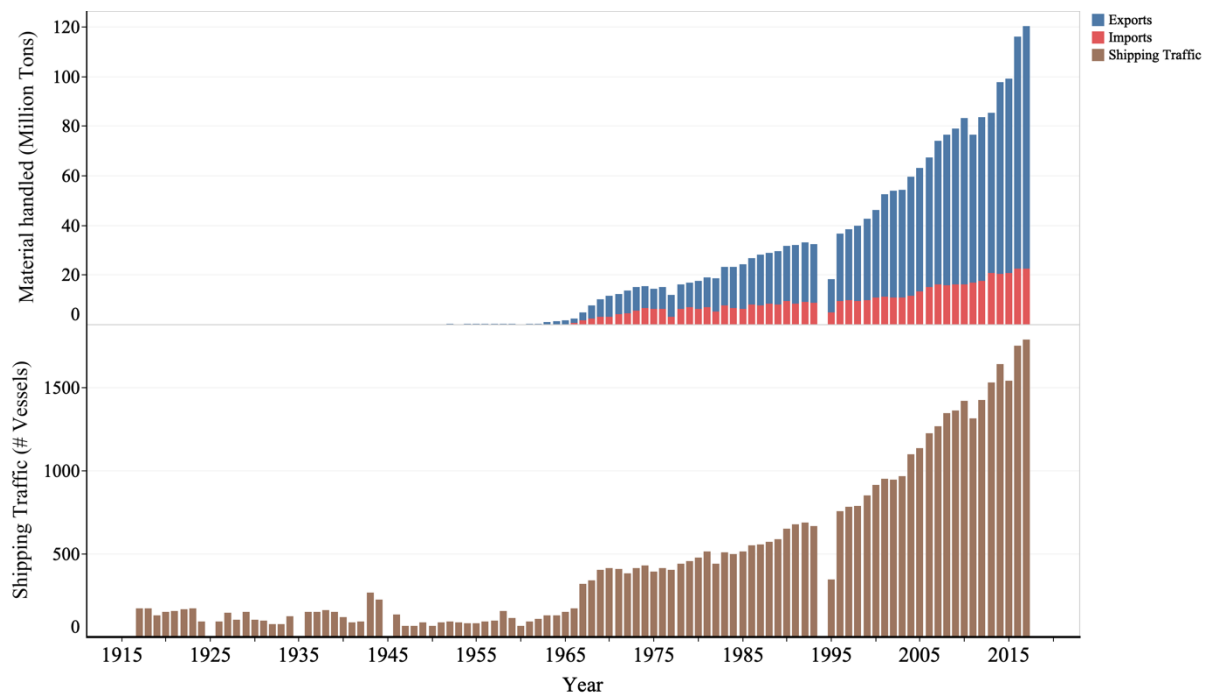


Figure 6.1 Industrial development and port expansion history of Gladstone Harbour from 1917 to 2017. Data show that shipping traffic (# of vessels/year) and commodities handled from international exports and imports (million tonnes/year) started to increase rapidly from 1960 (Cantin et al., 2018). Data source: Gladstone Ports Corporation (www.gpcl.com.au/about-us/our-history).

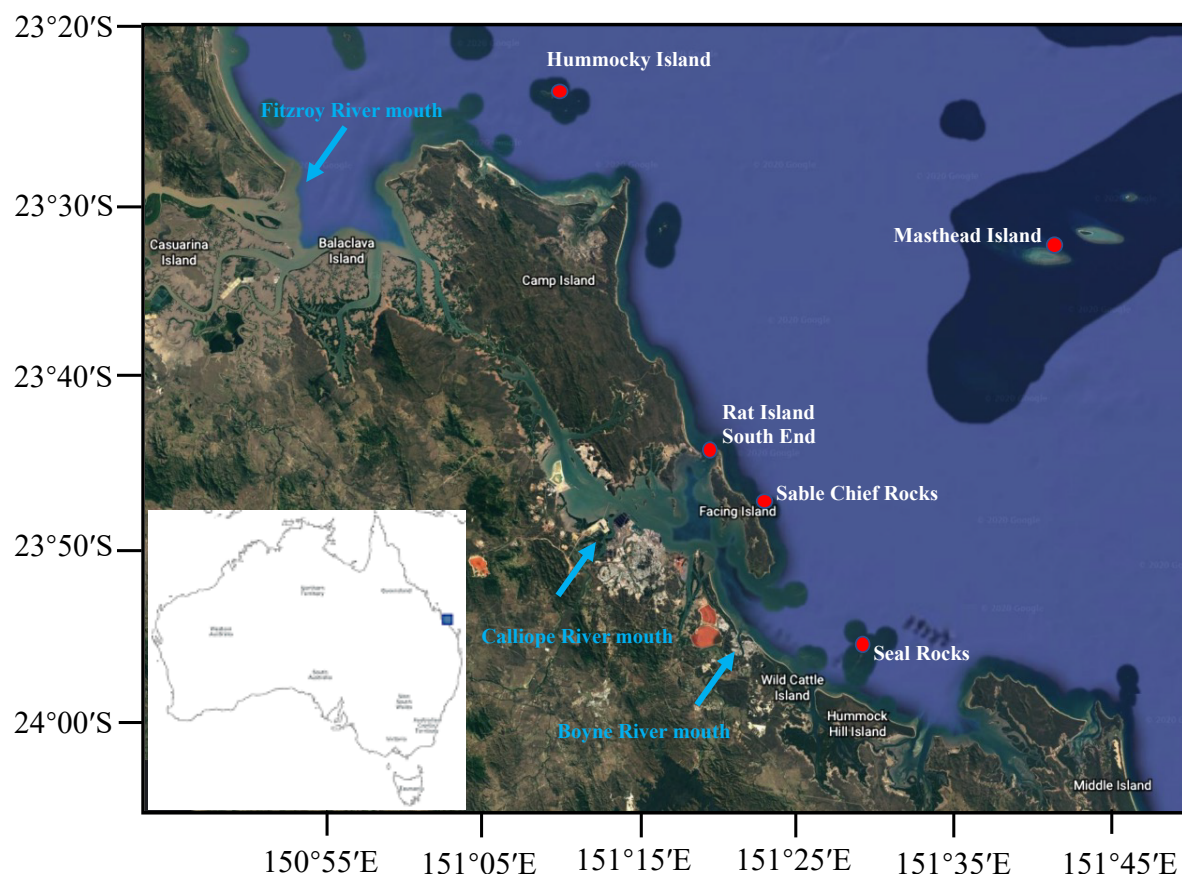
6.2 Research Methods

6.2.1 Study area

Porites spp. coral cores examined in this work were collected from 5 sites in and around Gladstone Harbour (Harbour Fringes Sable Chief Rocks (SAB05A), inshore control Hummocky Island (HUM02A, HUM03A), offshore control Masthead Island (MAS01E), mid-harbour South End Curtis Island (SEN01C) and outer-harbour Seal Rocks (SEA10A, SEA11A)) (Figure 6.2). Seal Rocks and Sable Chief Rocks are located within the port boundary limit of Gladstone Harbour. Seal Rocks is located near the Boyne smelter. Sable Chief Rocks is located on the open ocean side of Facing Island. South End Curtis Island is located in the channel between Facing Island and Curtis Island. Hummocky Island and Masthead Island are inshore control location and offshore control location.

Table 6.1 Geographic locations of *Porites* coral cores

Site	Core ID	Latitude (°)	Longitude (°)	Record period
Hummocky Island	HUM02A	-23.40341	151.14711	1902-2017
Hummocky Island	HUM03A	-23.40348	151.14716	1898-2017
Masthead Island	MAS01C	-23.53254	151.74602	1872-2017
South End Curtis Island	SEN01C	-23.7547	151.31693	1902-2016
Sable Chief Rocks	SAB05A	-23.81428	151.38417	1952-2017
Seal Rocks	SEA10A	-20.17447	148.9753	1959-2017
Seal Rocks	SEA11A	-20.0894	148.9076	1952-2017

**Figure 6.2** Coral sampling locations from the Gladstone Harbour and the main catchments in this region. Hummocky Island include two cores: HUM02A and HUM03A.

6.2.2 Geographic and hydrological setting

Gladstone Harbour lies in a macrotidal shoreline and has a complex estuarine system. The Fitzroy River catchment starts from Carnarvon Range and drains to Keppel Bay near the city of Rockhampton. The Calliope River drains to the north of Gladstone Harbour, near the Gladstone Power station. The Boyne River mouth is located in the south of Gladstone harbour

between Boyne Island and Tannum Sands. River flows (megalitres) data were obtained from Department of Natural Resources and Mines (DNRME) Water Monitoring Information Portal (WMIP) gauging stations (<https://water-monitoring.information.qld.gov.au/>) on the Fitzroy River at Yaamba (130001A) for the period 1915-1969 and at The Gap (130005A) for the period 1965-2016. River data were obtained for the Calliope River at Castlehope (132001A) for the period 1939-2016. Long-term river data for the Boyne River is not available, but the Boyne River, the Calliope River and the Fitzroy River are highly correlated with each other for the short overlapping periods. Annual river flow for the Calliope River and the Fitzroy River were calculated by combining the monthly data from October to September (Figure 6.3).

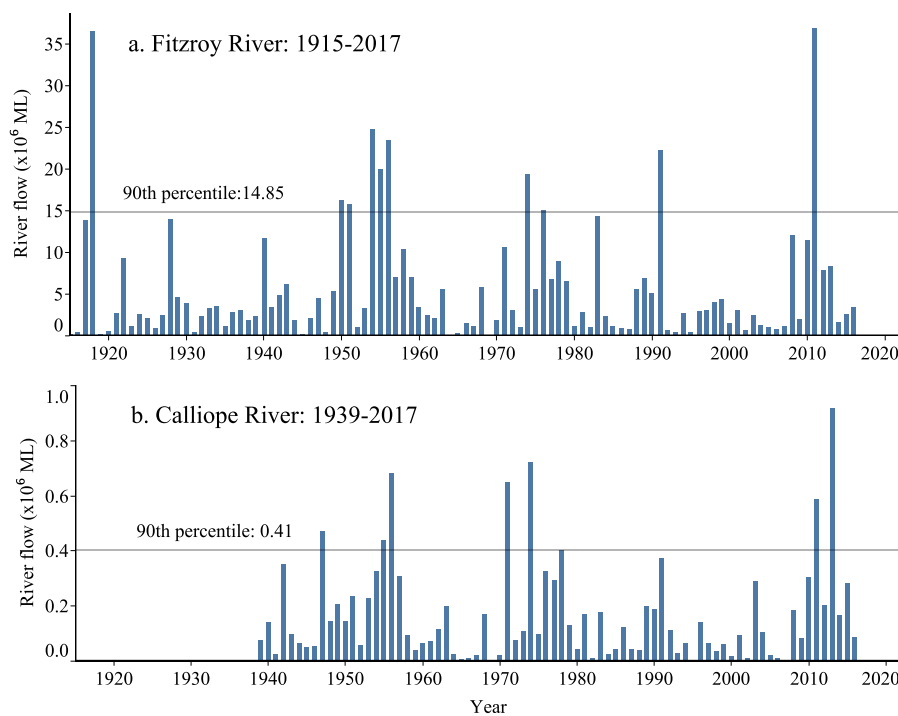


Figure 6.3 Annual River flow (x10⁶ ML) in (a) Fitzroy from 1915 to 2017 and in (b) Calliope from 1939 to 2017. Annual data were calculated from October-September (Cantin et al., 2018). Gray horizontal lines show 90th percentile of flows over respective record periods. Major flood years include 1918, 1950-1951, 1954-1956, 1971, 1974, 1991 and 2011, and drought years include the 1960s, mid-1990s and mid-2000s.

6.2.3 LA-ICP-MS

Laser ablation–inductively coupled plasma–mass spectrometry (LA–ICP–MS) was used to measure the abundance of ‘major’ trace elements (^{11}B , ^{24}Mg , ^{43}Ca , ^{84}Sr , ^{86}Sr , ^{137}Ba and ^{238}U) and ‘minor’ trace elements (^7Li , ^{27}Al , ^{47}Ti , ^{51}V , ^{53}Cr , ^{55}Mn , ^{57}Fe , ^{60}Ni , ^{63}Cu , ^{66}Zn , ^{75}As , ^{77}Se , ^{89}Y , ^{118}Sn , ^{121}Sb , ^{139}La , ^{140}Ce , ^{206}Pb , ^{207}Pb , ^{208}Pb) in corals. Raw data were processed using Python package *LAtools* (Branson et al., 2019). All isotopes were normalized to ^{43}Ca (element/Ca ratios) to present the trace element concentrations. Detailed procedures for sample preparation, machine set up and data process are described in chapter 2 and chapter 5.

6.2.4 Age model

A few elemental ratios (such as Sr/Ca, U/Ca and Li/Mg) have been shown to be effective geochemical proxies of sea surface temperature (SST) (see chapter 5). In this work, U/Ca outperformed other proxies in terms of long-term stability (see chapter 5). Therefore, peak (trough) values of U/Ca have been used to match SST minima (maxima) in winter (summer) to build the age model (Figure 6.4), coupled with the validation from Sr/Ca, Li/Mg and prominent runoff luminescent lines. After the construction of the age model, geochemical data were re-sampled by linear interpolation using Analyseries 2.0.8 (Paillard et al., 1996). Data resolution were reduced from weekly to monthly (12 points per year) or to seasonal (4 points per year) for better comparison.

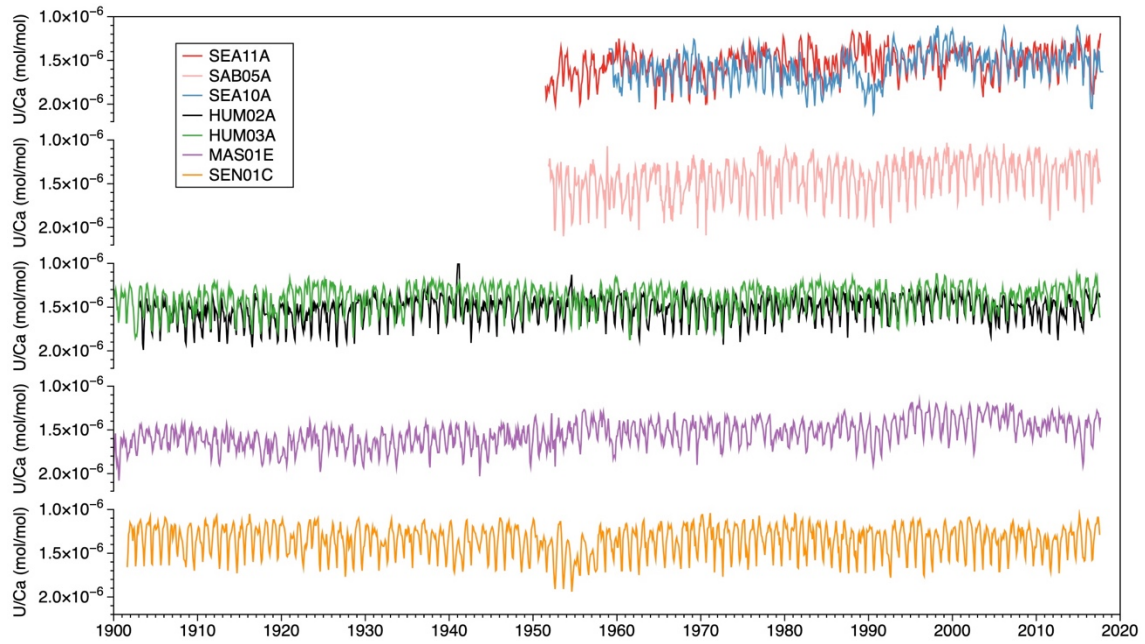


Figure 6.4 Uranium seasonal cycles from the Gladstone Harbour corals, which are used to make the age model (translation from distance to time-series) for each coral.

6.2.5 Statistical analyses

The dataset from this work contains 16 trace elements from 7 coral cores. Principal Component Analysis (PCA, computed using SPSS Statistics) has been performed to better understand the correlation between different trace metals and the grouping of trace metals from individual coral sites. PCA is based on linear classification. This classification system uses linear fitting to reduce high-dimensional data which are originally distributed in multiple dimensions, and project these transformed data onto several new axes. After extracting the major components using PCA analysis, these components were further rotated using Varimax with the Kaiser Normalization method to maximize the difference between variance (Richman 1986; Wold et al., 1987; Abdi et al., 2010). Compared to the unrotated eigenvectors, the rotated eigenvectors have a greater similarity to the actual physical/reasonable state although they account for a smaller variance.

6.3 Results: time-series of individual coral cores

6.3.1 Outer Harbour Seal Rocks: SEA10A and SEA11A

SEA10A has a geochemical record extending from 1959 to 2017 (Figure 6.5). Sustained spikes were recorded for Ti/Ca from 1960 to 1965. A spike around 1965 was recorded for Cu/Ca and Zn/Ca. Elevated ratios were recorded for Pb/Ca, V/Ca, Ti/Ca and Al/Ca from 1970 to 1978. A spike around 1985 was recorded for Pb/Ca and Zn/Ca. A spike in 2010 was recorded for As/Ca, V/Ca, Ti/Ca, Al/Ca, Sn/Ca, Cu/Ca and Ba/Ca. Indeed, the time-series for a 5-year period around 2010 are remarkably similar for V/Ca, Ti/Ca, Al/Ca, Sn/Ca, Cu/Ca, Ce/Ca and La/Ca. The times-series for Ce/Ca, La/Ca and Y/Ca are particularly consistent, showing coherent spikes around 1965, 1970, 1985 and 2010. Prior to the spikes around 2010, levels of Ce/Ca, La/Ca and Y/Ca declined around 1990 and remained at their lowest for a period of about 20 years. The levels for Mn were consistently low throughout the 60-year period, except for a small spike around 1985 and an even larger spike around 2000, which was accompanied by a large spike in V/Ca ratios and smaller spikes of As/Ca, Zn/Ca and Cu/Ca ratios.

SEA11A has a geochemical record extending from 1951 to 2017 (Figure 6.6). A few spikes were recorded for As/Ca, Zn/Ca, V/Ca and Al/Ca from 1951 to 1955. A consistent spike was recorded for all elements around 1965. Ti/Ca and Al/Ca showed fluctuations from 1965 to early 2000s with a few evident spikes around 1975, 1982-1985, 1989, 1995 and 2001. Three spikes of V/Ca occurred in 1989, 1995 and 2001. A spike was recorded for Pb/Ca and Zn/Ca around 1982. Sn/Ca and Cu/Ca remained relatively stable prior to 2000 and started to increase from 2002 and recorded an evident spike around 2011. Again, the times-series for Ce/Ca, La/Ca and Y/Ca are particularly consistent, showing coherent spikes around 1960, 1985-2005 and 2011. The levels for Mn/Ca remained low throughout the 60-year period, except for the two spikes around 1965 and 1991.

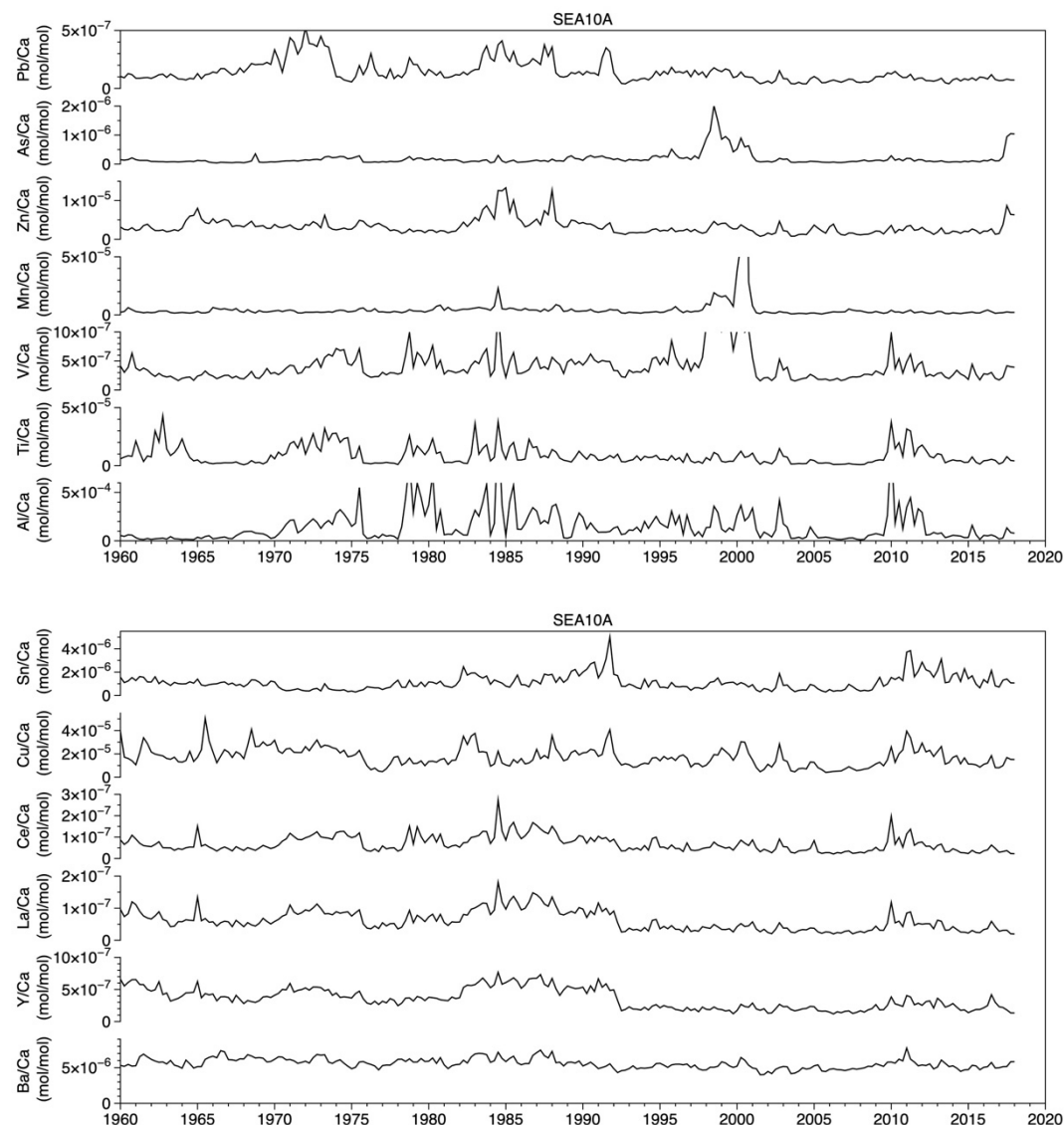


Figure 6.5 Geochemical time-series of Al/Ca, Ti/Ca, V/Ca, Mn/Ca, Cu/Ca, Zn/Ca, As/Ca, Y/Ca, Sn/Ca, La/Ca, Ce/Ca, Ba/Ca and Pb/Ca recorded in the *Porites* spp. skeleton from the Outer-Harbour Seal Rocks site (SEA10A) from 1959-2017.

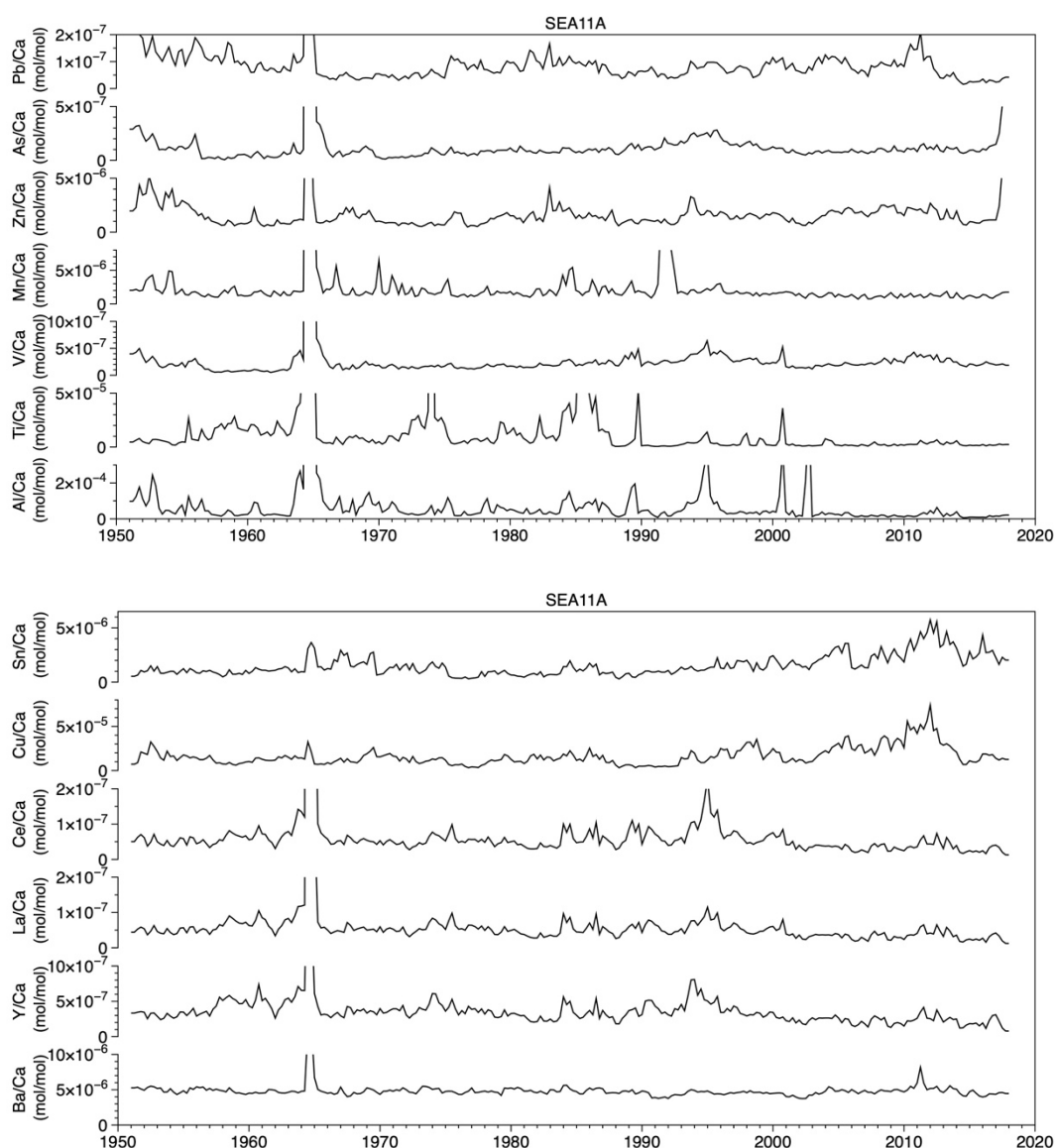


Figure 6.6 Geochemical time-series of Al/Ca, Ti/Ca, V/Ca, Mn/Ca, Cu/Ca, Zn/Ca, As/Ca, Y/Ca, Sn/Ca, La/Ca, Ce/Ca, Ba/Ca and Pb/Ca recorded in the *Porites* spp. skeleton from the Outer-Harbour Seal Rocks site (SEA11A) from 1952-2017.

6.3.2 Harbour Fringes Sable Chief Rocks: SAB05A

SAB05A has a geochemical record extending from 1951 to 2017 (Figure 6.7). Prior to 1958, most trace element ratios (Al/Ca, Ti/Ca, V/Ca, Mn/Ca, Zn/Ca, As/Ca, Cu/Ca, Sn/Ca) remained relatively stable while Pb/Ca, Ba/Ca, Y/Ca, La/Ca, and Ce/Ca showed some noticeable fluctuations. All elemental ratios except for Ba/Ca continuously recorded a few spikes from 1950 to 1970, and then the signals decreased back to baseline values in late 1970s. A few spikes were recorded for Pb/Ca, V/Ca, Ti/Ca, Al/Ca, Ce/Ca and La/Ca from 1988 to 1992. Two

significant spikes were recorded for Al/Ca in 2001 and 2005, and Ti/Ca also recorded a spike in 2005.

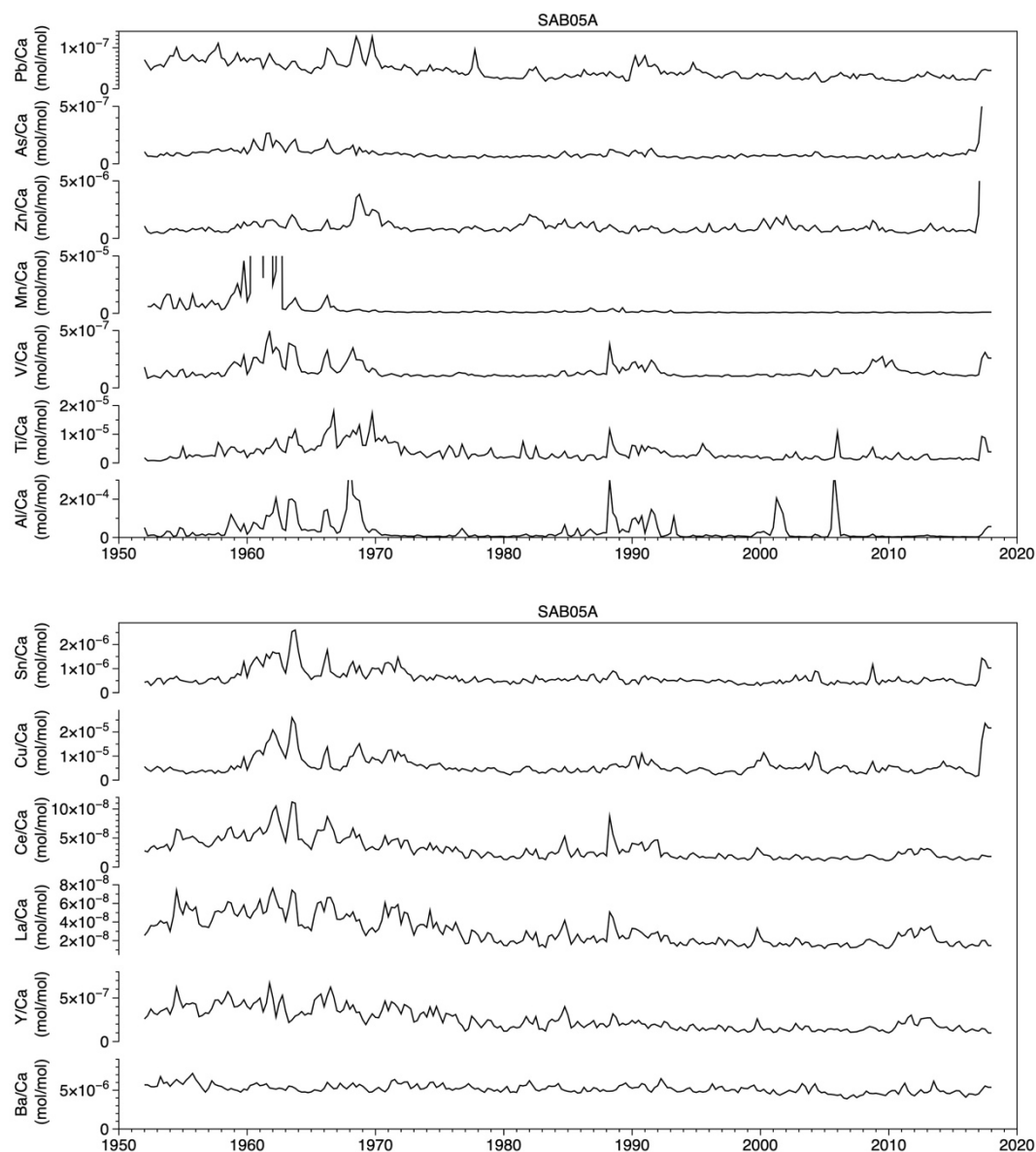


Figure 6.7 Geochemical time-series of Al/Ca, Ti/Ca, V/Ca, Mn/Ca, Cu/Ca, Zn/Ca, As/Ca, Y/Ca, Sn/Ca, La/Ca, Ce/Ca, Ba/Ca and Pb/Ca recorded in the *Porites* spp. skeleton from the Harbour Fringes Sable Chief Rocks site (SAB05A) from 1952-2017.

6.3.3 Mid-Harbour South End: SEN01C

SEN01C has a geochemical record extending from 1900 to 2017 (Figure 6.8). Prior to 1950, all trace element ratios stayed relatively stable while a few evident spikes were recorded for Ti/Ca around 1915 and 1922. Mn/Ca recorded frequent spikes throughout the periods from

1965 to 1990 and from 2005 to 2010. Ti/Ca recorded multiple spikes in the periods from 1955 to 1965, 1980-1990 and from 2005 to 2015. Two significant spikes were recorded for Al/Ca in 2006 and 2008. Time-series are remarkably similar for both Cu/Ca and Sn/Ca, and also for Ce/Ca, La/Ca and Y/Ca. Slightly elevated ratios for Cu/Ca, Sn/Ca, Ce/Ca, La/Ca and Y/Ca were recorded in 1922, 1927, 1952-1955, 1985 and 2011.

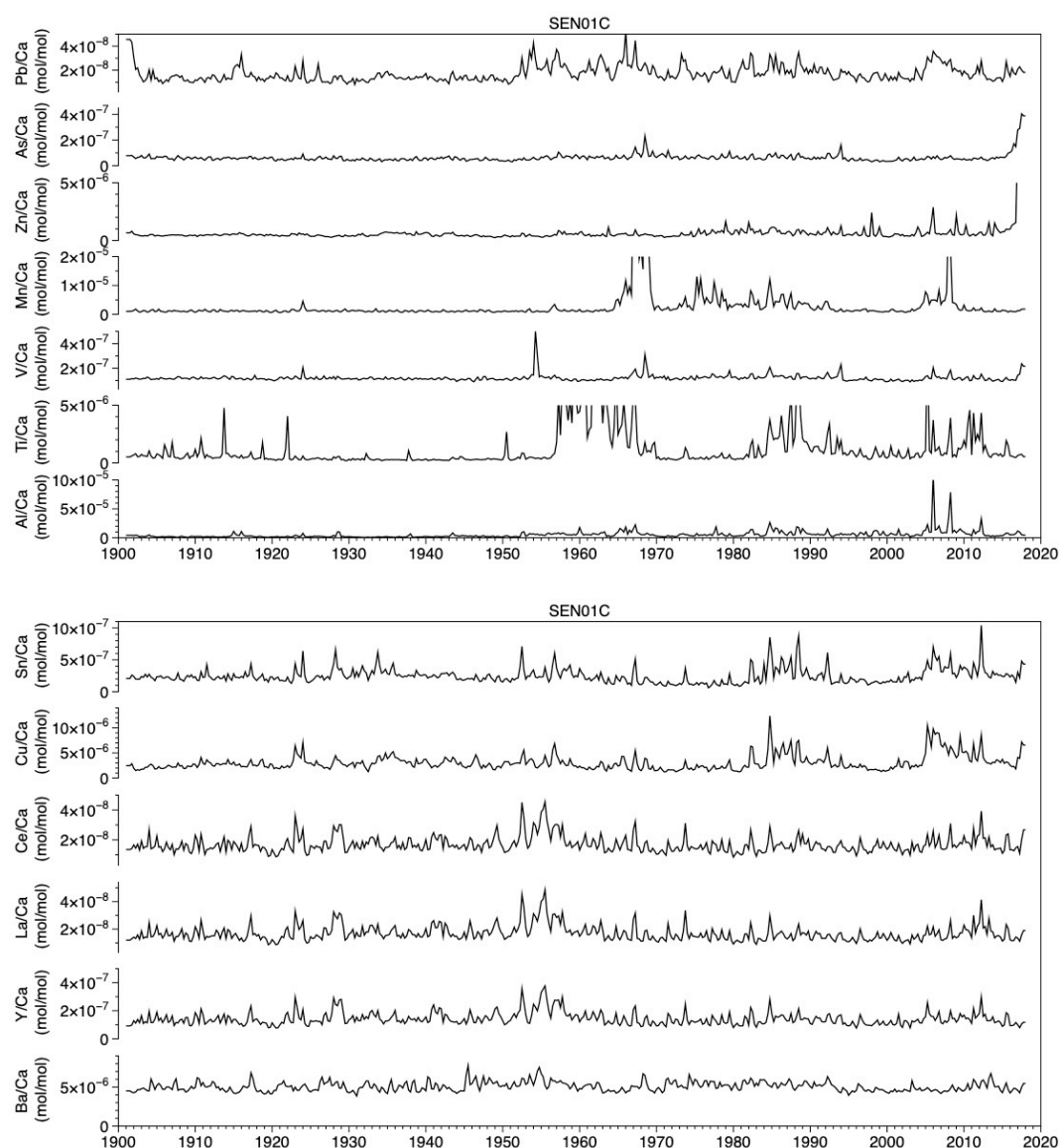


Figure 6.8 Geochemical time-series of Al/Ca, Ti/Ca, V/Ca, Mn/Ca, Cu/Ca, Zn/Ca, As/Ca, Y/Ca, Sn/Ca, La/Ca, Ce/Ca, Ba/Ca and Pb/Ca recorded in the *Porites* spp. skeleton from the Middle Harbour zone at South End Curtis Island (SEN01C) from 1901-2017.

6.3.4 Inshore control Hummock Island: HUM02A and HUM03A

HUM02A has a geochemical record extending from 1900 to 2017 (Figure 6.9). Element to Ca ratios for most elements (Pb, As, Zn, V, Al, Cu, Sn, Ce, La, Y and Ba) did not change significantly throughout the entire time-series even though a few spikes are observed. A spike was recorded for Pb/Ca and Zn/Ca around 1927. A spike was recorded for As/Ca in 1941. A few spikes were recorded for V/Ca in 1912, 1923, 1941 and 1958. Continuous spikes were recorded for Mn/Ca from 1920 to the mid-1930s, and another single spike was observed in 1965. Sustained spikes were recorded in Ti/Ca from 1935 to 1965 and from 1985 to 1995 along with some single spikes in 1912, 1932 and 2005. Al/Ca was found to be elevated around 1910 and from 1990 to 2010. Cu/Ca, Sn/Ca, Ce/Ca, La/Ca, Y/Ca and Ba/Ca displayed mostly natural variations throughout the entire time.

HUM03A has a geochemical record extending from 1905 to 2017 (Figure 6.10). Evident spikes were recorded for Zn/Ca, Mn/Ca, V/Ca, Ti/Ca, Al/Ca around 1911, 1918, 1930. Another spike was recorded for Mn/Ca around 1968. The levels for V/Ca were elevated from 1960 to 1970 and from 1990 to 2010. A few other spikes were recorded for Ti/Ca and Al/Ca around 1982, 1991 and 2002, while Ti/Ca also recorded a significant spike around 1955. Similar to the results from other corals, Cu/Ca and Sn/Ca (or Ce/Ca, La/Ca and Y/Ca) shared the concurrent variation throughout the time, as did Ce/Ca, La/Ca and Y/Ca. Consistently elevated levels were recorded for Cu/Ca and Sn/Ca from 1927 to 1935, as well as for Ce/Ca, La/Ca and Y/Ca during this time period. However, levels for Cu/Ca and Sn/Ca were also elevated from 1950 to 1960, from 1970 to 1975 and from 2005 to 2010. Ba/Ca displayed clear annual variations and showed an increase from baseline values from 1950 for about 20 years and from 1990 for about 10 years.

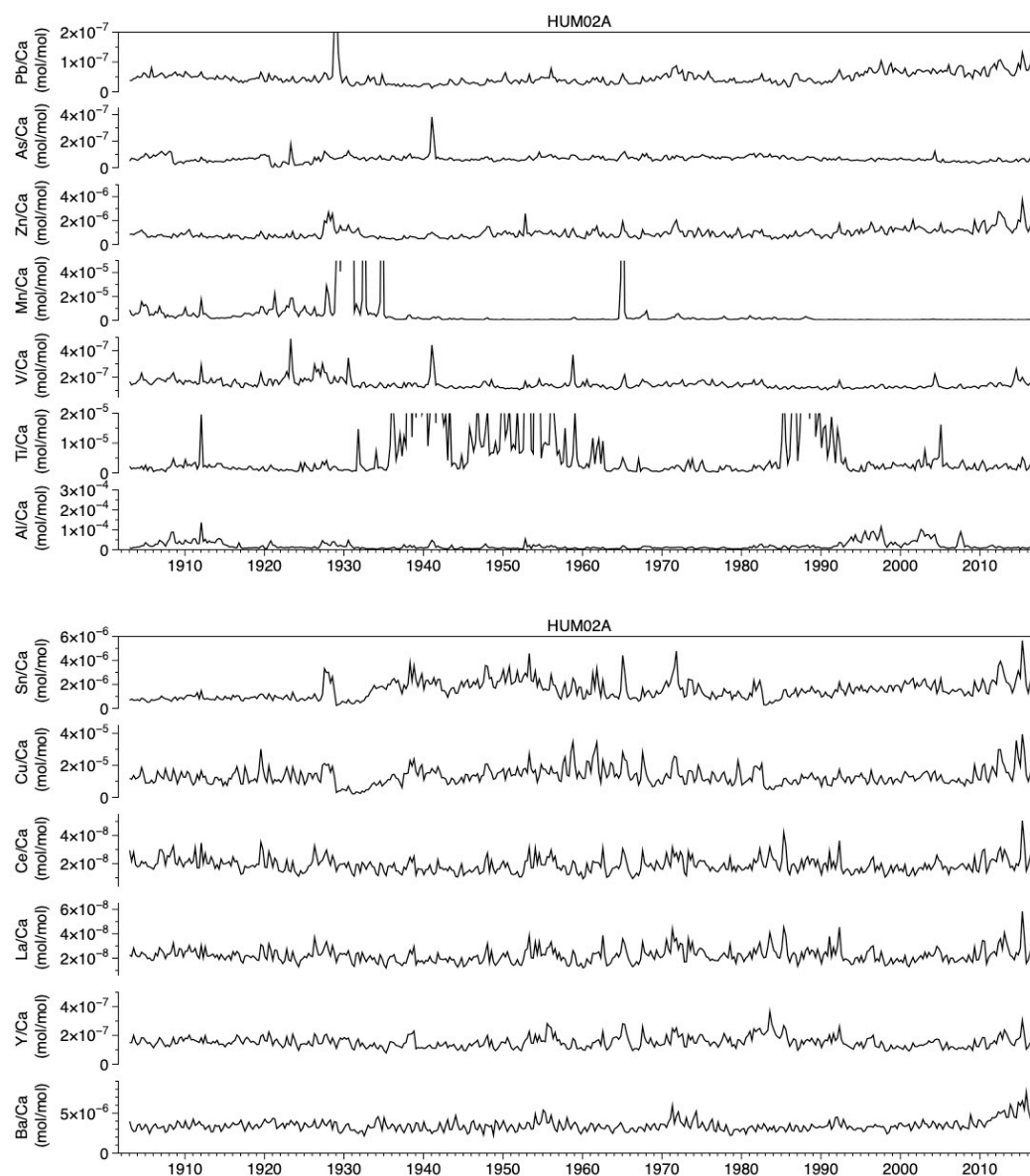


Figure 6.9 Geochemical time-series of Al/Ca, Ti/Ca, V/Ca, Mn/Ca, Cu/Ca, Zn/Ca, As/Ca, Y/Ca, Sn/Ca, La/Ca, Ce/Ca, Ba/Ca and Pb/Ca recorded in the *Porites* spp. skeleton from the inshore control Hummocky Island (HUM02A) from 1902-2017.

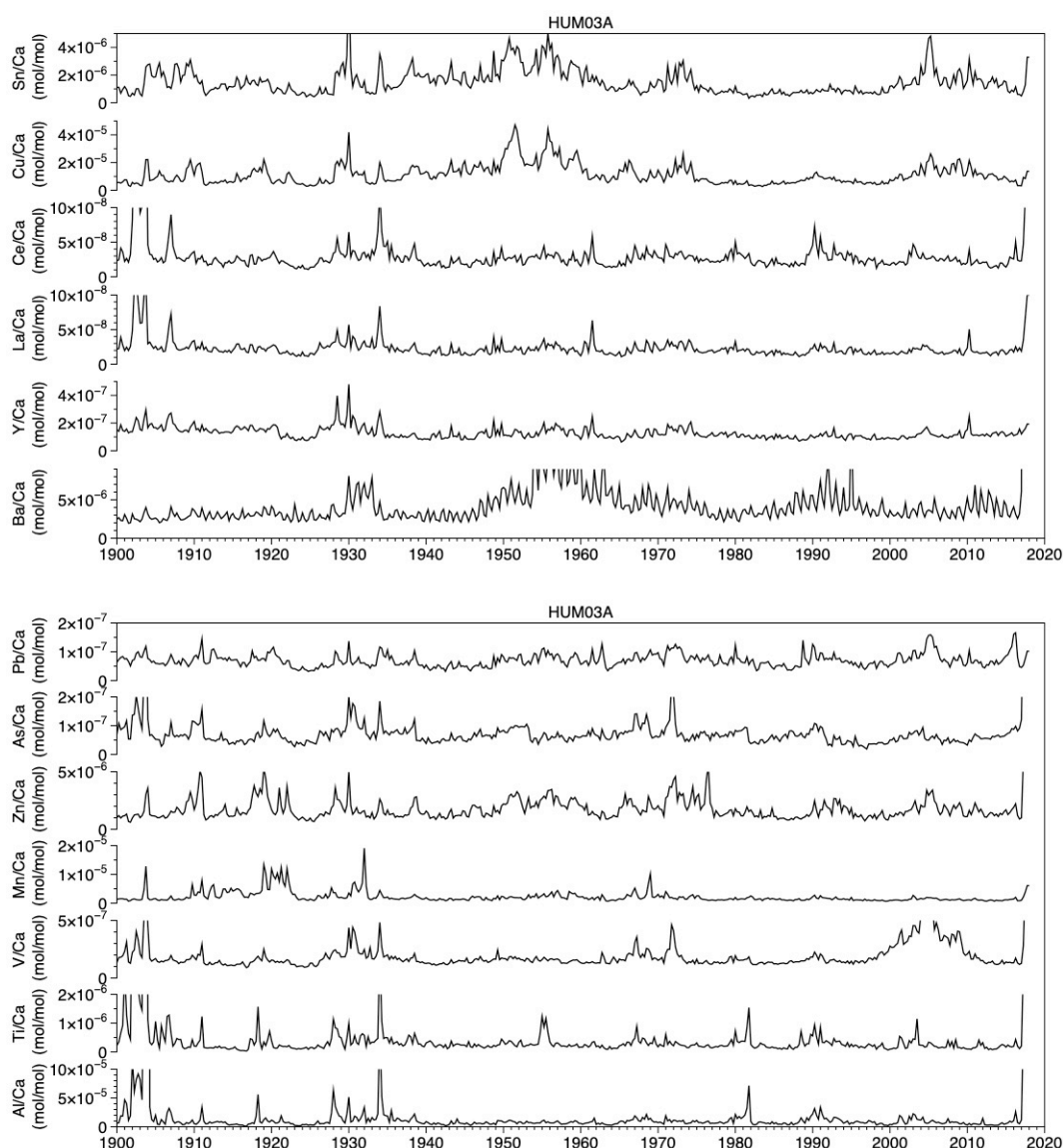


Figure 6.10 Geochemical time-series of Al/Ca, Ti/Ca, V/Ca, Mn/Ca, Cu/Ca, Zn/Ca, As/Ca, Y/Ca, Sn/Ca, La/Ca, Ce/Ca, Ba/Ca and Pb/Ca recorded in the *Porites* spp. skeleton from the inshore control Hummocky Island (HUM03A) from 1900-2017.

6.3.5 Mid-shelf offshore control Masthead Island: MAS01E

MAS01E has a geochemical record extending from 1880 to 2017 (Figure 6.11). Masthead Island is ~50km from Gladstone Harbour. Data lines for most trace elements remained flat throughout the entire period with some natural fluctuations. However, frequent spikes were recorded for Ti/Ca, and elevated levels were recorded for Zn/Ca from 1935 to 1960. Three prolonged spikes were recorded for V/Ca peaking around 1900, 1945 and 1990. Each V/Ca spike spanned 5-10 years long and reoccurred around every 45-year. A short-lived Al/Ca spike

was detected in 1987. Another spike was recorded for Al/Ca around 1991, which was also evident for Cu/Ca, Sn/Ca, Ce/Ca, La/Ca, Y/Ca and Ba/Ca. Cu/Ca and Sn/Ca showed a clear rise from baseline level from 2011 for about 6 years.

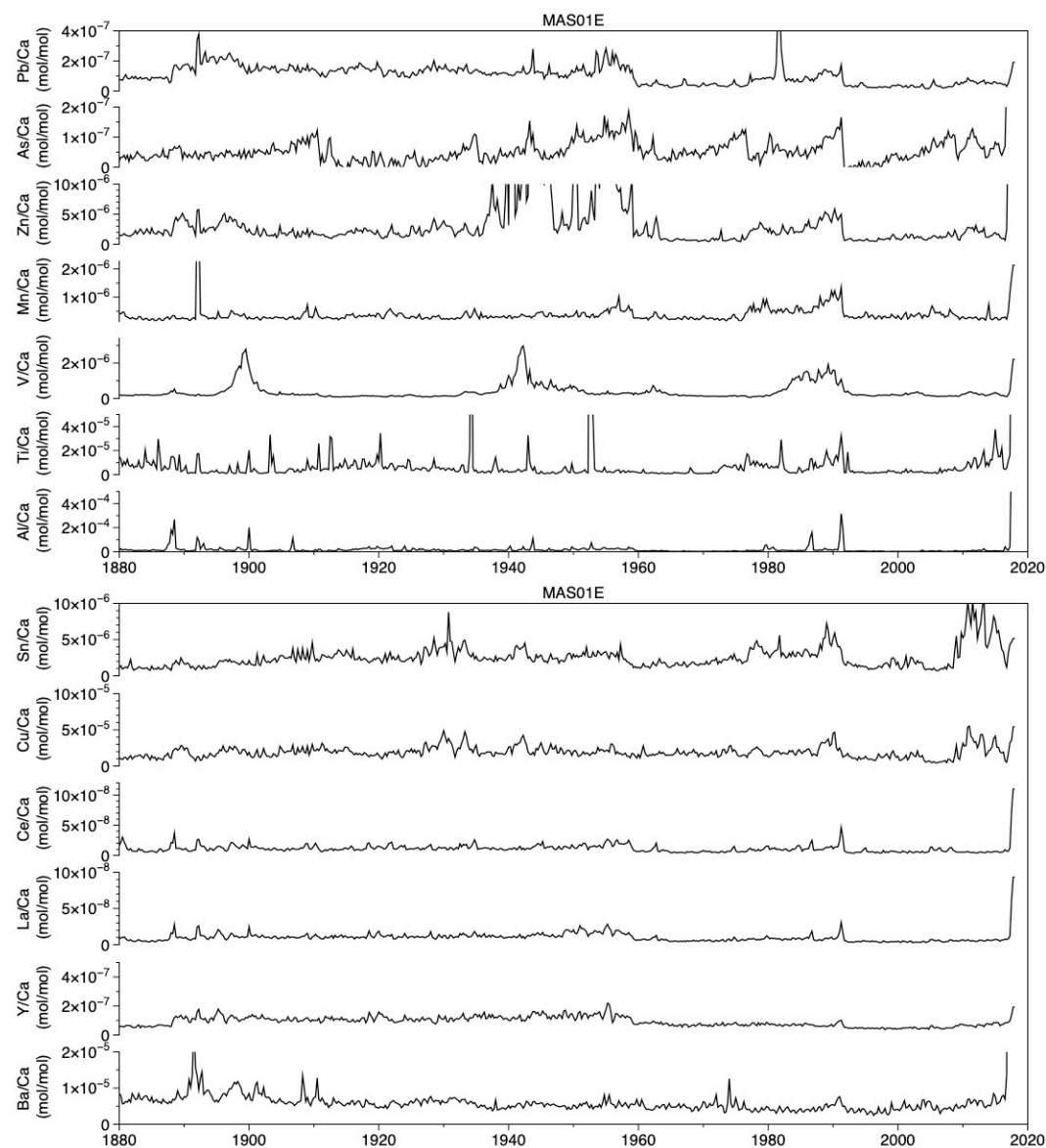


Figure 6.11 Geochemical time-series of Al/Ca, Ti/Ca, V/Ca, Mn/Ca, Cu/Ca, Zn/Ca, As/Ca, Y/Ca, Sn/Ca, La/Ca, Ce/Ca, Ba/Ca and Pb/Ca (mol/mol) recorded in the *Porites* spp. skeleton from the offshore control Masthead Island (MAS01E) from 1890-2017.

6.4 Discussion

6.4.1 Spatial variability of trace elements

The shape of Gladstone Harbour results in complex water circulation which influences the transport of dissolved metals and suspended particulates. Depending on their geographic

locations, corals are influenced by inputs from river runoff, shipping channels and industrial inputs to varying degrees. Figure 6.12 and Table 6.2 show the comparison of the statistical five-number summary (upper whisker, upper hinge, medium, lower hinge and lower whisker) for different elemental ratios (Al/Ca, Ti/Ca, V/Ca, Mn/Ca, Ba/Ca, Cu/Ca, Zn/Ca, Pb/Ca) in the coral skeletons from disparate locations. The spread and range of element/Ca ratios showed clear variability (Figure 6.12), with the median (or mean) values in some locations being several orders of magnitude higher than other locations (e.g., Al/Ca). Element/Ca ratios of replicate cores (SEA10A&11A, HUM02A&03A) from the nearby locations also differed, but the difference was less evident compared to corals from different locations (Figure 6.12). In general, most element/Ca ratios from different sampling locations followed a consistent spatial order with higher element/Ca ratios in the outer-harbour Seal Rocks (SEA10A&11A) and harbour fringes Sable Chief Rocks (SAB05A) than in the mid-harbour South End (SEN01C), inshore-control Hummocky Island (HUM02A&03A) and mid-shelf offshore control Masthead Island (MAS01E). This indicates that the seawater metal concentrations have a clear water quality gradient largely depending on the proximity to the harbour or the releasing sources of emerging contaminants/trace metals. A notable exception is Mn from the mid-harbour SEN01C which contains several periods of high Mn/Ca spikes. Overall, the disparities between different coral sites highlight the large spatial variability of metal concentrations in surface seawater around the Gladstone Harbour.

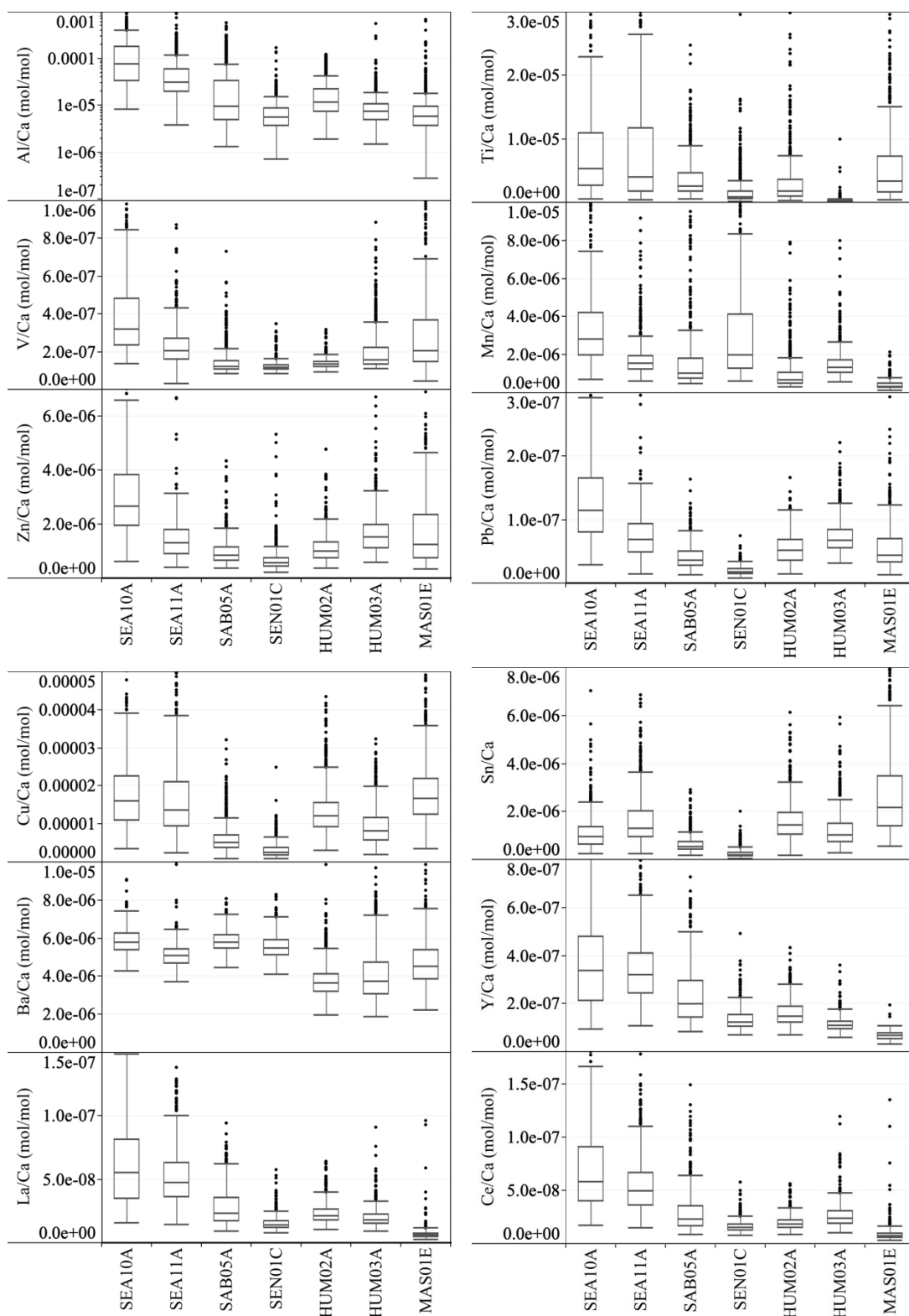


Figure 6.12 Comparison of Al/Ca, Ti/Ca, V/Ca, Mn/Ca, Zn/Ca, Pb/Ca, Cu/Ca, Zn/Ca, Ba/Ca, Y/Ca, La/Ca and Ce/Ca elemental ratios in coral skeletons along the geographic gradients from near harbour sites to offshore sites. From the top to bottom, this box and whisper plot presents the five-number summary of upper whisker, upper hinge, medium, lower hinge and lower whisker. Note: Whiskers extend to data within 1.5 times the IQR.

Table 6.2 Comparison of average, minimum, maximum, median, standard deviation, first quartile and third quartile for selected elemental ratios in different coral sites.

	SEA10A	SEA11A	SAB05A	SEN01C	HUM02A	HUM03A	MAS01E
Al/Ca (mol/mol)							
Average:	1.5E-04	3.1E-04	3.6E-05	8.1E-06	2.0E-05	1.5E-05	1.7E-05
Minimum:	9.0E-06	0.0E+00	1.3E-06	7.0E-07	2.0E-06	2.0E-06	0.0E+00
Maximum:	1.6E-03	6.5E-02	5.9E-04	1.7E-04	1.2E-04	1.8E-03	1.6E-03
Median:	7.8E-05	3.0E-05	9.6E-06	5.6E-06	1.2E-05	7.0E-06	6.0E-06
Standard deviation:	2.0E-04	3.3E-03	6.5E-05	1.2E-05	2.3E-05	7.9E-05	8.8E-05
First quartile:	3.4E-05	2.0E-05	5.1E-06	3.8E-06	7.4E-06	5.0E-06	4.0E-06
Third quartile:	1.8E-04	6.0E-05	3.4E-05	8.7E-06	2.2E-05	1.1E-05	1.0E-05
Ti/Ca (mol/mol)							
Average:	5.8E-06	5.2E-06	5.9E-06	5.6E-06	7.0E-06	7.0E-06	1.7E-05
Minimum:	4.3E-06	3.7E-06	4.5E-06	4.1E-06	2.0E-06	1.9E-06	2.0E-06
Maximum:	9.1E-06	2.5E-05	8.1E-06	8.3E-06	1.7E-03	7.5E-04	3.1E-03
Median:	5.8E-06	5.1E-06	5.8E-06	5.5E-06	4.0E-06	3.7E-06	5.0E-06
Standard deviation:	6.7E-07	1.2E-06	5.6E-07	6.4E-07	6.6E-05	3.7E-05	1.5E-04
First quartile:	5.4E-06	4.7E-06	5.5E-06	5.1E-06	3.0E-06	3.1E-06	4.0E-06
Third quartile:	6.3E-06	5.4E-06	6.2E-06	5.9E-06	4.0E-06	4.7E-06	5.0E-06
V/Ca (mol/mol)							
Average:	5.6E-06	3.6E-06	2.4E-05	5.5E-06	2.0E-06	1.6E-06	4.1E-07
Minimum:	7.0E-07	6.0E-07	0.0E+00	6.0E-07	3.0E-07	5.9E-07	1.2E-07
Maximum:	8.9E-04	5.9E-04	1.7E-03	7.4E-04	4.9E-04	1.8E-05	2.1E-06
Median:	2.8E-06	1.5E-06	1.0E-06	2.0E-06	7.0E-07	1.3E-06	3.2E-07
Standard deviation:	3.4E-05	2.4E-05	1.6E-04	3.0E-05	2.0E-05	1.1E-06	2.6E-07
First quartile:	2.0E-06	1.2E-06	1.0E-06	1.3E-06	5.0E-07	1.0E-06	2.5E-07
Third quartile:	4.2E-06	1.9E-06	2.0E-06	4.1E-06	1.0E-06	1.7E-06	4.6E-07
Mn/Ca (mol/mol)							
Average:	8.6E-06	2.1E-05	3.7E-06	1.7E-06	6.0E-06	3.2E-07	6.8E-06
Minimum:	5.9E-07	0.0E+00	5.7E-07	1.9E-07	3.0E-07	5.0E-08	4.0E-07
Maximum:	8.8E-05	2.1E-03	2.5E-05	4.7E-05	4.3E-04	1.5E-05	5.7E-04
Median:	5.2E-06	4.0E-06	2.5E-06	8.2E-07	1.7E-06	2.0E-07	3.2E-06
Standard deviation:	9.9E-06	1.2E-04	3.3E-06	3.0E-06	2.4E-05	7.8E-07	2.4E-05
First quartile:	2.6E-06	2.0E-06	1.6E-06	4.9E-07	9.0E-07	1.4E-07	1.6E-06
Third quartile:	1.1E-05	1.2E-05	4.6E-06	1.7E-06	3.5E-06	3.0E-07	7.1E-06
Ba/Ca (mol/mol)							
Average:	4.1E-07	5.4E-07	1.5E-07	1.2E-07	1.4E-07	2.1E-07	3.7E-07
Minimum:	1.4E-07	3.0E-08	8.5E-08	8.5E-08	9.4E-08	1.1E-07	4.2E-08
Maximum:	2.6E-06	6.6E-05	7.3E-07	3.5E-07	3.2E-07	1.3E-06	2.2E-06
Median:	3.2E-07	2.0E-07	1.2E-07	1.2E-07	1.3E-07	1.6E-07	2.0E-07
Standard deviation:	2.9E-07	3.7E-06	7.2E-08	3.1E-08	2.6E-08	1.3E-07	4.0E-07
First quartile:	2.3E-07	1.6E-07	1.1E-07	1.1E-07	1.2E-07	1.3E-07	1.5E-07
Third quartile:	4.8E-07	2.7E-07	1.5E-07	1.3E-07	1.5E-07	2.2E-07	3.7E-07

Table 6.3 Comparison of metal contents in *Porites* corals between this work and other studies

Coral location	Period	Al	Mn	Fe	Ni	Cu	Zn	Y	Pb	Reference
		ug/g coral	ug/g coral	ug/g coral	ug/g coral	ug/g coral	ug/g coral	ug/g coral	ug/g coral	
HUM02A, GBR	1960-2017	4.16	4.22	43.03	0.47	7.48	0.58	0.12	0.09	This study
MAS01E, GBR	1960-2017	2.24	0.08	42.15	0.46	4.32	0.38	0.04	0.04	This study
SAB05A, GBR	1960-2017	17.52	7.92	42.82	0.81	7.11	4.39	0.21	0.10	This study
SEA10A, GBR	1960-2017	11.96	0.95	51.81	0.52	5.81	1.98	0.10	0.09	This study
SEA11A, GBR	1960-2017	5.22	0.65	48.16	0.50	6.09	2.38	0.10	0.11	This study
SEN01C, GBR	1960-2017	1.11	0.82	42.81	0.47	2.29	3.46	0.10	0.03	This study
Xiaodonghai Bay	1910-2006	-	1.02	1190	6.18	3.8	5.93	0.103	2.09	Jiang et al., 2017
Longwan Bay	1853-2011	-	0.027	-	-	0.32	-	-	-	Chen et al., 2015
Snaya, Hainan Island	1870-2006	-	0.88	-	6.04	3.21	3.43	-	11.32	Song et al., 2014
Nha Trang Bay	1995-2009	-	2.92	35.77	-	5.53		0.14	0.24	Nguyen et al., 2013
Daya Bay	1976-2007	-	1.77	80	-	-	3.57	-	-	Chen et al., 2010
Gulf of Aqaba, Jordan	1925-2005	-	2.46-8.22	34.81-25.76	-	4.7-5.36	5.40-5.52	-	41.51-47.91	Al-Rousan et al., 2007
Magnetic Island, Australia	1813-1986	-	0.41-9.64	-	-	-	-	0.14-0.24		Lewis et al., 2007
Dafangji Island	1982-2001	-	4.27	-	9.5 2	11.7 1	4.2	-	1.62	Peng et al., 2006
Ihatub reef, Marinduque Island, Philippines	-1999	-	7.1	160	-	9.6	1	-	-	David, 2003
Misima Island, Papua New Guinea	1986-1995	-	0.19-0.49	-	-	-	0.35-36.5	0.02-0.05	0.05-1.22	Fallon et. al., 2002
Low sediment Venezuela	1960-1995	1.44-86.11	-	88.68	-	3.53-36.95	0.83-23.1	-	0.029-4.74	Bastidas and Garcia, 1999
High sediment Venezuela	1960-1995	1.54-846.49	-	1.32-369	-	3.33-89.57	3.59-42.25	-	0.031-1.413	Bastidas and Garcia, 1999

Note: For comparison between individual sites within this study during the same time period, metal concentrations were only averaged for the period 1960-2017. The actual geochemical records for each site are longer and may extend back to 1880 (See Table 6.1).

Table 6.4 Factor loadings on rotated principal components for 16 elemental ratios in each coral core and the percentage variance explained by each component. Note principal components were extracted based on eigenvalues > 1.

(a)	SEA11A			SEA10A				SAB05A					SEN01C			
	PC1	PC2	PC3	PC1	PC2	PC3	PC4	PC1	PC2	PC3	PC4	PC5	PC1	PC2	PC3	PC4
Ba/Ca	0.90	-	-	0.69	-	-	-	0.44	-	-	0.40	-	-	0.53	-	-
U/Ca	-	-	0.97	0.48	-	-0.34	-	0.75	-	-	-	-	-	0.48	-	-
Al/Ca	0.98	-	-	-	0.85	-	-	-	0.89	-	-	-	0.70	-	0.34	-
Ti/Ca	0.89	-	-	-	0.78	-	-	0.44	0.57	0.31	-	-	0.50	-	-	-
V/Ca	0.98	-	-	-	0.60	0.73	-	-	0.77	0.35	-	0.33	-	-	0.39	0.41
Mn/Ca	0.43	-	-	-	-	0.50	-	-	-	-	-	0.92	-	-	0.57	-
Fe/Ca	0.96	-	-	0.75	0.40	-	-	-	-	-	0.88	-	-	-	0.65	-
Ni/Ca	0.81	-	0.34	0.89	-	-	-	-	-	-	0.90	-	-	-	0.72	-
Cu/Ca	-	0.94	-	0.45	-	-	0.71	-	0.55	0.64	-	-	0.77	-	-	-
Zn/Ca	0.86	-	-	0.70	-	-	-	-	-	0.94	-	-	-	-	-	0.88
As/Ca	0.98	-	-	-	-	0.85	-	-	-	0.85	-	-	-	-	-	0.89
Y/Ca	0.88	-	-	0.83	-	-	-	0.88	-	-	-	-	0.47	0.84	-	-
Sn/Ca	-	0.92	-	-	-	-	0.90	0.46	0.55	0.48	-	-	0.78	0.33	-	-
La/Ca	0.99	-	-	0.77	0.49	-	-	0.84	0.34	-	-	-	0.44	0.85	-	-
Ce/Ca	0.98	-	-	0.59	0.72	-	-	0.72	0.56	-	-	-	0.51	0.79	-	-
Pb/Ca	0.96	-	-	0.73	-	-	-	0.57	-	-	0.48	-	0.62	-	0.44	-
% Variance	66.57	12.06	7.31	31.52	17.83	11.84	10.11	23.37	18.41	16.15	14.12	7.25	20.16	17.69	11.66	11.62

(b)	HUM02A						HUM03A				MAS01E					
	PC1	PC2	PC3	PC4	PC5	PC6	PC1	PC2	PC3	PC4	PC1	PC2	PC3	PC4	PC5	PC6
Ba/Ca	-	-	-	0.78	-	-	-	0.79	-	-	0.91	-	-	-	-	-
U/Ca	0.57	0.32	-	-	-0.37	-	-	-	-	0.79	-	0.73	-	-	-	-
Al/Ca	-	-	0.75	-	-	-	-	0.62	-	-	0.85	-	-	-	-	-
Ti/Ca	-	-	-	-	0.79	-	0.32	0.70	-	-	0.44	-	-	-	-	-
V/Ca	-	0.42	-	0.36	0.34	0.44	0.50	0.57	-	-	-	-	-	-	-0.62	0.35
Mn/Ca	-	-	-	-	-	0.87	0.69	-	-	-	-	-	-	0.80	-	-
Fe/Ca	-	0.93	-	-	-	-	0.73	-	-	-	0.37	-	-	-	0.69	-
Ni/Ca	-	0.91	-	-	-	-	0.60	-	-	-	-	-	-	0.33	0.64	0.31
Cu/Ca	0.65	-	-	0.36	-	-	-	-	0.90	-	-	-	0.91	-	-	-
Zn/Ca	0.38	-	0.52	0.49	-	-	0.89	-	-	-	-	-	-	-	-	0.88
As/Ca	-	-	-	0.57	0.55	0.34	-	0.89	-	-	0.80	-	-	-	-	-
Y/Ca	0.88	-	-	-	-	-	-	-	-	0.79	-	0.87	-	-	-	-
Sn/Ca	0.52	-0.49	-	-	-	-	-	-	0.93	-	-	-	0.93	-	-	-
La/Ca	0.92	-	-	-	-	-	0.70	0.33	-	0.51	0.60	0.65	-	0.35	-	-
Ce/Ca	0.89	-	-	-	-	-	0.94	-	-	-	0.62	0.49	-	0.41	-	-
Pb/Ca	-	-	0.79	-	-	-	0.94	-	-	-	-	0.71	-	0.37	-	-
% Variance	23.20	15.29	10.18	9.27	8.91	7.94	30.90	18.14	12.48	10.79	20.93	16.02	11.47	9.27	8.24	6.62

6.4.2 Pre-industrial periods vs post-industrial periods

The average concentrations for the majority trace elements in the Gladstone Harbour were within the wide range compared to other reported *Porites* corals from over the world (Table 6.3). However, a few heavy metals (e.g., Al, Ti, Mn) were clearly elevated within coral skeletons in the Mid-Harbour (SEN01C), Harbour Fringes (SAB05A) and Outer Harbour zones (SEA10A, SEA11A) during the post-industrial/port expansion era (1950-present) as opposed to pre-industrial era (before 1950) (Figure 6.13). In order to quantify the comparison between trace element concentrations after the coastal development and natural environmental levels, enrichment factors for individual elements were determined (Figure 6.13).

Trace element concentrations of aluminium (Al), titanium (Ti), vanadium (V), manganese (Mn), copper (Cu), zinc (Zn), arsenic (As), tin (Sn) and lead (Pb) in coral skeletons were found elevated in the post-industrial era (1950-present) relative to pre-industrial era (before 1950) in the nearshore sites (Figure 6.1). Aluminium was the most enriched metal in coral skeletons with an enrichment factor higher by one order of magnitude (Figure 6.13). Outer-harbour SEA10A and SEA11A recorded the highest Al enrichment factor (8-16-fold > pre-industrial baseline), followed by the mid-harbour SEN01C (3-fold > pre-industrial baseline), and harbour fringes SAB05A (2-fold > pre-industrial baseline). Titanium was the second most enriched metal, with enrichment factors being 2-6-fold > pre-industrial baseline at outer-harbour SEA10A and SEA11A, and 4-fold > pre-industrial baseline at mid-harbour SEN01C respectively. Manganese was enriched by a factor of 3-4 in harbour fringes SAB05A and mid-harbour SEN01C. Yttrium, lanthanum and cerium were also enriched (3-5-fold > pre-industrial baseline) in the outer-harbour SEA10A and SEA11A. Enrichment factors for other trace elements (e.g., Cu, Sn, Zn, Pb, Ba) were generally small (<2) and lower than the baseline levels (<1) in some corals. In contrast, inshore control Hummocky Island corals (HUM02A &

HUM03A) and mid-shelf Masthead Island coral (MAS01E) did not record significantly higher trace element concentrations in the post-industrial era compared to pre-industrial era because these sites are relatively away from the urban contaminations.

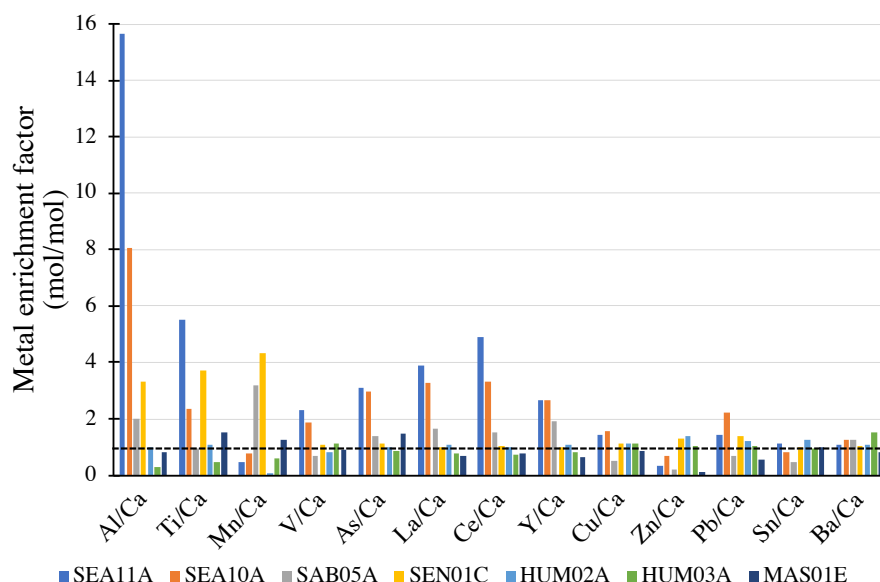


Figure 6.13 Comparison of trace element enrichment within the coral skeletons from five reef locations surrounding the Gladstone Harbour. Mid-Harbour: South End Curtis Island (SEN01C), Outer Harbour: Seal Rocks (SEA10A and SEA11A), Harbour Fringes: Sable Chief Rocks (SAB05B), Inshore controls: Hummocky Island (HUM02A and HUM03A) and Offshore Control: Masthead Island (MAS01E). Average element/Ca ratios before 1950 from individual sites were used as the respective pre-industrial/port expansion baselines. Enrichment factors were calculated by dividing ‘mean element/Ca ratios in the post-industrial era (1950-present)’ by ‘mean element/Ca ratios in the pre-industrial era (-1950)’. For the consistency in comparison, average element/Ca ratios before 1950 from individual sites were used as the respective pre-industrial/port expansion baselines when data were available. However, SEA10A, SEA11A and SAB05A have shorter records which do not have long-term pre-industrial baseline. In that case, pre-industrial baseline values from SEN01C, HUM02A, HUM03A and MAS01E were averaged to serve as the pre-industrial ‘baseline value’ for SEA10A, SEA11A and SAB05A. Trace element concentrations were elevated during the post-industrial era (1950-present) if the post:pre (mol/mol) ratio exceeds 1 (black dashed line). Several trace elements (e.g., Al, Cu, Pb, Ti, Zn, Mn, As) are elevated during the recent era, with Al being the most significant.

6.4.3 Individual trace elements

Aluminium (Al)

Aluminium (Al) was found to be the most enriched trace element in Gladstone corals during the post-industrial era (>1960) (Figure 6.14). The Al concentrations from the corals at mid-harbour SEN01C and distant locations (inshore control HUM02A and HUM03A, offshore control MAS01E) were much lower compared to Outer Harbour SEA10A & 11A and Harbour Fringes SAB05A (Figure 6.14). Corals from SEA10A&11A have been exposed to sustained

pulses of Al from 1960 to 2010. The Al/Ca ratios in the SAB05A showed three sustained periods of enrichment (1960-1970, 1990-1993 and 2000-2008). Only occasionally short-lived Al spikes were recorded in SEN01C (2005, 2008) and in MAS01E (1987, 1991). HUM02A, however, recorded sustained elevated Al inputs from 1993-2008 which coincides with the timing of Al spikes in corals at Seal Rocks. Elevated Al/Ca ratios have been recorded in coral skeletons across all the sites, suggesting that the Al contamination is not limited to the Gladstone Harbour region but can be transported further into more pristine environments (e.g., Hummocky Island and Masthead Island are located in the Great Barrier Reef Marine Park).

Al/Ca ratios in coral skeletons in the region of Gladstone Harbour are variable, however, the timing of when the Al/Ca signal started to rise coincides with the environmental changes and anthropogenic developments in Gladstone region (Figure 6.14). The elevated Al/Ca ratios measured in corals from the Outer Harbour (SEA) and the Harbour Fringes (SAB) are most likely linked to the initial start of the alumina import and refinery industry in the late 1960s and the subsequent opening of the aluminium smelting facility at the Boyne Island in 1982 (Cantin et al., 2018). The Al/Ca pulses in the 1960s and 1980s reflects recent inputs from industrial development, but the elevated Al/Ca ratios were still detected after these pulsed events which suggest a large amount of Al has been attached or deposited on suspended particulates and were ultimately accumulated in sediments. Angel et al. (2012) performed a linear regression analysis between total Al concentrations in seawater and the total suspended solids ($R^2=0.7$) showing Al affinity to bind to particles. Therefore, the re-suspension of particulates is a major pathway of Al release, transport and mobilization. The Al-rich sediments can release Al back to the water column when environmental conditions become favourable. These conditions include the re-suspension by dredging, cyclones and major flood periods. Besides, Al/Ca spikes do not always correspond to industrial events (Figure 6.14). Al is also

abundant in clay minerals; therefore, future work needs to consider the degree to which Al reflects alumina versus clay from enhanced catchment clearing. Few studies have reported the Al concentration in corals (Table 6.3). This might be partially attributed to the low toxicity of Al in marine waters (Angel et al., 2012). Thus, this study will be the precursor in examining how the development of Alumina industry at Gladstone affects the coastal aquatic environments by using the geochemical signatures recorded in coral skeletons.

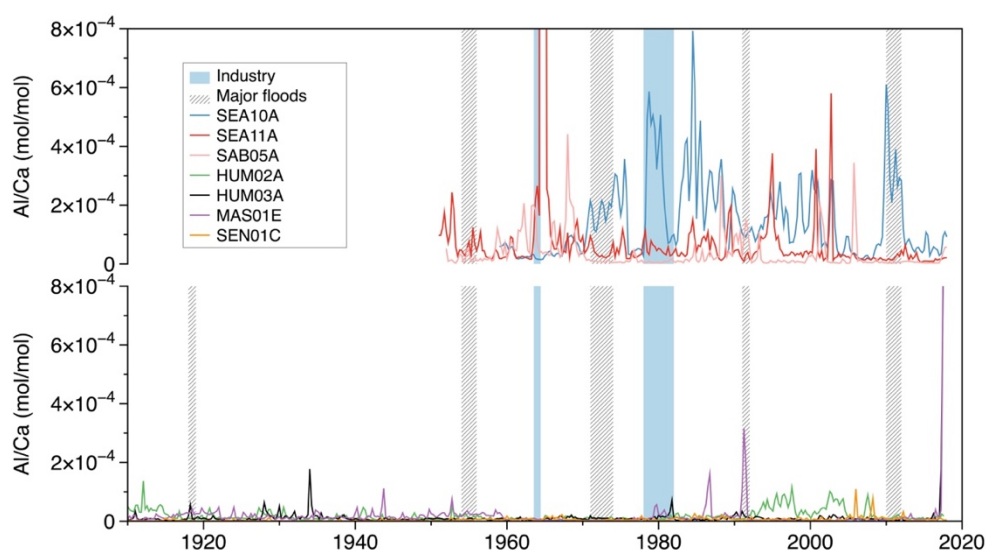


Figure 6.14 Comparison of Al/Ca ratios at different coral sites, and their correspondence with major port development and floods. Blue shaded area indicates the manufacturing of alumina by Queensland Alumina Ltd. (QAL) and the construction of the aluminium smelting facility at Boyne Island. Gray shaded area indicates the major floods.

Titanium (Ti)

The Ti/Ca ratios in the corals from the Gladstone Harbour showed a few sustained periods of enrichment (1940-1960 and 1985-1993 at HUM02A, 1958-1970 at SEN01C, 1950-1960 and 1970-1990 at SEA10A and SEA11A, and 1985-1993 at MAS01E). Ti concentrations in natural coral skeletons have not been reported before. A published study has demonstrated that coral exposure to excessive nano-TiO₂ induce stress and possibly the decrease in the exposed coral population (Jovanovic and Guzman, 2014). All coral colonies in the Gladstone Harbour region recorded pulsed high-amplitude Ti/Ca spikes relative to baseline values (Figure 6.15). The occurrence of the elevated Ti/Ca signals was neither not concurrent in timing with industrial

activities or large discharge events nor were they typically correlated across sites, thus making it difficult to identify their common sources. TiO_2 and ZnO nanoparticles are the main ingredients in sunscreens (Giokas et al., 2007; Labille et al., 2020). The presence of titanium (Ti) in seawater has been proposed to come from the wide use of sunscreens which people used to protect against ultraviolet rays during recreational activities in the beach (Giokas et al., 2007; Hopkins and Blaney, 2016; Labille et al., 2020). However, this is highly unlikely for the Gladstone corals as the high Ti/Ca spikes would need a lot of people using sunscreen. Therefore, the exact sources of Ti detected in the Gladstone corals need further investigation.

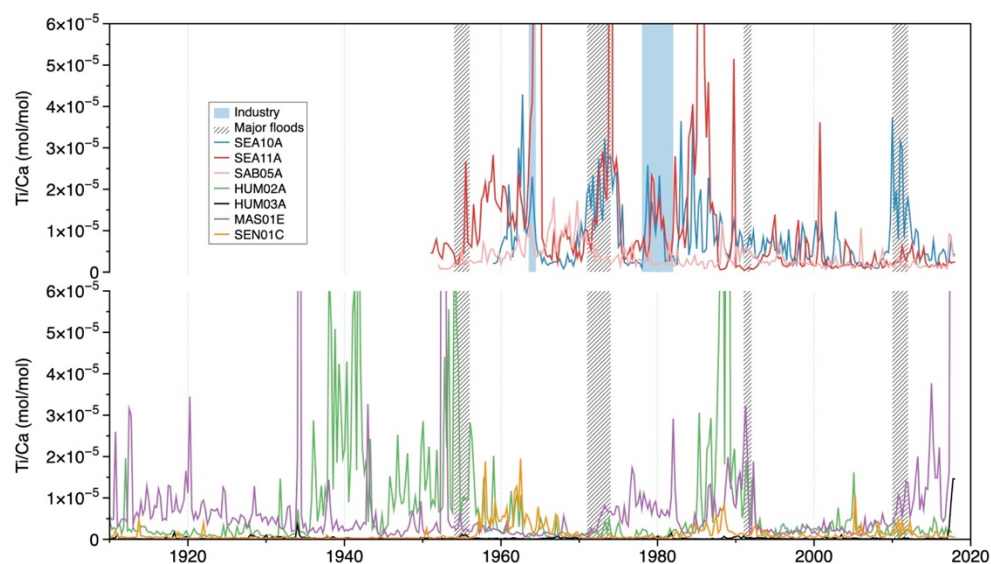


Figure 6.15 Comparison of Ti/Ca ratios at different coral sites, and their correspondence with major port development and floods.

Vanadium (V)

Vanadium has been investigated in few coral studies and the measured V concentrations reflect historical oil pollution (Guzman and Jarvis, 1996; Tanaka et al., 2013) and historical wood clearing and burning (Saha et al., 2019a). Prolonged inputs of V were detected in the corals obtained at SEA10A from 1960 onward. SEA11A also recorded an increase in vanadium concentrations from 1985-1995 and from 2005-2012. Corals from the mid-shelf offshore control site, MAS01E, however, recorded three spikes of V peaking around 1900, 1942 and 1990 (Figure 6.16). This ~45-year V cycle at MAS01E was not observed at other sites. These

large V/Ca spikes might reflect the influence of oil spills around Masthead Island. Oil compounds are resistant to biodegradation. However, it is unlikely that the oil plume can hang around for years on a reef on a mesotidal shelf because the dominantly north-eastern winds would drive inshore waters north and drive the oil spills to the coast.

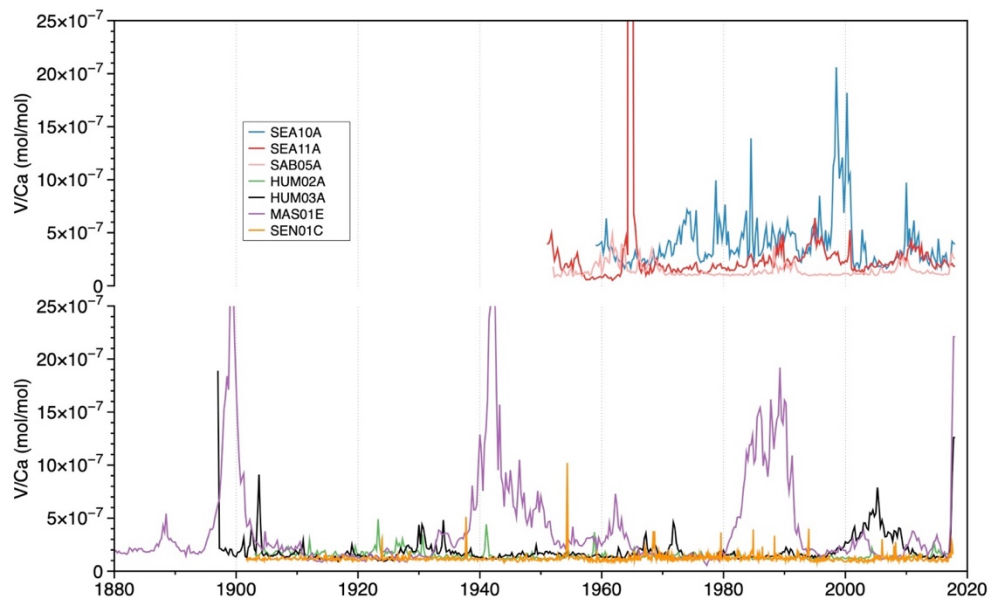


Figure 6.16 Comparison of V/Ca ratios at different coral sites.

Manganese (Mn)

The Mn concentration in seawater, usually derived from river runoff or shelf sediments, is controlled by redox cycles initiated by sunlight and mediated by microorganisms (Hunt, 1983; Schoemann et al., 1998; Sunda et al., 1983). In this study, Mn/Ca does not have a strong correspondence with either river runoff or Ba/Ca. Instead, Mn/Ca seems to be seasonally driven (zoom in figures in chapter 7) and consistent with other published studies (Alibert et al., 2003; Delaney et al., 1993; Lewis et al., 2012; Shen et al., 1991; Wyndham et al., 2004).

Even though Mn/Ca remained low most of the time, several Mn/Ca spikes were measured. Sustained elevation of Mn/Ca ratios were measured at HUM02A from 1928-1932, at SAB05A from 1950-1962, and at SEN01C from 1962-1992 and from 2008 to 2011. A few pulsed spikes of Mn/Ca were measured at SEA11A in 1965 and 1991 and at SEA10A in 1985 and 2011.

Frequent Mn/Ca spikes in late 1920, 1965, 1970, 1980, 1985 were measured at HUM02A, with Mn/Ca spikes in 1968 and 2009 at SEN01C, and a large Mn/Ca spike around 1962 at SAB05A corresponding to several major dredging operations (1918, 1953-1954, 1967, 1981-1986, 2011) and jetty expansion (1920) (Figure 6.17). Short lags between the coral records and the major harbour events may result from the diffusion of metals or metal desorbed from particulates caused by water mixing.

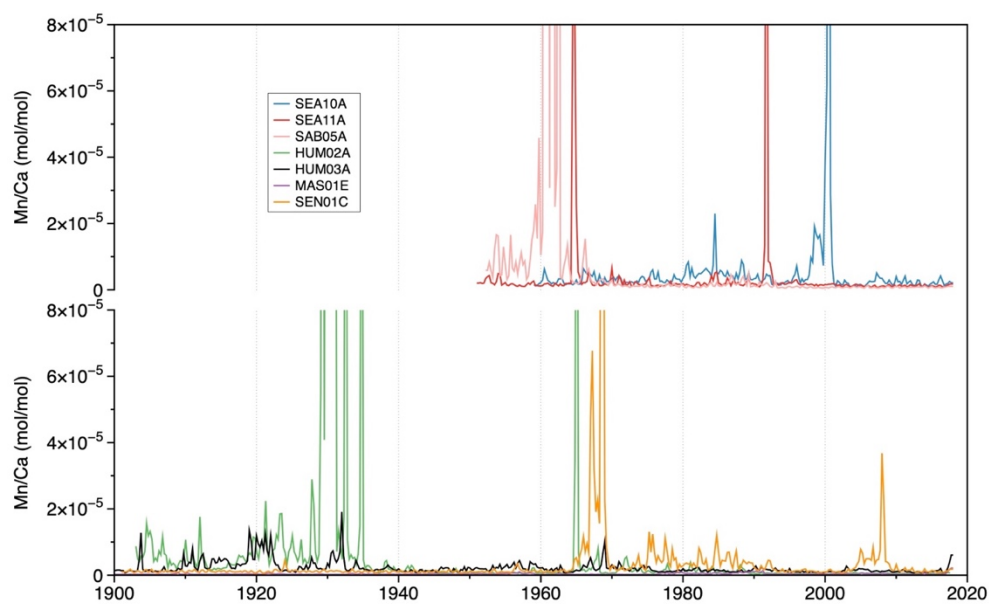


Figure 6.17 Comparison of Mn/Ca ratios at different coral sites.

Barium (Ba), Yttrium (Y), Lanthanum (La) and Cerium (Ce)

Ba/Ca, Y/Ca and rare earth elements (REEs) have been widely used to reconstruct land use changes, sediment inputs and river runoff (Leonard et al., 2019; Lewis et al., 2018; Lewis et al., 2007; McCulloch et al., 2003; Moyer et al., 2012; Saha et al., 2018a; Saha et al., 2016; Saha et al., 2019b; Sinclair, 2005b; Sinclair and McCulloch, 2004; Walther et al., 2013). Corals at the Outer harbour, SEA10A&11A and harbour fringes, SAB05A sites have captured the flood events with a correspondence between Ba/Ca, Y/Ca, La/Ca, Ce/Ca and large river discharge in 2011 and 2014 (Figures 6.18, 6.19). The inshore control sites, HUM02A and HUM03A, both recorded increases in Ba/Ca concentrations from baseline values which were in line with floods

in 1955, 1971, 1974, 1991 and 2011 (Figure 6.18). Similarly, the mid-harbour site, SEN01C recorded slight increases in Ba/Ca ratios during a few flood years, 1918, 1955, 1975, 1991, and 2011 (Figure 6.18). In most cases, Ba/Ca, Y/Ca, La/Ca, and Ce/Ca showed concurrent fluctuations coincident with the timing of river floods. The correspondence between Y/Ca, La/Ca, Ce/Ca and river runoff, however, is less significant compared to Ba/Ca (e.g., see data for HUM02A, HUM03A). Future work can analyse the full range of REEs and use the shale-normalized patterns to better understand the river and sediment discharges (Fallon et al., 2002; Leonard et al., 2019; Saha et al., 2019b; Wyndham et al., 2003).

Luminescence lines from coral records in the Gladstone Harbour correlated well with the historic river discharge (Cantin et al., 2018), consistent with previous studies (Jupiter et al., 2008; Lough et al., 2002; Lough et al., 2015; Rodriguez-Ramirez et al., 2014). However, Ba/Ca spikes did not always reflect river discharge. For example, SEA10A&11A and SAB05A recorded frequent Ba/Ca spikes from 1950 onwards. These sites are near the shipping channel (Figure 6.2), so they are more susceptible to sediment resuspension by annual dredging. Figure 6.12 also suggests the long-term accumulation of Ba in the near harbour sites, with higher Ba/Ca and Y/Ca concentrations recorded at SEA10A&11A, SAB05A and SEN01C. On the other hand, not all river runoff can be reconstructed by Ba/Ca signals. For example, 22.3×10^6 ML of river flow was recorded in 1991, however, corals from Seal Rocks (SEA10A&11A) did not record significantly high Ba/Ca signals corresponding to this flood event (Figure 6.18). Besides, Ba records from the Hummocky Island (HUM02A&03A) and the South End (SEN01C) failed to track the flood in 1918 either (Figure 6.18). This potentially shows the limited supply of Ba to the coastal environments in certain years and in certain regions (Sinclair and McCulloch, 2004). Of note, Ba/Ca displayed clear seasonal cycles at a few sites (e.g., HUM02A&03A) with the Ba peaks (troughs) consistent with Austral summers (Austral

winters), although the seasonal amplitude varied (Figure 6.18). The timing of summer Ba/Ca peaks is most likely due to greater precipitation and river runoff in summer compared to winter. Ba in corals can also be controlled by environmental factors such as sea surface temperature and phytoplankton blooms (Fallon et al., 1999; Lewis et al., 2018; Saha et al., 2018b; Sinclair, 2005b; Walther et al., 2013). These distinct Ba signatures have been further examined in corals collected from the Whitsunday Islands (see chapter 7).

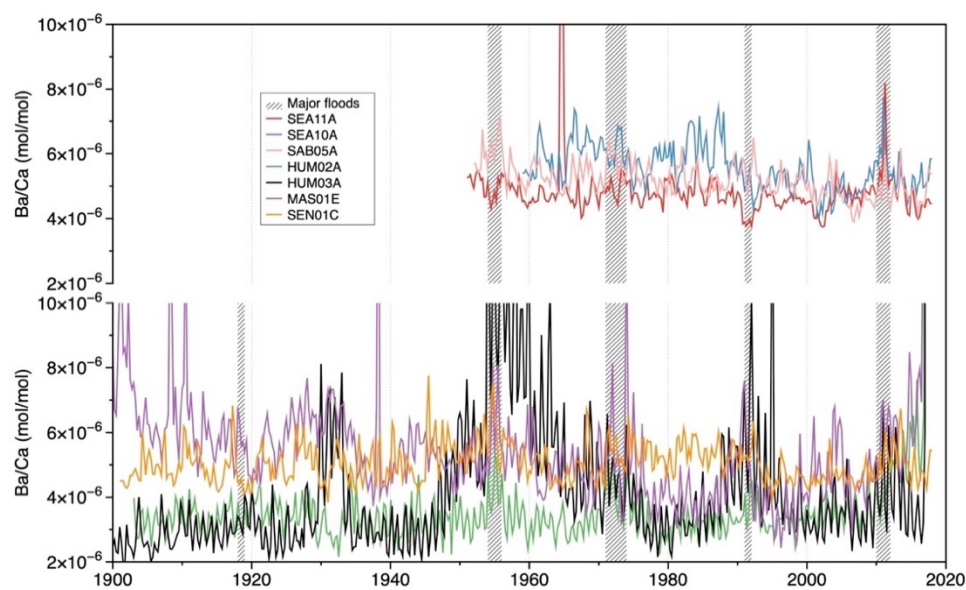


Figure 6.18 Comparison of Ba/Ca ratios at different coral sites, and their correspondence with major floods.

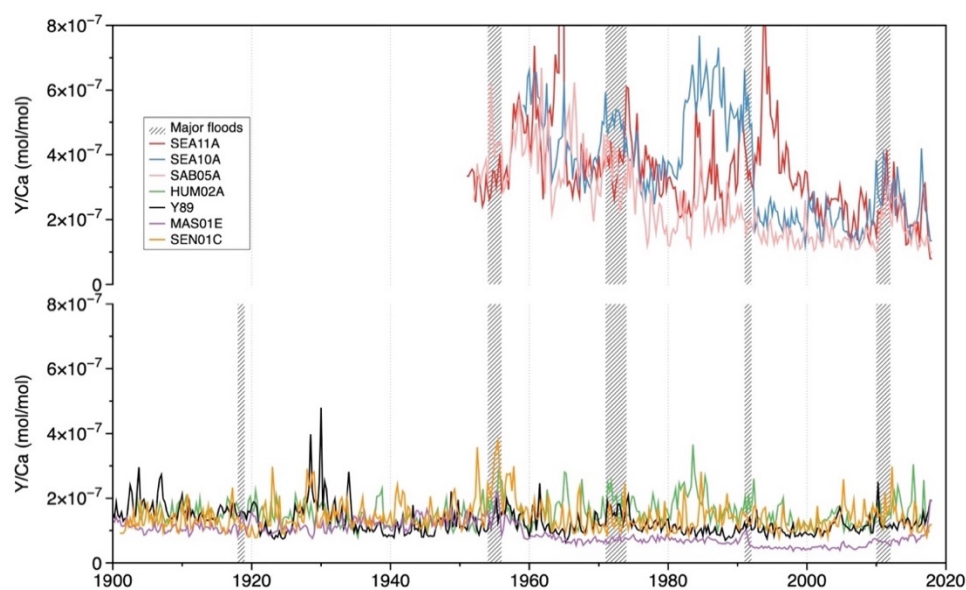


Figure 6.19 Comparison of Y/Ca ratios at different coral sites, and their correspondence with major floods.

Copper (Cu) and Tin (Sn)

Cu/Ca and Sn/Ca ratios remained relatively stable at all coral sampling sites (Figure 6.20). However, both Cu/Ca and Sn/Ca showed an increase in late 2000s, reaching a peak around 2011, and then gradually decreasing back to the baseline. This event corresponds to dredging and a flood in 2011. Unlike other trace elements, Cu/Ca and Sn/Ca ratios at the offshore control site, MAS01E and at the inshore control sites, HUM02A&03A are similar to the metal ratios at nearshore coral sampling sites (e.g., SEA10A&11A) (Figure 6.20). Of note, corals at MAS01E recorded the highest Sn concentrations. Major sources of Cu in this region are the use of antifouling and anticorrosive paints on vessels (Kroon et al., 2020). Other sources may include domestic and industrial wastewater discharge; runoff from power plants and terrestrial runoff (Ali et al., 2011). Sn concentrations in corals has not been studied extensively. The major source of Sn in seawater has been suggested to be from eolian input rather than riverine inputs (Byrd and Andreae, 1982).

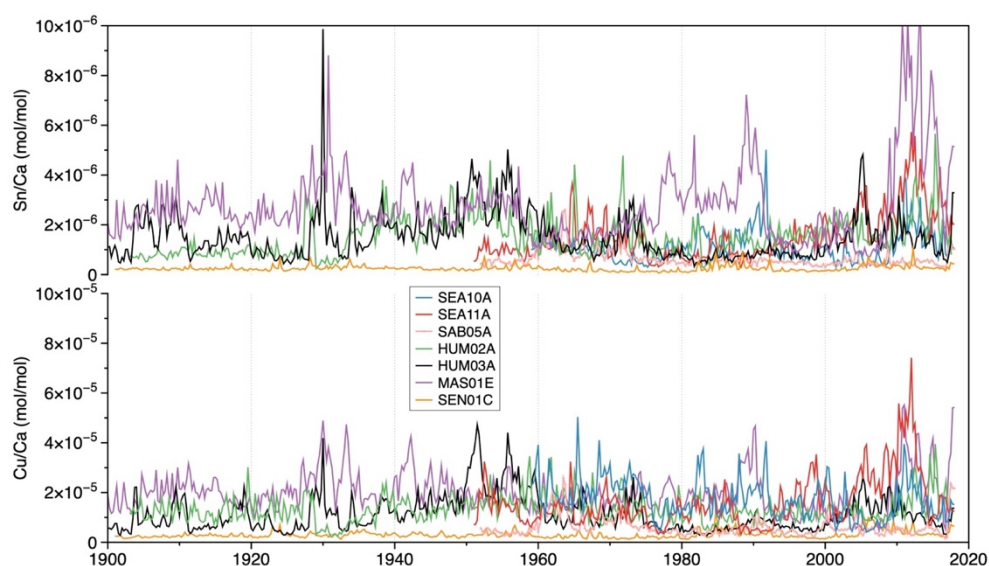


Figure 6.20 Comparison of Cu/Ca and Sn/Ca ratios at different coral sites.

Zinc (Zn) and Lead (Pb)

Zn/Ca and Pb/Ca ratios for the majority corals mostly exhibited natural fluctuations (Figure 6.21). Corals from both SEA10A and MAS01E recorded some elevated Zn/Ca signals in the 1980s, and corals at MAS01E also recorded frequent Zn spikes from 1935 to 1960. Zn and Pb concentrations in corals showed a clear spatial distribution. Outer harbour corals from sites SEA10A&11A recorded higher Zn/Ca and Pb/Ca ratios than mid-harbour, harbour fringes or control site corals, suggesting that the near Harbour coral sites are more susceptible to chronic contamination from urbanization, industrial development and harbour activities. Overall, mean Zn and Pb concentrations in the corals collected from the Gladstone Harbour were lower than other locations from over the world (Table 6.3), so the Gladstone region is presumed to be a locally contaminated area.

Pb in seawater can also come from the use of antifouling and anticorrosive paints on marine vessels. Pb is widely used for weatherproofing buildings, water pipes and cooking vessels. Domestic sewage, industrial waste and car exhaust emissions all contain Pb (Fallon et al., 2002). Pb would have a primary control from leaded petrol use. It should have increased with cars and then decreased when unleaded fuels were mandated. Therefore, the detection of Pb in seawater or coral skeletons mainly reflect anthropogenic activities. Some random peaks of Pb, however, may come from local upwelling, atmospheric deposition, or other sources (Chen et al., 2016). Future work can precisely measure the different Pb isotopes and identify the specific Pb sources (Chen et al., 2016).

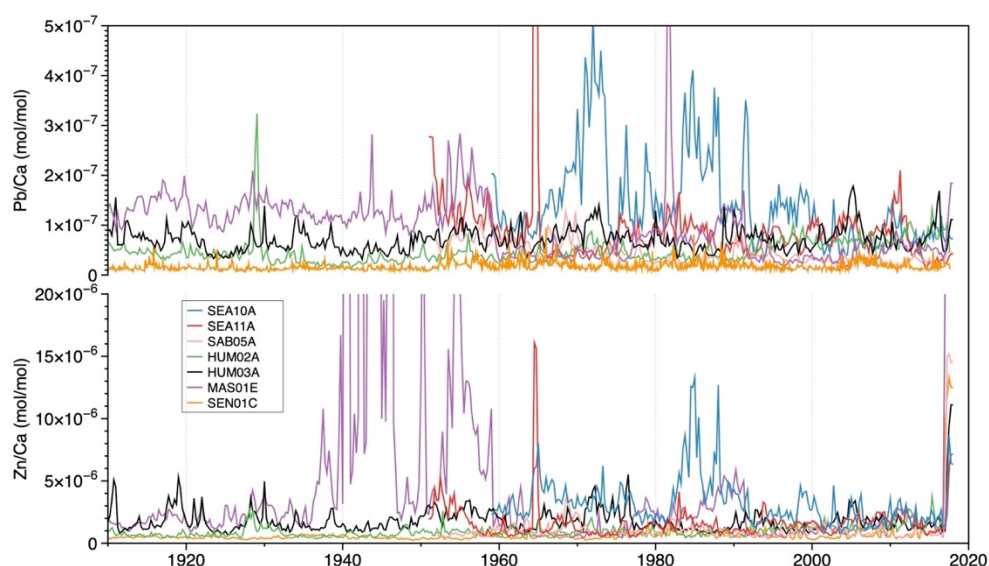


Figure 6.21 Comparison of Zn/Ca and Pb/Ca ratios at different coral sites.

6.4.4 Metal covariance and delivery pathways

PCA analysis showed that the time series were not random and some metals covaried together (Table 6.4). The occurrence of different metals at the same historic time indicate that large scale environmental changes coupled with intimate geochemical correlation between certain elements lead to the simultaneous fluctuations of these elements in corals. Some trace elements are consistently grouped together showing similar leaching sources or coherent geochemical signatures (Table 6.4, Figure 6.22). These groups include (1) Y/Ca, La/Ca and Ce/Ca and/or Ba/Ca that represent terrestrial river runoff; (2) Al/Ca and Ti/Ca that are industrially derived; (3) Cu/Ca and Sn/Ca that are potentially associated with paintings in vessels; (4) Zn/Ca and As/Ca that are potentially nutrients and (5) Mn/Ca and V/Ca that are pulsed sources due to random events. The high association between some metal contaminants (e.g., Al, Ti) and terrestrial runoff proxies (Ba/Ca, Y/Ca, La/Ca, Ce/Ca) at some coral sampling sites (e.g., SEA10A, SEA11A) has confirmed the prominent river influence at the coastal coral sampling sites. However, it is not possible to clearly separate the trace elements associated with alumina-mining activities, coal-mining activities, land use change, terrestrial runoff and seasonally

varying environment factors from PCA because these signals were mixed together at some coral sites.

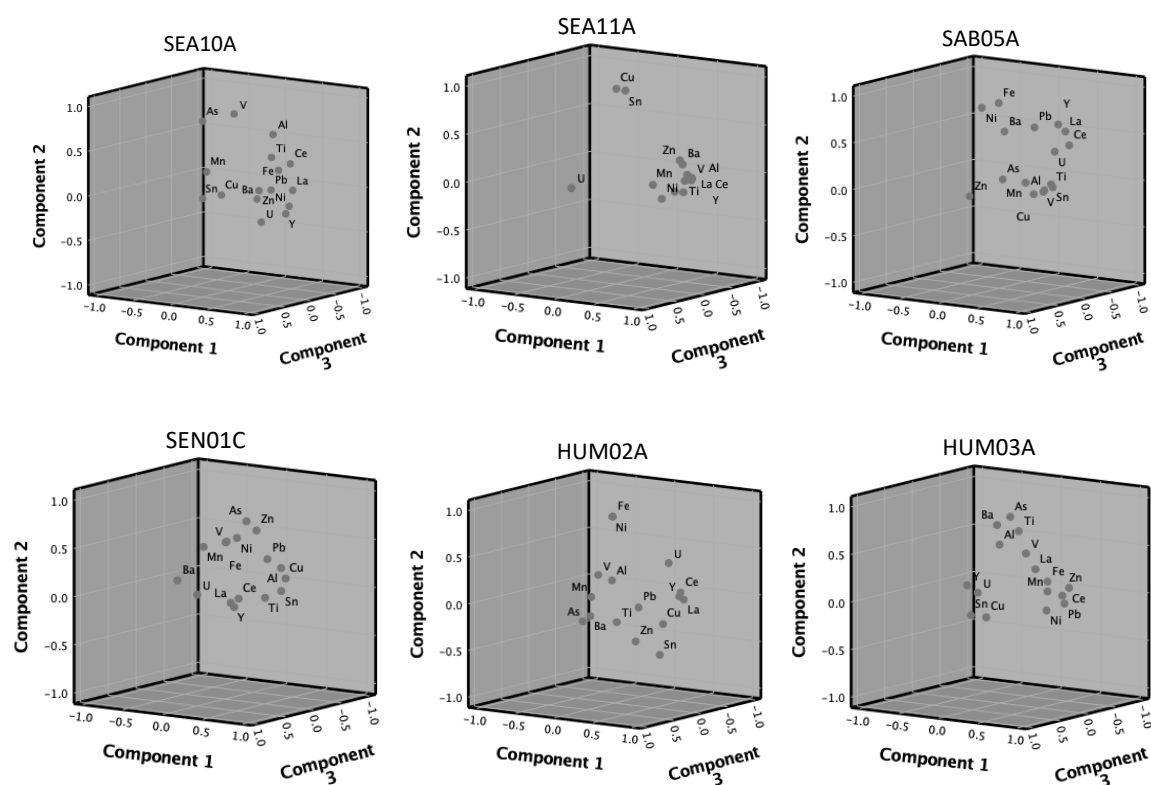


Figure 6.22 Loading plots in rotated space for 16 elemental ratios in each coral core with Varimax rotation solution. This plot shows several evident groupings of trace elements.

6.4.5 Distribution coefficient (K_d)

Historical seawater sampling and long-term monitoring programs for industrially sourced contaminants in the marine environment around the Gladstone Harbour region only existed after 2003 (Apte et al. 2005). Reconstructing trace element concentrations in seawater from trace element concentrations in coral skeletons can be an effective way to monitor both spatial (inshore vs offshore) and temporal (back to 1900) marine contamination. Due to the complicated process of coral calcification, metal fractionation from seawater to coral skeletons has not yet been established. In order to better understand how trace elements are incorporated into coral skeletons, empirical distribution coefficients (K_d) were calculated as follows (Shen and Boyle, 1988):

$$K_{d_{Me}} = (Me/Ca)_{coral} / (Me/Ca)_{seawater}$$

Where Me represents the trace element (metal), and Me/Ca is the molar ratio. A large *Kd* indicates that corals favour the uptake of this trace element and vice versa.

In order to calculate the *Kd*, Ca^{2+} levels in seawater and coral skeletons are desirable. Average Ca^{2+} concentrations in seawater were estimated to be $\sim 415 \text{ mg/kg}$ or 10.3 mmol/kg and Ca^{2+} in corals was $\sim 350 \text{ mg/g}$ (Jiang et al., 2020; Kelly et al., 2009; Song et al., 2014). Since seawater monitoring data in Port Curtis (near the Gladstone Harbour) were publicly available in December 2011 (Angel et al., 2012) and from November 2012-August 2015 (Kroon et al., 2020), trace element concentrations in coral skeletons were averaged for the same period to calculate the *Kd* (Table 6.5).

According to Shen and Boyle (1987,1988), cations with 2+ valence and with similar atomic size (ionic radius: $0.90\text{-}1.48 \text{ \AA}$) to Ca (ionic radius: $1.12 \text{ \AA}$) can substitute for Ca in coral aragonite, which leads to a unity in distribution coefficient (=1). A distribution coefficient equal to 1 indicates that the ratio of trace elements to calcium in coral aragonite is the same as that in seawater. That is, the precipitation process did not remarkably alter the concentration of trace elements to calcium. In other words, no significant biological regulation occurred. A distribution coefficient much smaller than 1 means that the metal is discriminated by the coral while a distribution coefficient much larger than 1 means that the metal is taken up by the coral preferentially than calcium. A comparison between literature *Kd* and the *Kd* in this work was shown in Table 6.6.

Aluminium (Al)

The only published *Kd* for Al (Antwertinger 2010) is 0.3-0.39 that is similar to the median and mean values in this study (0.31 and 0.40). The *Kd* at site SEA10A has an abnormally higher

value which is due to a pulsed Al/Ca spike during the calculation period (November 2012-August 2015). Kd values for Al suggest that the uptake of Al is discriminated by corals. The ionic radius of Al ranges from 0.39 Å (coordination IV) to 0.535 Å (coordination VI), along with the 3+ valence, making it incompatible with aragonite lattice. Therefore, the Al may be taken up as Al bearing particulates or adsorbed to coral skeleton instead of dissolved Al in seawater so the Kd values could be illusory.

Manganese (Mn)

The Kd_{Mn} calculated in this work, (median and mean values of 0.20 and 0.21 respectively), is similar to that calculated by Shen and Boyle (1988) ($Kd_{Mn}=0.1$). This suggests the uptake of Mn is discriminated by corals. However, Linn et al. (1990) reported a Kd_{Mn} close to unity, and Antwertinger (2010) reported a much higher Kd_{Mn} (~3) as the Mn in coral skeletons were relatively constant from various locations, but the dissolved Mn concentration in seawater had large variations (Table 6.5).

Copper (Cu)

Kd_{Cu} calculated in this study ranged from 4.3 to 31. Kd_{Cu} values reported by Jiang et al (2020) were 2.7 (*Porites lutea*), 4.4 (*Favia palauensis*) and 3.0 (*Pavona decussata*). Other studies also reported a wide range of Kd_{Cu} from 0.3 to 7.2 for various coral species (Linn et al., 1990; Livingston, 1971). The higher Kd_{Cu} values calculated from the Gladstone Harbour may be due to the higher Cu concentrations in coral skeletons as the seawater Cu concentrations remained relatively constant from different sites (Table 6.5). The variable Kd_{Cu} suggests that the relatively smaller ionic radius (0.73 Å, coordination VI) of Cu makes Cu less compatible with the aragonite lattice making it harder to consistently be substituted in aragonite lattice.

Zinc (Zn)

The median and mean Kd_{Zn} from seven locations in the Gladstone Harbour were 0.91 and 0.81 respectively. These values are close to unity, similar to the estimation by Shen (1986) for *Diploria strigosa*. Jiang et al. (2020) reported the coefficients of Zn for three different species, which were 1.8 (*Porites lutea*), 1.4 (*Favia palauensis*) and 1.2 (*Pavona decussata*) respectively. Antwertinger (2010) and Shen and Boyle (1988), in contrast, reported higher Zinc coefficients of 6-7 and 11 for corals collected from Darwin Harbour and from Bermuda. Coral Zn concentration ranges from 0.46-1.15 mg/Kg in the Gladstone Harbour which are comparable to the reported literature values (Table 6.3). Seawater Zn concentration from the Darwin Harbour is lower than that in the Gladstone Harbour or the South China Sea by one order of magnitude. Therefore, the differences are caused by different seawater Zn concentrations.

Lead (Pb)

The median and mean Kd_{Pb} from seven locations in the Gladstone Harbour were 1.62 and 1.67 respectively. These values are similar to those reported by Jiang et al. (2020) and Shen and Boyle (1988) which are 1.1, 1.1, 1.9 and 2.1-2.3 for *Porites lutea*, *Favia palauensis*, *Pavona decussata*, and *Diploria strigose* respectively. Kd_{Pb} calculated by Antwertinger (2010) have a larger range (9.5-14.2) which suggests that a small portion of Pb in the corals from the Darwin Harbour was in particulate forms rather than in dissolved form. Pb concentrations in coral skeletons were relatively constant among different sites (Table 6.5) even though the ambient Pb concentrations varied greatly, covering the wide water conditions. Shen and Boyle (1988) performed a rigorous cleaning of crushed coral samples and yielded a similar coefficient of Pb, which suggests that the Pb is bound in aragonite skeletons. Overall, the coefficients of Pb are consistently higher than 1 in the literatures (Table 6.6), suggesting the preferential uptake of Pb by corals.

Vanadium (V) and Arsenic (As)

The median and mean Kd_V in the Gladstone Harbour were 0.05 and 0.06, respectively. The median and mean Kd_{As} in the Gladstone Harbour were 0.04 and 0.06, respectively. These low values suggest both V and As are significantly discriminated by corals. There are no literature values for Kd_V and Kd_{As} for comparison. The ionic radius of V (0.79 Å, coordination VI) and As (0.58 Å, coordination VI) are small and As has 3+ and 6+ charges. The incompatibility of ionic radius and charge make V and As not suitable for incorporation into aragonite. The mechanism of V incorporation into aragonite remains speculative. Anionic vanadate HVO_4^{2-} in seawater may substitute for the CO_3^{2-} because they have the same charge, but this process may be difficult due to the significantly larger size of vanadate anion than that of carbonate anion. Other modes of incorporation may include the deposition of V in skeletal defects or intracrystalline organic matrix like Mg (Saha et al., 2019).

***Kd* summary**

Kd values calculated in this work were in the range of reported literature values, showing preferential uptake of Pb and discrimination against Al, V, Mn, As. Cu is the only element that varies quite a bit. The discrepancy of *Kd* between this study with others could be primarily due to the differences in seawater data. Seawater sampling usually represents a snapshot of the water composition which cannot precisely cover the long-term average of coral trace metal concentrations. Besides, the water sampling locations were not exactly at the coral sampling location. Shen and Boyle (1988) took typical metal levels in the western North Atlantic or Sargasso Seawater. Antwertinger (2010) used the seawater data measured in Darwin Harbour in 2001, and this work used the seawater data in Gladstone Harbour from 2011 to 2015 (Angel et al., 2012; Kroon et al., 2020). Metal incorporation into coral skeletons is not a simple process. That is, the *Kd* is supposed to be 1 if metals in corals come directly from precipitation. Instead,

the K_d can be influenced by environmental factors such as water temperature, aragonite saturation index and biological factors (Gonneea et al., 2017).

Table 6.5 The mean concentrations of trace metals ($\mu\text{g}\cdot\text{g}^{-1}$) in coral skeletons from seven sites around the Gladstone Harbour (this study) and average trace metals ($\mu\text{g}\cdot\text{L}^{-1}$) in seawater from the Port Curtis (Kroon et al., 2020) for the same period November 2012 - August 2015. SEA11A, SEA10A and SAB05A are considered as outer-harbour sites. SEN01C is considered as mid-harbour site. HUM03A, HUM02A and MAS01E are considered as offshore sites.

Element	Control ¹	Outer-Harbour	Mid-Harbour	SEA11A	SEA10A	SAB05A	SEN01C	HUM03A	HUM02A	MAS01E
Seawater ($\mu\text{g/L}$)				Coral skeleton ($\mu\text{g/g}$)						
Aluminium	5.6	15	11	3.96	15.23	1.43	0.94	1.13	2.27	1.79
Vanadium	1.7	1.7	1.8	0.10	0.12	0.05	0.05	0.06	0.07	0.18
Manganese	2.4	2.4	6.2	0.57	0.88	0.41	0.56	0.49	0.24	0.15
Iron	2.8	11	4.2	45.34	49.47	44.61	47.07	171.49	44.93	128.78
Nickel	0.5	0.5	0.51	0.52	0.58	0.56	0.49	1.42	0.25	0.79
Copper	0.46	0.46	0.49	9.76	8.66	3.04	1.78	5.05	12.10	9.21
Zinc	1	1.5	1	0.68	1.15	0.46	0.51	0.78	1.05	0.95
Arsenic	0.67	1.2	1.1	0.06	0.06	0.05	0.04	0.04	0.03	0.02
Lead ²	0.016	0.019	0.016	0.16	0.18	0.15	0.10	0.09	0.15	0.06
Tin	0.5	0.5	0.5	2.96	1.79	0.55	0.27	1.40	2.84	1.75
Uranium	2	3	3	2.96	2.81	2.86	2.65	2.42	3.10	2.72

Note: ¹ Offshore seawater control is not available so the minimum metal concentration among different sites was picked up to serve as offshore control; ² Seawater lead concentration used for calculation is from Angel et al. (2012)

Table 6.6 Distribution coefficients (*K_d*) of selected metals in corals (seawater metal data from Angel et al., 2012 and Kroon et al., 2020)

Species	Sample ID	Al/Ca	V/Ca	Mn/Ca	Fe/Ca	Cu/Ca	Zn/Ca	As/Ca	Sn/Ca	Pb/Ca	U/Ca	References
<i>Porites</i> spp.	SEA11A	0.31	0.07	0.28	4.85	25.01	0.53	0.06	6.97	1.01	1.16	This work
<i>Porites</i> spp.	SEA10A	1.20	0.09	0.43	5.30	22.20	0.91	0.06	4.22	2.17	1.10	This work
<i>Porites</i> spp.	SAB05A	0.11	0.04	0.20	4.78	7.79	0.36	0.05	1.29	0.91	1.13	This work
<i>Porites</i> spp.	SEN01C	0.10	0.03	0.11	13.20	4.27	0.60	0.04	0.65	0.50	1.04	This work
<i>Porites</i> spp.	HUM03A	0.24	0.04	0.24	72.12	12.95	0.92	0.07	3.31	2.63	0.95	This work
<i>Porites</i> spp.	MAS01E	0.38	0.13	0.07	54.16	23.62	1.12	0.04	4.13	1.62	1.07	This work
<i>Porites</i> spp.	HUM02A	0.48	0.05	0.12	18.90	31.03	1.24	0.06	6.70	2.86	1.22	This work
<i>Porites</i> spp.	Median	0.31	0.05	0.20	13.20	22.20	0.91	0.06	4.13	1.62	1.10	This work
<i>Porites</i> spp.	Mean	0.40	0.06	0.21	24.76	18.13	0.81	0.06	3.89	1.67	1.10	This work
<i>Gaspera</i>	n/a	0.3	-	2.83	-	1.34	6.69	-	-	9.5	-	Antwertinger (2011)
<i>Porites</i> spp.	n/a	0.39	-	3.01	-	1.5	6.37	-	-	14.2	-	Antwertinger (2011)
<i>Porites</i> spp.	n/a	-	-	-	-	2.6	-	-	-	-	-	Livingston and Thompson (1971)
<i>Favia palauensis</i>	n/a	-	-	-	-	4.4	1.4	-	-	1.1	-	Jiang et al., 2020
<i>Porites</i> spp.	n/a	-	-	-	-	2.7	1.8	-	-	1.1	-	Jiang et al., 2020
<i>Pavona decussata</i>	n/a	-	-	-	-	3	1.2	-	-	1.9	-	Jiang et al., 2020
<i>Pavona clavus</i>	n/a	-	-	-	-	0.3	-	-	-	-	-	Linn et al.,1990
<i>Various species</i>	n/a	-	-	-	-	0.3-7.2	-	-	-	-	-	Livingston and Thompson (1971)
<i>Diploria strigosa</i>	n/a	-	-	-	-	-	1	-	-	-	-	Shen (1986)
<i>Diploria strigosa</i>	n/a	-	-	0.1	-	-	11	-	-	-	-	Shen and Boyle (1988)

6.5 Conclusion

This work has generated seven long geochemical records from *Porites* corals sampled in the Gladstone Harbour region. These records have provided a long historical baseline for seawater chemistry in the Gladstone Harbour. Results also show that *Porites* corals are effective recorders of environmental disturbance by capturing the pulsed or sustained inputs of contaminants associated the industrial development of the Gladstone Harbour. Elevated metal concentrations (e.g., Al, Ti, Mn, V) recorded in corals relative to their background values imply that coastal seawater in the Gladstone Harbour was affected by various natural and anthropogenic impacts, even though the contamination is not as great as some other regions in the world.

By grouping different metals in the corals via PCA, several major natural and anthropogenic impacts on corals can be identified including shipping, dredging, industrial operations and river runoff. Dredging mainly contributes to the disturbance of sediment deposits, the increase in turbidity, and the remobilization of toxic or non-toxic metals/colloids. Shipping has increased the chance of metal release from boats. Industrial operations greatly enhanced the disposal of chemical wastes which contain high concentrations of heavy metals, and river runoff facilitates the delivery of those contaminants from the land to the marine environments.

This work also determined the distribution coefficient (K_d) values of ten trace elements (Al, V, Mn, Fe, Cu, Zn, As, Sn, Pb, U). Knowledge regarding the partition of trace elements between coral and seawater is quite limited, but most K_d values determined in this work are within the range of previously reported estimates, consistently showing that corals preferentially uptake Cu and Pb but discriminate Al and Mn. The poor constraints of seawater data, however, may

limit the accurate determination of K_d . In order to better understand the incorporation mechanisms of trace metals into coral skeletons and obtain more accurate K_d values, a plausible way is to grow corals in sea simulation tanks which better controls the environmental parameters.

Chapter 7: Environmental and biological controls on seasonal to interannual Ba/Ca variations recorded in *Porites* corals from the Great Barrier Reef

Chapter overview:

Since European settlement, increased sediment loads from human activities have been a major threat to the Great Barrier Reef (GBR) ecosystem. Ba/Ca ratio in coral skeletons has been documented to track terrestrial runoff in coastal waters. Due to the lack of continuous records for river discharge and seawater quality, use of coral skeletons to reconstruct long-term spatial and temporal coastal changes becomes critical. In this study, century-long *Porites* corals were collected from the Southern GBR and Central GBR to reconstruct past environmental changes. Variations of coral Ba/Ca were compared to coral luminescence, local river discharge records and environmental data. Results showed that spatially variable geochemical signals highlighted the influence of complex ocean dynamics. The major fluctuations of Ba/Ca were well correlated to historic discharge records or other environmental perturbations. Besides, distinct Ba/Ca seasonal cycles, with different peak timings, were preserved in corals from Hummock Island, South Molle Island and Whitsunday Island which may not be simply associated with river discharge. Instead, temperature-dependant incorporation of Ba and biogeochemical cycling of Ba in ambient seawater may play a role. The correlation between coral Ba/Ca ratios and river discharge records established in this study can be used to reconstruct environmental changes in the pre-instrumental era but should be approached with careful site selections. Supplemental tables and figures associated with this chapter have been put at the end of this chapter for easy reading.

7.1 Introduction

Over the past decades, the intensive anthropogenic activities (e.g., mining and agriculture) along the Great Barrier Reef (GBR) has significantly modified the coastal river catchments and increased the input of land-based runoff of sediments, nutrients and other contaminants into oceans (Bartley et al., 2018; Kroon et al., 2016; McCulloch et al., 2003; Neil et al., 2002). It is feared that the health of the GBR and the coastal ecosystems will be severely degraded due to changes of coastal water quality (Ainsworth et al., 2016; De'ath et al., 2012; Fabricius et al., 2005; Wooldridge et al., 2006; Wooldridge, 2009). Due to the lack of long-term high-precision instrumental records, it is essential to develop appropriate proxies to understand and reconstruct past climatic and environmental changes.

Trace metals in the skeletons of massive corals (e.g., *Porites* spp.) originate from the chemical compositions of surface seawaters, thus faithfully record climatic and environmental conditions otherwise difficult to be obtained by instruments (Amiel et al., 1973; Fallon et al., 1999; Lewis et al., 2007; Sinclair et al., 1998). Coral barium/calcium (Ba/Ca), manganese/calcium (Mn/Ca) and yttrium/calcium (Y/Ca) ratios have been widely used as geochemical proxies for terrestrial runoff, which is a general term that includes both river discharge and/or sediment load (Carilli et al., 2009; Lewis et al., 2018; Liu et al., 2019; Shen et al., 1992; Walther et al., 2013). Although a number of publications have shown Ba/Ca variability in coral skeletons, they are still not fully understood as Ba incorporation is influenced by both internal biomineralization and external environmental processes (e.g., terrestrial runoff) (Gonneea et al., 2017). These complex processes need to be decoupled to better understand Ba/Ca signatures.

Considerable work has been done in the Northern GBR to link coral geochemical records to terrestrial runoff (Alibert et al., 2003; Fallon et al., 2003b; Lewis et al., 2018; Lough, 2007; McCulloch et al., 2003; Sinclair, 2005b; Sinclair and McCulloch, 2004; Wyndham et al., 2003) while the Central and Southern GBR only have limited coral geochemical data (Lewis et al., 2012; Saha et al., 2018a; Saha et al., 2018b). This chapter has examined 10 corals sampled in the Central and Southern GBR which cover a wide latitudinal range and coastal conditions. This provides an opportunity to comprehensively assess the impacts of multiple environmental drivers on coral Ba/Ca signatures in these specific sites. The behaviour of Ba/Ca ratios was critically evaluated and compared to previous studies to unravel the corresponding environmental drivers over different time scales. Results from this study provide additional insights into coral Ba/Ca signatures under diverse water conditions and can be used to reconstruct past environmental conditions when instrumental records are not available.

7.2 Study sites and methods

7.2.1 Study area and sample collection

Porites corals were collected from Hummocky Island (HUM02A&03A) to the north of the Gladstone region and six additional sites (Hook Reef (HOO81A), Stonehaven Bay (SNH84A), Whitsunday Island (WHI84A), South Molle Island (SMI81A), Shaw Island (SHW82C), Scawfell Island (SCF81B)) in the Whitsunday Islands in August 2017 and February 2018 (Figure 7.1, Table 7.1). Additionally, two long cores (Humpty Island (HMP01B), South Molle Island (SMI01C)) were obtained from the Australian Institute of Marine Science (AIMS) Coral Core Archive (Figure 7.1). These sites were assumed to receive varying degrees of freshwater impacts from nearby river systems (Fitzroy River, Proserpine River, O'Connell River and Pioneer River). The Fitzroy River catchment starts from Carnarvon Range and drains into the Keppel Bay near Rockhampton. Proserpine and O'Connell rivers are the primary rivers

influencing Whitsunday reefs (Lewis et al., 2012). Occasionally, this region can also be influenced by the Pioneer River (to the south) and Burdekin River (to the north) (Lewis et al., 2012).

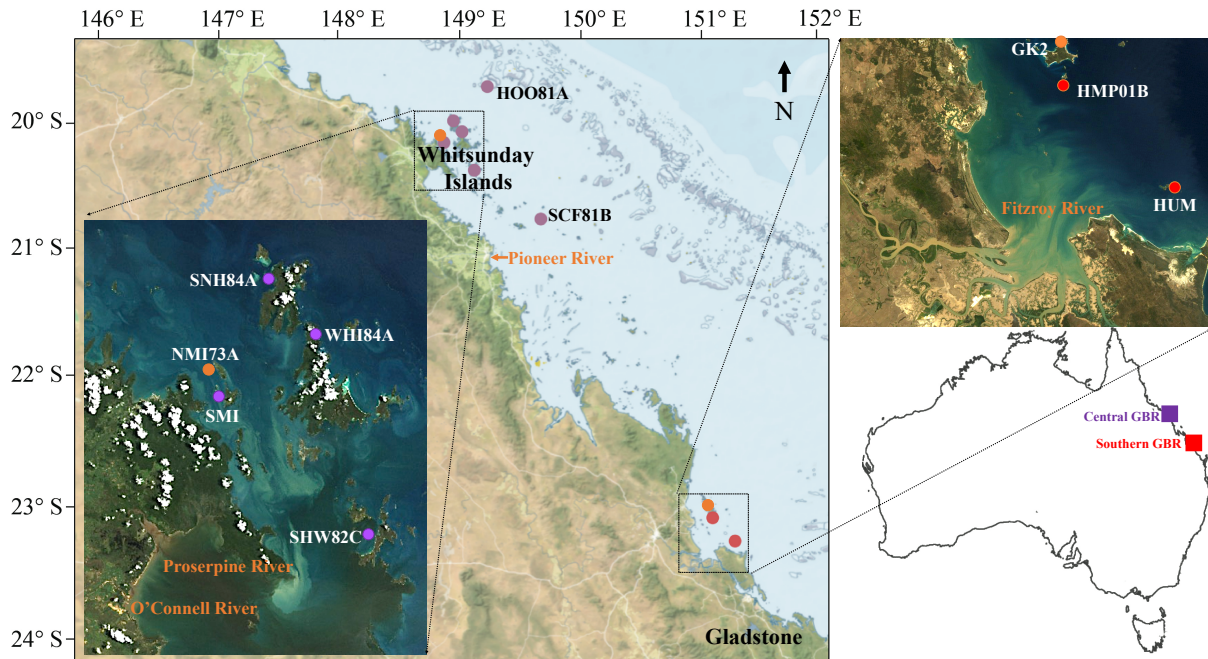


Figure 7.1 Coral sampling sites in the Central GBR (purple rectangle and purple circles) and in the Southern GBR (red rectangle and red circles) as well as satellite images for major rivers of influence. Cores (SMI01C and SMI81A) from South Molle Island were collected from the same colony in 1984 and for this study in 2018. HOO81A is short for Hook Island; SNH84A is short for Stonehaven Bay; WHI84A is short for Whitsunday Island; SMI is short for South Molle Island; SHW82C is short for Shaw Island; SCF81B is short for Scawfell Island; HMP01B is short for Humpy Island; HUM is short for Hummocky Island. North Molle Island coral (NMI73A; Lewis et al., 2012) and Great Keppel Island coral (GK2; Saha et al., 2018a) are also plotted for regional comparison. Landsat 5 image in the Southern GBR was taken on 11/09/2011 showing the bifurcation of Fitzroy flood plume.

Table 7.1 Geographic locations of *Porites* coral cores examined in this work

Site	Core ID	Latitude (°)	Longitude (°)	Record period
Hummocky Island	HUM02A	-23.40341	151.14711	1902-2017
Hummocky Island	HUM03A	-23.40348	151.14716	1898-2017
Humpy Island	HMP01B	-23.219	150.968	1666-1999
Scawfell Island	SCF81B	-20.86196	149.6024	1956-2017
Shaw Island	SHW82C	-20.4796	149.0691	1947-2017
Whitsunday Island	WHI84A	-20.17447	148.9753	1979-2017
Stonehaven Bay	SNH84A	-20.0894	148.9076	1978-2017
Hook Island	HOO81A	-19.81582	149.1766	1978-2017
South Molle Island	SMI01C	-20.25878	148.8283	1860-1986
South Molle Island	SMI81A	-20.25878	148.8283	1975-2017

7.2.2 Geochemical analysis

Laser ablation–inductively coupled plasma–mass spectrometry (LA–ICP–MS) was utilized in order to measure the abundance of ^7Li , ^{11}B , ^{24}Mg , ^{43}Ca , ^{55}Mn , ^{86}Sr , ^{89}Y , ^{137}Ba and ^{238}U in coral skeletons. Elemental concentrations were reported as ratios normalized to ^{43}Ca (element/Ca in mol/mol). Raw counts were background subtracted, drift corrected and calibrated from standards using Python code (*LAtools*) (Branson et al., 2019). The machine set up, data process and analytical uncertainty are described in chapter 2.

7.2.3 Environmental data

Records of daily and monthly river discharge (megalitres, ML) were obtained from the Queensland Department of Natural Resources, Mines and Energy (DNRME) Water Monitoring Portal (<https://water-monitoring.information.qld.gov.au>) for the Proserpine, O’Connell, Pioneer and Fitzroy Rivers. Data were totalled from October - September to represent a water year (Cantin et al., 2018). Rainfall data were obtained from the Australian Bureau of Meteorology (www.bom.gov.au/climate/data/) for Pacific Height, site # 033077, 1966-2019; Letherbrook, site # 033041, 1923-2019 and Proserpine Airport, site # 033247, 1978-2019 (Figure 7.2).

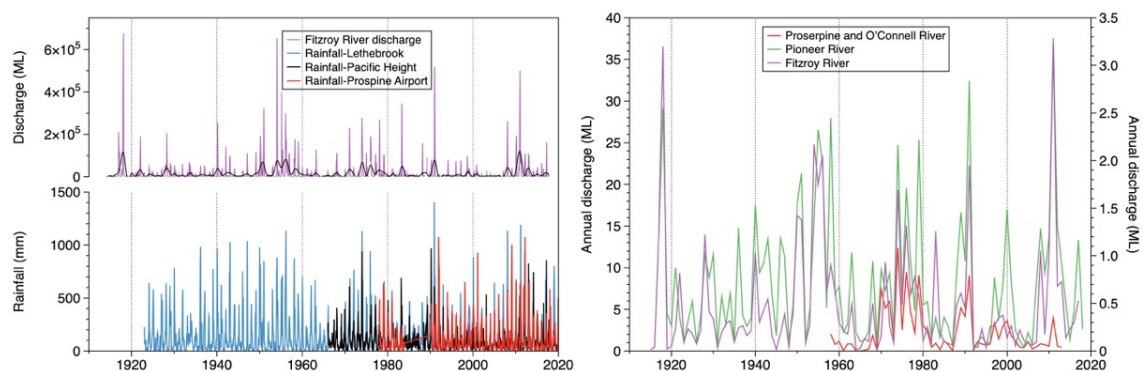


Figure 7.2 (a) Comparison between Fitzroy River discharge and rainfall in the study region (Letherbrook, Pacific Height and Proserpine Airport) (b) Comparison of annual River discharge from Fitzroy River, Pioneer River and the combination of Proserpine and O’Connell River

7.2.4 Age model

Coral elemental ratios were translated from length to time to reveal temporal variations. Similar to chapters 4-6, the robust chronologies were made from luminescent lines, annual high-low density bands and temperature-dependent proxies (e.g., U/Ca) (Figure S7.1). Coral luminescent lines are excellent markers for historic large flood events in the GBR region (e.g., 1974, 1991, 2011) (Lough et al., 2015).

7.3 Results

Average annual skeletal extension and luminescence characteristics are listed in Table 7.2. Calcification rates for the seven Central GRB (Whitsunday) corals ($1.65\text{-}2.18\text{ g.cm}^{-2}\text{.yr}^{-1}$) were higher than those for the Southern GBR corals ($1.61\text{-}1.66\text{ g.cm}^{-2}\text{.yr}^{-1}$). Tissue layer thickness from the two locations was relatively comparable (Table 7.2). The unusually high tissue layer thickness in SMI01C may be due to difference in collecting month compared to other sites as tissue layer thickness was found to be related to the monthly lunar cycle (Rotmann and Thomas, 2012). Annual luminescence ranges were moderate-strongly correlated to river discharge (October-September) with the exception of Hook Island (Table 7.3) (Cantin et al., 2018, 2019a, 2019b, Lough et al., 2020).

Geochemical records for the ten coral cores (Table 7.1), ranged from 37 years in WHI84A to >300 years in HMP01B including major flood years (e.g., 1918, 1950-1951, 1954-1956, 1971, 1974, 1991 and 2011). Geochemical profiles of Ba/Ca, Mn/Ca and Y/Ca are presented in Figures 7.3-7.4 and Figures S7.2-S7.3. All Ba/Ca profiles displayed large peaks but with different timing throughout the year. Ba/Ca values were affected by the upper tissue layers in most of the analyzed cores where ratios were elevated ~ 100 -fold in the core-top (Figures 7.3-7.4, values out of axis range). This effect cannot be eliminated by rigorous chemical cleaning and has been documented in a few other studies (Lewis et al., 2018; Sinclair, 2005b). For a

common period of 35 years (1980-2015), geochemical records for Ba/Ca, Mn/Ca and Y/Ca displayed spatial differences (Figure 7.5). The mid-shelf Hook reef (HOO81A) recorded the lowest Mn/Ca and Y/Ca and the third lowest Ba/Ca (Figure 7.5) potentially due to its mid-shelf location distant from inshore inputs (Figure 7.1). SHW82C recorded the second lowest Ba/Ca values (Figure 7.5) even with its proximity to river mouth (Figure 7.1). Overall, monthly Ba/Ca, Mn/Ca and Y/Ca values for all sites were consistent with the published values in the literature (Lewis et al., 2012; Sinclair, 2005; Sinclair and McCulloch, 2004; Alibert et al., 2003; Jupiter et al., 2008; McCulloch et al., 2003).

Table 7.2 Average annual skeletal growth and luminescence characteristics

Location	Core ID	Tissue layer thickness (mm)	Extension (cm.yr ⁻¹)	Density (g.cm ⁻³)	Calcification (g.cm ⁻² .yr ⁻¹)	Luminescence range
Hummocky Island	HUM02A ¹	4.42	15.57±3.64	1.04±0.05	1.61±0.38	0.17±0.14
Hummocky Island	HUM03A ¹	5.47	14.30±2.73	1.16±0.04	1.66±0.32	0.17±0.15
Humpy Island	HMP01B ²	4.50	0.99 ± 0.25	1.27 ± 0.07	1.26 ± 0.31	0.27 ± 0.16
Hook Reef	HOO81A ³	4.69	1.31±0.41	1.43±0.05	1.87±0.58	0.08±0.05
Stonehaven Bay	SNH84A ³	5.63	1.24±0.38	1.55±0.26	1.87±0.51	0.19±0.08
Whitsunday Island	WHI84A ³	6.16	1.22±0.36	1.41±0.07	1.73±0.53	0.17±0.09
South Molle Island	SMI81A ³	7.79	1.26±0.24	1.31±0.06	1.65±0.33	0.16±0.08
South Molle Island	SMI01C ³	10.35	1.38±0.35	1.29±0.05	1.78±0.46	0.23±0.14
Shaw Island	SHW82C ³	4.77	1.19±0.46	1.59±0.11	1.89±0.74	0.15±0.07
Scawfell Island	SCF81B ³	4.13	1.68±0.33	1.30±0.14	2.18±0.50	0.11±0.04

¹ For the base period from 1987-2016 (± 1sd) (Cantin et al., 2018)

² For the base period, 1961-1990 (growth) and 1947-1996 (luminescence), ± 1 sd (Cantin et al., 2019a).

³ For the base period, 1959-1984 (growth) and 1960-1983 (luminescence), ± 1 sd (Cantin et al., 2019a).

Table 7.3 Correlations (r values, $p < 0.05$) between (a) coral annual luminescence range and annual river discharge (October-September), and (b) annual average coral Ba/Ca ratio and annual river discharge (October-September).

Coral ID	(a) Luminescence vs river discharge		(b) Ba/Ca vs river discharge	
	Fitzroy River	Pioneer River	Fitzroy River	Pioneer River
HUM02A ¹	0.73	-	0.17	-
HUM03A ¹	0.63	-	0.35	-
HMP01B ²	0.5	-	0.51	-
WHI84A ³	0.38	0.37	-0.05	-0.05
SHW82C ³	0.44	0.5	0.12	0.19
SNH84A ³	0.21	0.22	0.08	0.08
SCF81B ³	0.56	0.41	0.12	0.19
SMI81A ⁴	0.72	0.83	0.72 ⁵	0.69 ⁵
SMI01C ⁴	0.68	0.64		
HOO81A ⁴	-0.08	0.18	-0.11	-0.04

Note: The respective correlation periods are: ¹HUM02&03A: 1915-2016; ²Humpy coral (HMP01B): 1915-1996; ³WHI84A, SHW82C, SNH84A, SCF81B: 1949-2016; ⁴SMI81A, SMI01C, HOO81A: 1960-1983 (Cantin et al., 2019a, 2019b); ⁵SMI01C and SMI81A were combined to calculate the correlation between Ba/Ca and river discharge.

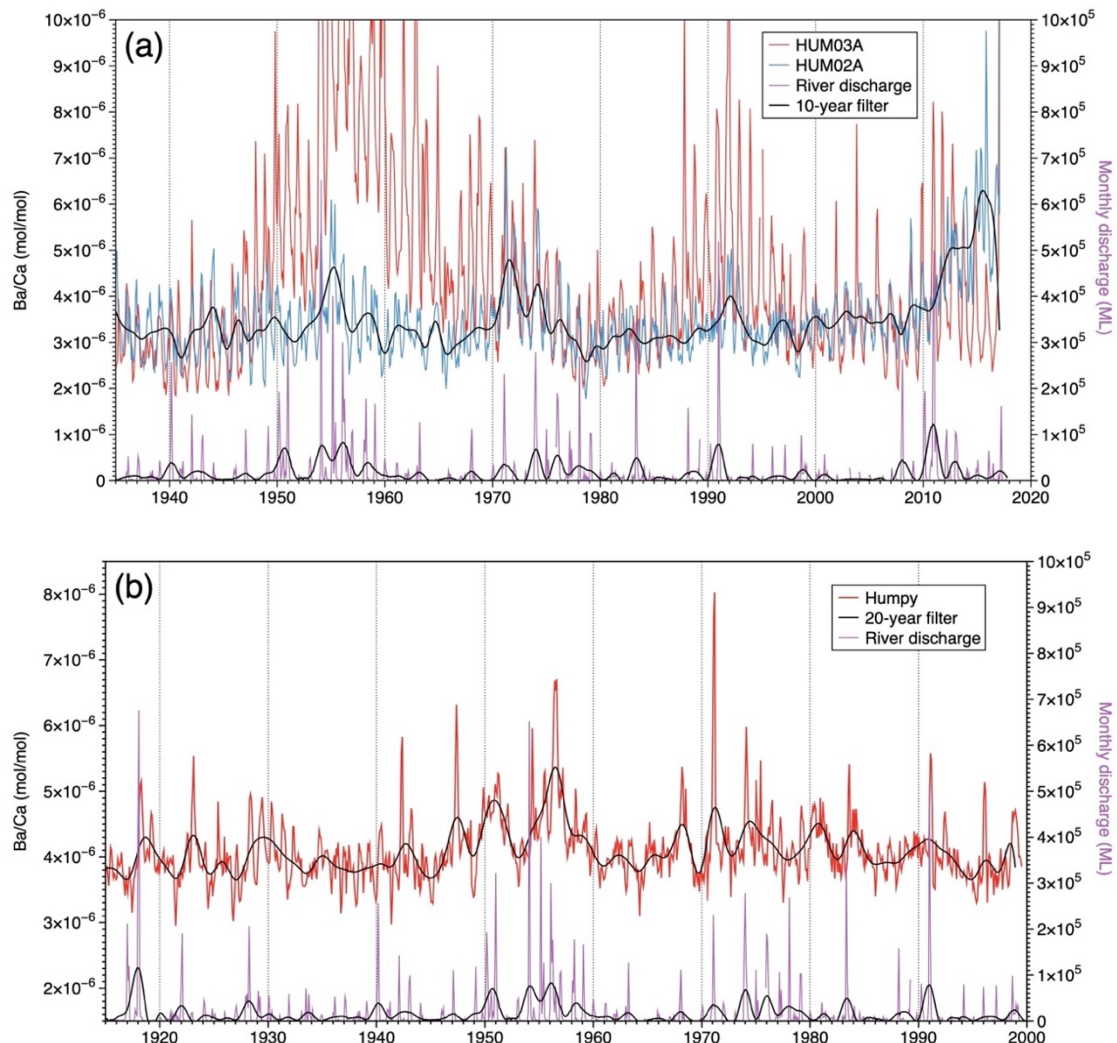


Figure 7.3 Coral Ba/Ca records from (a) Hummocky Island (HUM02A&03A) and (b) Humpy Island (HMP01B) to the north of Gladstone (Southern GBR)

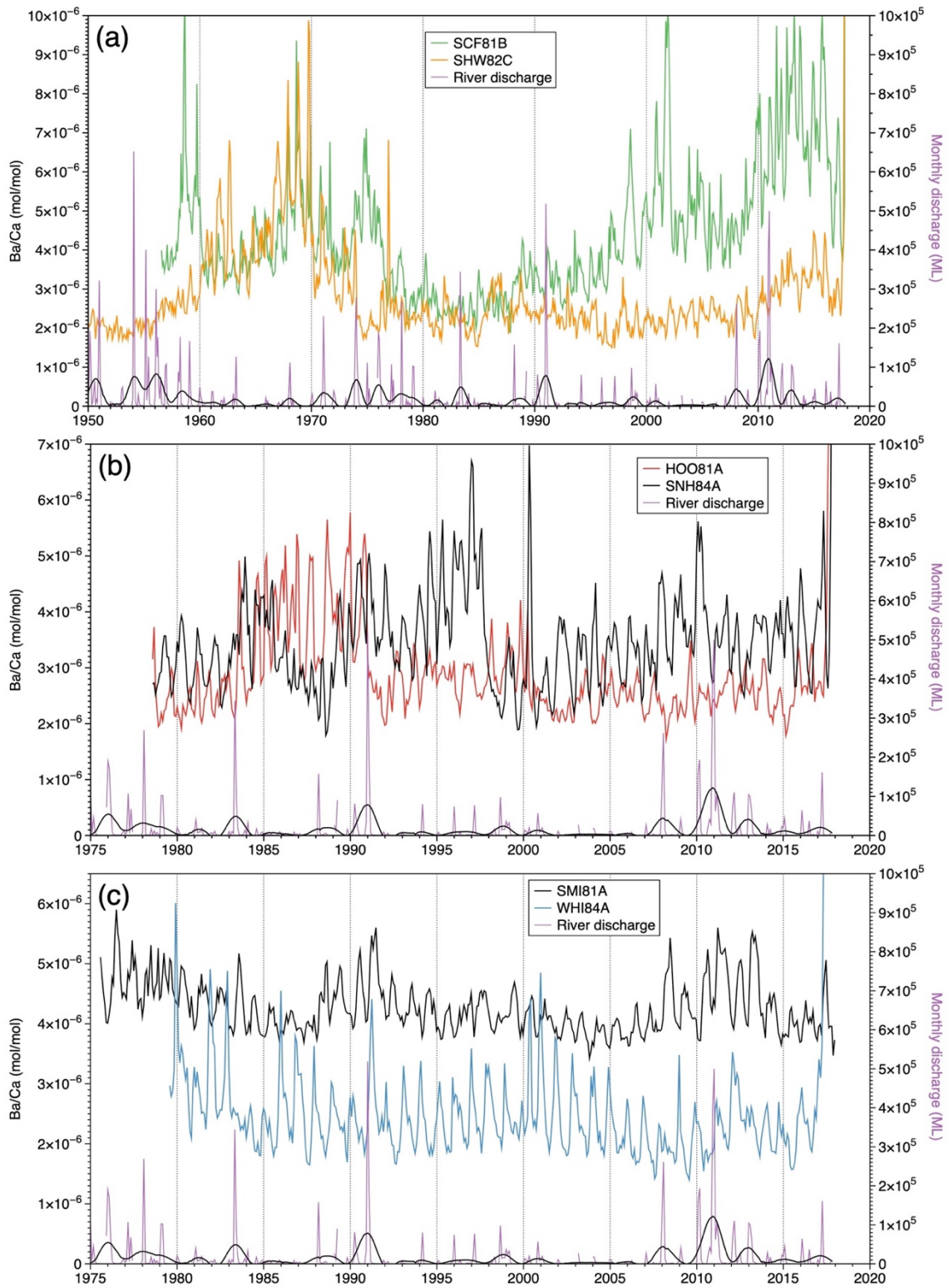


Figure 7.4 Coral Ba/Ca records from the Whitsunday Islands (Central GBR), showing evident seasonal Ba/Ca cycles but with different Ba/Ca peak timing.

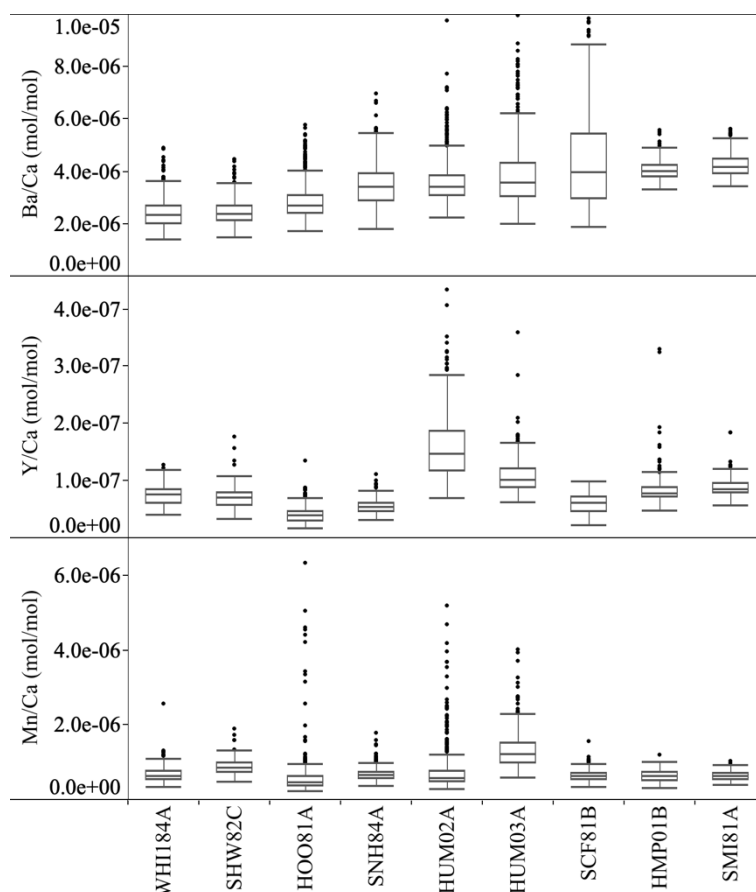


Figure 7.5 Comparison of Ba/Ca, Mn/Ca and Y/Ca elemental ratios in coral skeletons from the Central GBR (WHI184A, SHW82C, HOO81A, SNH84A, SCF81B, SMI81A) and Southern GBR (HUM02A, HUM03A, HMP01B). For direct comparisons only data from 1980-2015 were plotted. Site order is based on Ba/Ca gradients from low to high. From the top to bottom, this box and whisker plot presents the five-number summary of upper whisker, upper hinge, medium, lower hinge and lower whisker. Note: Whiskers extend to data within 1.5 times the interquartile range (IQR).

7.4 Discussion

7.4.1 Ba incorporation into coral skeletons

In order to understand the coral Ba/Ca signals, Ba incorporation mechanisms and the associated influencing factors need to be elucidated. Although the ionic radius of Ba^{2+} is slightly larger than that of Ca^{2+} (Shannon, 1976), Ba^{2+} can readily substitute for Ca^{2+} in the coralline aragonite, similar to Sr^{2+} due to their similar ionic radii (Lea et al., 1989; Zhong and Mucci, 1989). Ba/Ca incorporation into coral skeletons has been shown to be proportional to Ba/Ca in the seawater (Alibert et al., 2003; Gonneea et al., 2017). External sources of seawater Ba/Ca come from (1) Ba enriched estuarine freshwater input (Lewis et al., 2018; Moyer et al., 2012); (2) Ba enriched

suspended sediment flux (Alibert et al., 2003; McCulloch et al., 2003; Sinclair et al., 1998); (3) ocean upwelling (Fallon et al., 1999; Lea et al., 1989; Montaggioni et al., 2006; Walther et al., 2013); and (4) by-products of biological activities. Coral Ba/Ca ratio was also found to be inversely correlated to temperature in experimentally precipitated aragonite, aquaria reared corals and field samples (Dietzel et al., 2004; Fallon et al., 2003b; Gaetani and Cohen, 2006; Gonneea et al., 2017; Grove et al., 2012). Temperature related Ba/Ca oscillations were suggested to be caused by changes in distribution coefficient and precipitation efficiency (Gaetani and Cohen, 2006; Gonneea et al., 2017).

7.4.2 Spatially different timings of Ba/Ca peak and regional reproducibility

It is essential to identify the timing of Ba/Ca peaks in order to identify the major Ba sources for each coral site. The wet season in tropical Queensland normally occurs from November to April, bringing in river floods and monsoonal and cyclonic rainfall. Ba/Ca peaks associated with terrestrial runoff therefore coincide with the timing of summer months (warm SST) and prominent luminescent lines. Coincidentally, the summer season also has the highest upwelling intensity in the mid-shelf of GBR (Berkelmans et al., 2010; Wolanski and Pickard, 1983). Therefore, high Ba/Ca signals recorded in offshore corals (e.g., Myrmidon) usually reflect the upwelled dissolved Ba/Ca during summertime (Walther et al., 2013).

For simplicity, Ba/Ca annual peaks which correlate with coral luminescence, river discharge and precipitation (in phase with SST maximum or U/Ca minimum) are called ‘normal’ Ba/Ca peaks in the following discussion. These ‘normal’ Ba/Ca peaks follow a normal distribution which is characterized by a rapid rise starting from early spring, peaking in summer, and followed by a decline over several months (Figures 7.3-7.4, 7.6). The tail-off period sometimes can last up to 6 months (Sinclair 2005). On the other hand, Ba/Ca peaks sometimes are not

correlated with the timing of terrestrial runoff or upwelling events (out of phase with SST maximum or U/Ca minimum). These ‘anomalous’ Ba peaks may be explained by a few environmental factors. Firstly, seasonal SST oscillations lead to the changes in Ba incorporation dynamics with Ba/Ca peaks (troughs) occurring in winter (summer). Over SST range of ~20-29 °C in the GBR, an increase of 10°C in SST would lead to ~1.2 $\mu\text{mol/mol}$ Ba/Ca decrease for *Favia fragum* (Gonneea et al., 2017) and ~2 $\mu\text{mol/mol}$ Ba/Ca decrease for *Diploria* (Gaetani and Cohen, 2006). However, temperature driven Ba/Ca changes are normally insignificant compared to other driven factors which result in much higher annual Ba/Ca difference (~2-10 fold higher than baseline) (Gonneea et al., 2017). Secondly, ‘anomalous’ Ba peaks can result from short-lived biological events such as phytoplankton blooms, *Trichodesmium* blooms and/or endogenous process such as coral mass spawning (Saha et al., 2018b; Sinclair, 2005b). Phytoplankton start to bloom in spring as a result of rising SST, solar exposure and nutrient supply in the GBR. These phytoplankton take up dissolved Ba and/or adsorb dissolved Ba onto cell surfaces, leading to the initial stage of Ba depletion. Decaying phytoplankton during post-bloom periods favor the formation of particulate barite (BaSO_4), resulting in a further removal of dissolved Ba (Saha et al., 2018b; Sinclair, 2005b).

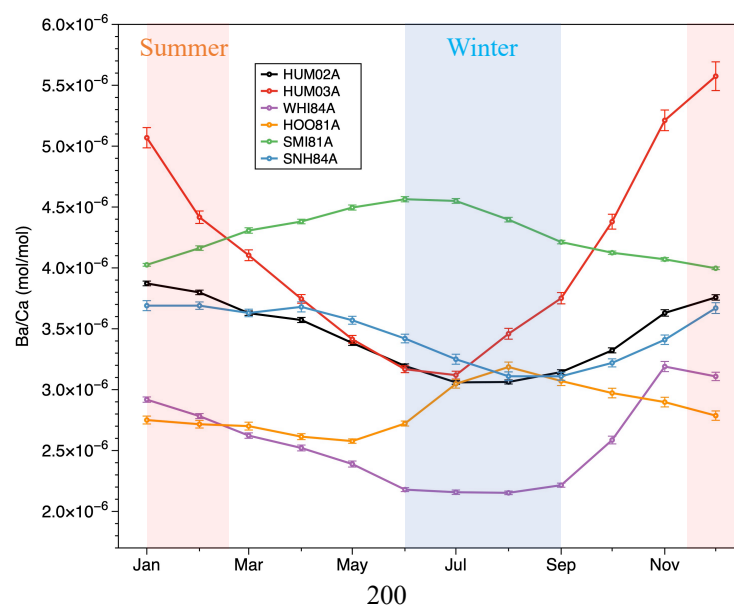


Figure 7.6 Monthly averages of coral Ba/Ca showing two common patterns (1) Ba/Ca peak in phase with the timing of SST maxima or river discharge maxima which normally occurred in summer months (pink region) (2) Ba/Ca peak out of phase with the timing of SST maxima or river discharge such as winter months (blue region). Note: Only corals with clear Ba annual periodicity were plotted (Figures 7.3-7.4).

‘Normal’ Ba/Ca peaks

Two Hummocky corals (HUM02A, HUM03A) near the Fitzroy river mouth recorded ‘normal’ annual Ba signals, which peaked in summer months (Figure 7.6). The good correlation ($r > 0.7$, Table 7.3) between Fitzroy River discharge and annual luminescence ranges suggests that Hummocky Island was influenced by pulsed freshwater inputs. The Ba/Ca baselines for HUM02A and HUM03A were identical and their respective timings of summer Ba peaks could match (Figure 7.3). However, the amplitudes of seasonal variations were significantly different for HUM02A and HUM03A even though they were within a 30-meter swim of each other. In contrast to the Hummocky corals, the nearby Humpy coral (HMP01B) did not record the regular seasonal time-scale Ba/Ca signals even though HMP01B is also in the direct path of Fitzroy river plume or its bifurcated plumes (Figure 7.1). Discrepancies between Humpy Island and Hummocky Island suggest the significant bifurcation of Fitzroy flood plume as shown in satellite images (Figure 7.1, insert). Therefore, flood plumes may have been diluted only reaching Humpy Island occasionally. However, a comparison between HMP01B and a nearby Great Keppel Island coral GK2 (Saha et al., 2018a) demonstrates high regional reproducibility in Ba/Ca variability (Figure 7.7). The Ba/Ca baselines were similar and both sites displayed evident summer Ba/Ca peaks in major flood years (e.g., 1968, 1971, 1974-1979, 1983, 1991).

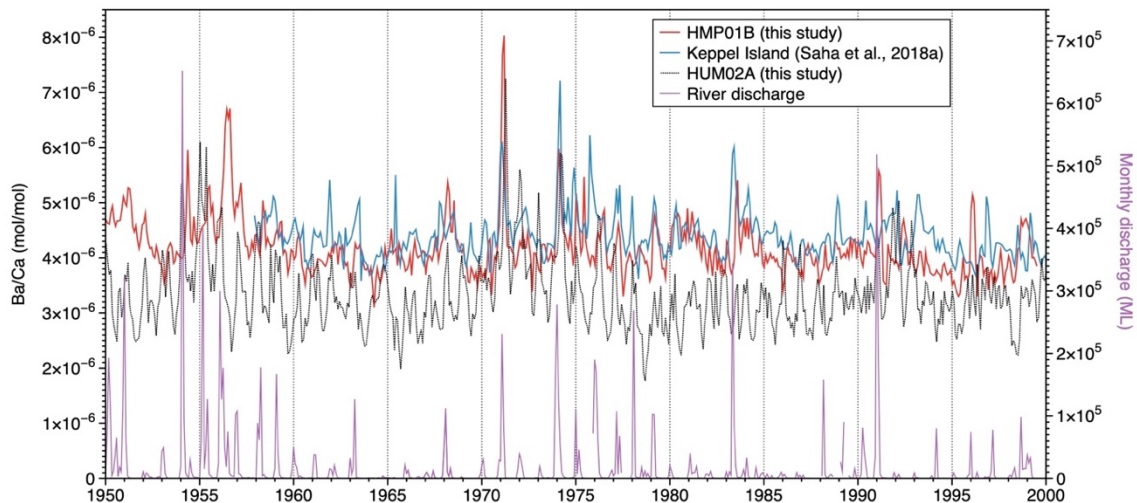


Figure 7.7 Comparison of coral Ba/Ca profiles from Hummocky Island, Humpy Island and Keppel Island

Annual Ba/Ca peaks were also evident in the Whitsunday corals (Figure 7.4). WHI84A, SNH84A, and SHW82C all displayed ‘normal’ summer Ba/Ca peaks (Figure 7.6). The hydrodynamics of the inshore Whitsunday Islands are complicated, with major currents and river plumes deflected around the islands (Lewis et al., 2012). Shaw Island (SHW82C) is geographically close to river mouth (Figure 7.1) and showed marked luminescent lines which are characteristic of flood plumes (Table 7.3). In contrast, SNH84A and WHI84A are located at the outer edge of Whitsunday Islands (Figure 7.1). These two sites are too distant to be influenced by flood plumes from the Proserpine and O’Connell Rivers. Their weaker luminescent lines also prove that freshwater rarely reached those sites. One possibility is that a much-diluted flood plume from the Burdekin river (to the north) or Pioneer river (to the south) may reach SNH84A and WHI84A but the direct influence from Fitzroy river seems unlikely as discussed for the Humpy Island (HMP01B). Annual Ba/Ca concentration in WHI84A is poorly correlated with luminescent range or annual discharge (Table 7.3), therefore the seasonally regular ‘normal’ Ba/Ca peaks should be caused by wind-induced resuspension or other unknown seasonally reoccurring events.

“Anomalous” Ba/Ca peaks

SMI01C, SMI81A and HOO8A displayed ‘anomalous’ Ba/Ca peaks with slightly different peak timings (Figure 7.6). An outstanding feature for these ‘anomalous Ba/Ca peaks’ is their consistent seasonal regularity. Given its mid-shelf location distant from inshore flood events, Hook Island (HOO81A) showed no evidence of intense luminescent lines so the direct impact from freshwater flood plumes can be ruled out. HOO81A did not record the seasonal upwelling signals either which are characterised by high Ba in summer. Instead, ‘anomalous’ annual Ba/Ca peaks were persistent across all years. The annual Ba peaks of HOO81A were in perfect timing with SST minima (August) (Figure 7.6). Seasonal Ba differences (maximum-minimum) varied from $\sim 1\text{--}2\ \mu\text{mol/mol}$ from 1992 to 2018 (Figure 7.4), within the range of change due to temperature dependence (Gaetani and Cohen 2006; Gonneea et al., 2017). However, higher annual variabilities ($\sim 3\ \mu\text{mol/mol}$) were noticed from 1983 to 1991 (Figure 7.4). A single temperature control should be consistent and cannot account for inter-annual Ba variabilities. Therefore, local-scale biological productivity may play a role. Ba/Ca ratios in HOO81A started to decline from early-spring, concurrent with the timing of phytoplankton bloom in the GBR region (Saha et al., 2018b; Sinclair, 2005b).

South Molle Island corals (SMI01C_81A hereafter) are located in a semi-enclosed coastal embayment at the exit of Whitsunday passage (Figure 7.1). Annual Ba/Ca peaks from the two SMI cores occurred regularly in June/early winter and annual Ba/Ca differences were within a consistently narrow range ($\sim 1\text{--}1.5\ \mu\text{mol/mol}$) (Figures 7.4, 7.6). These ‘anomalous’ Ba/Ca signals (winter maxima and summer minima) in SMI01C_81A were initially thought to be either controlled by temperature or due to biological scavenging of Ba during the phytoplankton blooming seasons, similar to Hook Island, Rat Island and Cow and Calf Island (Saha et al., 2018b; Sinclair, 2005b). The similar timing of winter Ba/Ca peaks was also

documented in a coral collected from North Molle Island (Figure 7.8) (Lewis et al., 2012), suggesting that these ‘anomalous’ Ba signals were reproducible regionally and they were not caused by the artefacts of age model. However, in comparison to other corals, SMI01C_81A revealed the strongest correlation with river discharge in terms of luminescent range and annual Ba/Ca concentration (Table 7.3). Therefore, another possibility is that the South Molle Island has been regularly recharged with dissolved or particulate Ba via river runoff, but the timing of coral Ba/Ca peaks can be offset by a few months. The significantly thicker tissue layers in SMI cores may have resulted in a ‘smoothing effect’ (Taylor et al., 1995). The above contradictory explanations of the regionally reproducible winter Ba/Ca peaks suggest this region (the transect from North Molle-South Molle-Cow and Calf Island) needs further investigation to be fully understood.

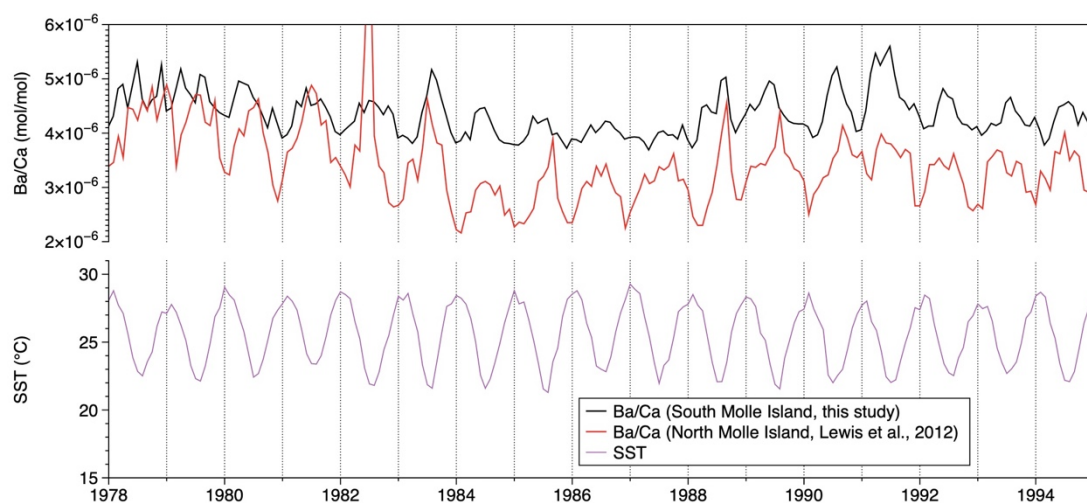


Figure 7.8 Regional comparison of seasonal Ba/Ca cycles between SMI81A (this work) and North Molle Island (Lewis et al., 2012). SST is used as marker for the timing, with peaks (troughs) representing wet period (dry period) in summer (winter) months. Normal Ba/Ca peaks occurred during wet period in summer months.

7.4.3 Long term Ba/Ca signals

Interannual to decadal oscillations were evident in all sites throughout the years analyzed (Figures 7.3-7.4), which were related to rainfall and river discharge (Figure 7.2). For example,

SHW82C, SMI01C, HUM03A and HMP01B clearly recorded a dramatic Ba/Ca increase in the 1950s, 1970s, 1991, late 2000s to early 2010s (Figures 7.3-7.4), suggesting that a greater amount of terrigenous sediment was transported in these ‘drought-breaking’ floods (McCulloch et al., 2003; Saha et al., 2018a). The preceding years of drought resulted in the loss of plant cover, thus making soils more susceptible to erosion in these wet years when rainfall and river discharge was most aggressive (McCulloch et al., 2003; McCulloch et al., 2002; Saha et al., 2018a). Over the centennial scale, the time series of Ba/Ca at HMP01B had generally stable and low baseline values from the late 17th century, followed by an initial increase in the late 19th century (Figure 7.9a) which coincided with European settlement (~1870). Similarly, the baseline values of Ba/Ca at SMI01C also revealed a long-term increase from 1870 and returned back to the pre-1870 baseline value in 1900 (Figure 7.9b). These temporal variations are consistent with the sediment input associated with the initial land clearing activities after European settlement in the late 19th century, which has also been noted in other studies (e.g., Cid Harbour Island, Round Top Island and Havannah Island) (Lewis et al., 2012; McCulloch et al., 2003).

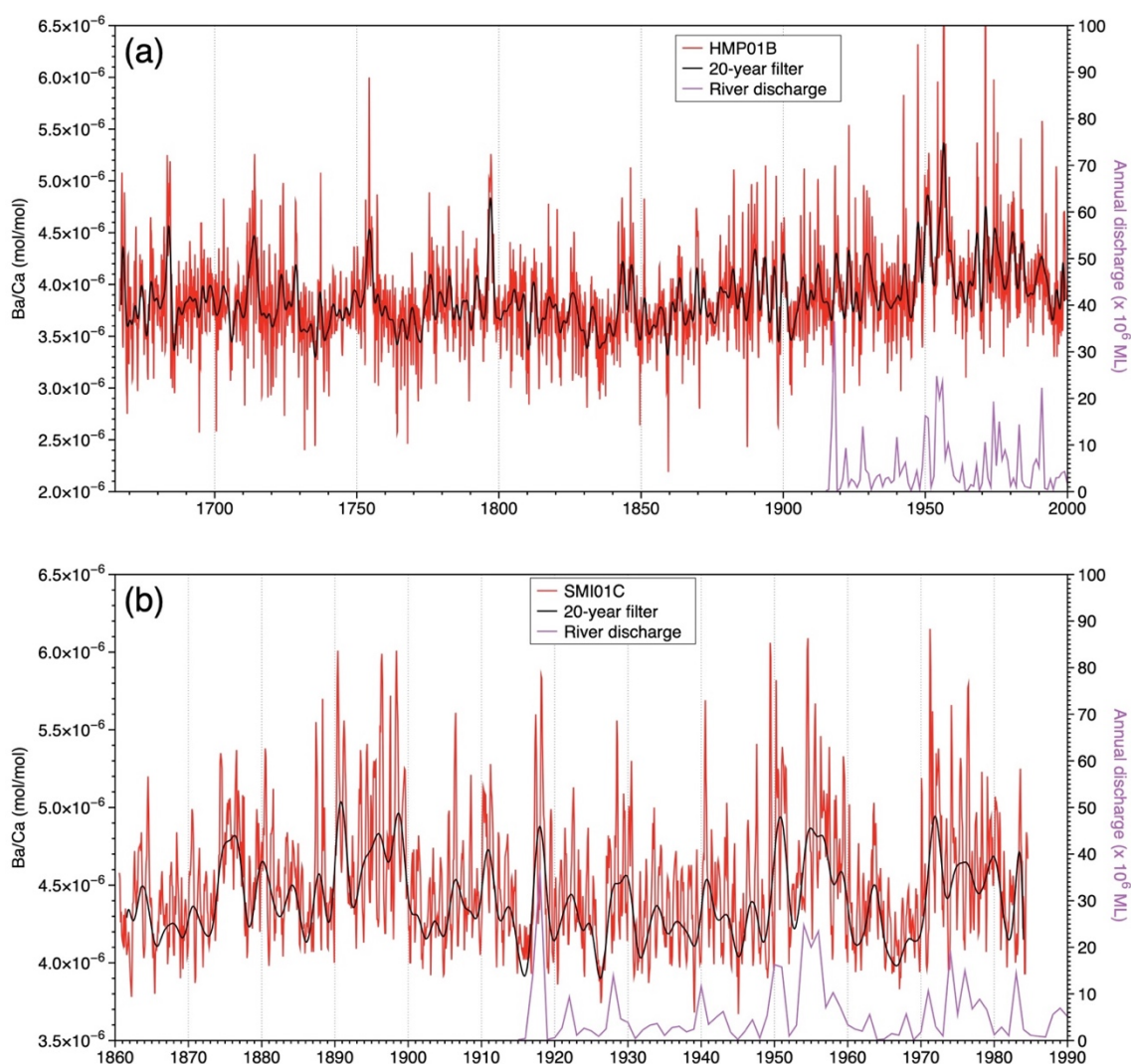


Figure 7.9 Long-term coral Ba/Ca records from the Humpy Island (HMP01B, 1665-2000) and South Molle Island (SMI01C, 1860-1985)

7.4.4 Translating Ba signals

The relationship between coral Ba/Ca ratios and river discharge from SMI01C_81A, HMP01B, HUM02A and HUM03A were further examined because the annual luminescence ranges from these sites were correlated with annual river discharge (Table 7.3). Results showed that SMI01C_81A and HMP01B were moderately correlated with river discharge (R^2 : 0.3-0.5, $p < 0.0001$) while HUM02A and HUM03A were weakly correlated (Figure 7.10). This suggests that Ba/Ca ratios in some corals cannot be used to quantify river discharge even though these corals receive the direct impact of flood plume. Terrestrial Ba/Ca sources can derive from the

dissolved Ba in freshwater or Ba enriched suspended sediments which release Ba upon seawater mixing (Lewis et al., 2018; Saha et al., 2016). Therefore, the translation of coral Ba/Ca signals requires the separation of impacts from river water discharge and suspended sediment load. Due to the absence of water chemistry data from the Whitsunday Islands and limited water data in the Fitzroy river catchment, the proportion of Ba desorption cannot be fully analyzed. Lewis et al. (2018) sampled the Fitzroy River estuarine mixing zones over two flood years in 2007/2008 and 2008/2009. They found that 40% of dissolved Ba in the flood plumes came from desorption therefore coral Ba/Ca may record changes in sediment loads in the Fitzroy River estuarine mixing zones. Besides, drought-breaking floods normally deliver more suspended sediments than other water years due to higher availability of terrestrial sediments. In future work, water monitoring in the estuarine mixing zone especially during flood years is encouraged which can provide additional insights into the coral Ba/Ca signals.

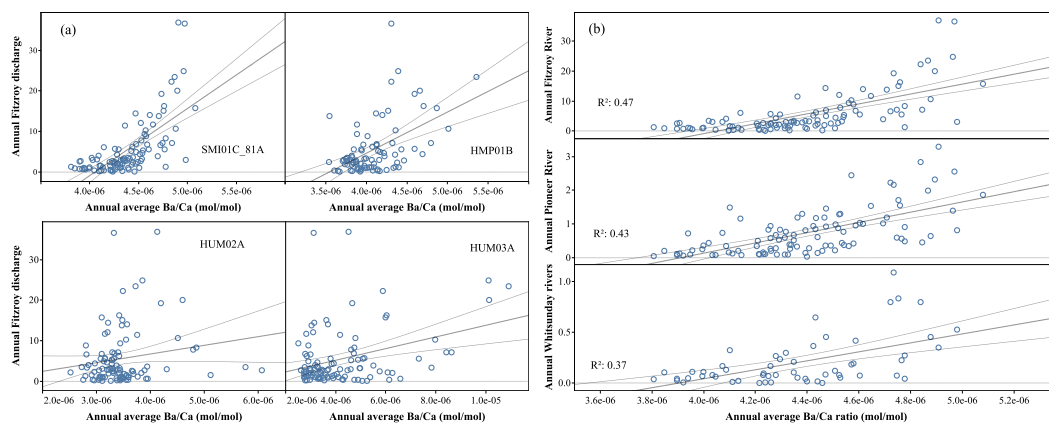


Figure 7.10 (a) Scatterplot of annual average Ba/Ca ratios from SMI01C_81A, HMP01B, HUM02A and HUM03A vs Fitzroy river discharge ($\times 10^6$ ML) from 1917-2017; (b) Scatterplot of annual average Ba/Ca ratios from SMI01C_81A vs Fitzroy River discharge, Pioneer River discharge and sum of Proserpine River and O'Connell River discharge ($\times 10^6$ ML) from 1917-2017. All plots show positive trend in increased Ba/Ca with increasing river discharge. Linear regression is plotted with line and confidence band at $p < 0.05$.

7.4.5 Implications from coral Mn/Ca and Y/Ca records

Similar to Ba, the primary sources of Mn and Y in coastal seawater are riverine particulate matters (Shen et al., 1991) and both Mn/Ca and Y/Ca in coral skeletons are closely linked to major terrestrial runoff events and/or other kinds of environmental disturbances (Lewis et al., 2012; Lewis et al., 2007; Sinclair, 2005b). Mn^{2+} was suggested to be able to substitute for Ca^{2+} in the lattice and the incorporation of Mn in coral skeleton was found to be proportional to Mn concentration in seawater (Alibert et al., 2003; Lewis et al., 2007; Saha et al., 2016; Wyndham et al., 2003). Mn in coral skeletons has also been found to be unaffected by organics (Lewis et al., 2007) making coral Mn a reliable geochemical proxy to record seawater chemistry. However, Mn concentrations in flood plumes were found to vary greatly depending on local catchment geology (Lewis et al., 2018) and Mn desorption from sediments were found to be controlled by various factors such as salinity (Stolpe and Hasselov, 2007), light intensity (Sunda and Huntsman, 1994) and pH (Xyla et al., 1992) in seawater. Other sources of dissolved Mn include photo-reductive dissolution of Mn particulates, diagenetic release in benthic zone and decomposition of organic matter transforming less soluble Mn (IV) to soluble Mn (II). Similarly, Y incorporated in coral skeletons was found to be proportional to its concentration in the surrounding seawater (Luo and Byrne, 2004), but skeletal Y was irrelevant to primary productivity which potentially affected Ba and Mn incorporation (Lewis et al., 2007).

Overall, annual skeletal Y/Ca and Mn/Ca ratios in this study did not show significant correlation with river discharge patterns even though synchronous behaviour of Mn/Ca and Y/Ca with river discharge was observed in some flood events (Figures S7.2-S7.3). Mn/Ca, and Y/Ca ratios in the replicate cores from the same/nearby sampling location (e.g., South Molle Island, Hummocky Island) failed to demonstrate good replication either (Figures S7.2-S7.3). However, statistical distribution of Mn/Ca across all sites from 1980-2015 was quite

comparable while Y/Ca displayed slightly higher regional variability (Figure 7.5). In this work, coral Mn/Ca ratios consistently revealed a 12-month seasonal-timescale cycle (e.g., Figure 7.10) with short-lived or prolonged high intensity spikes occurring randomly at certain years. All Gladstone corals (SEN01C, SAB05A, HUM02A&03A) displayed a few large Mn peaks after 1960 (see chapter 6) which were related to large environmental disturbances such as dredging and mining activities. Even though the seasonal-timescale record of Y/Ca was noisy, the extraction of monthly mean data showed that the timing of Y/Ca peaks occurred regularly in late winter (Figure S7.4), ahead of the timing for river runoff. It has been documented in a few other studies that Y/Ca was not always correlated with coral luminescence or river runoff and the intensity of Y/Ca spikes did not match the river discharge volumes (Alibert et al., 2003; Lewis et al., 2012; Moyer et al., 2012; Saha et al., 2018a). However, coral Y/Ca ratios are still good recorder for long-term changes in baseline concentrations (e.g., SCF81B and SHW82C in Figure S7.3). The poor correlation between Mn/Ca (or Y/Ca) and pulsed flood events suggests that the geochemical cycling of Mn and Y and their incorporation into coral skeletons are more complex than Ba. Lewis et al. (2018) found the desorption of both Mn and Y occurred over a wide salinity range, suggesting the residence time of Mn and Y may be longer than Ba (Brodie et al., 2012).

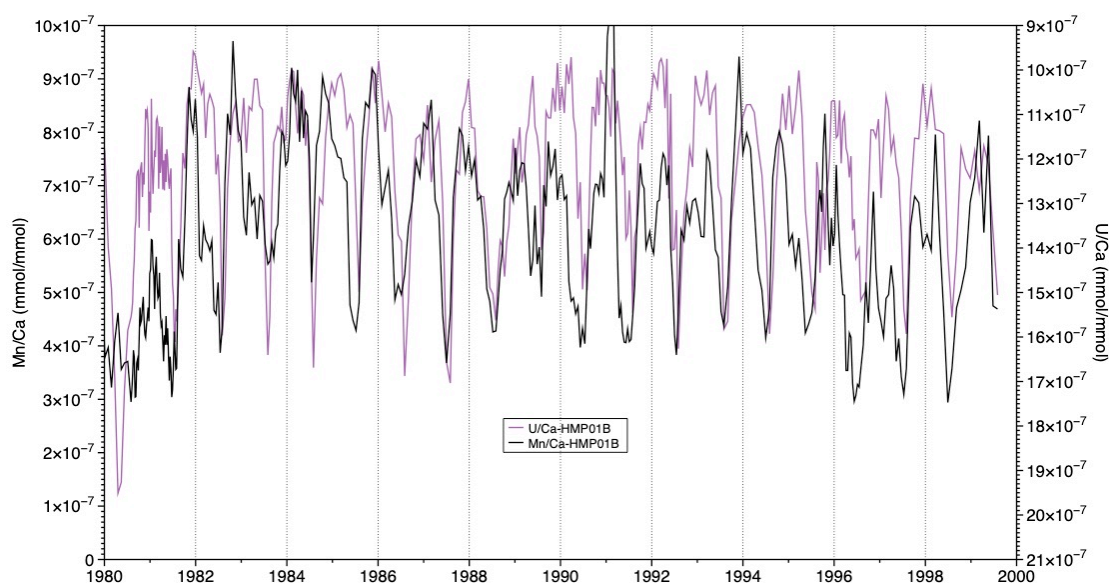


Figure 7.11 Seasonal cycles of Mn/Ca and U/Ca for HMP01B from 1980 to 2000. U/Ca indicates SST seasonality, with peaks representing warm water conditions in mid-summer.

7.5 Conclusion

In this study, significant spatial differences were found in Ba/Ca signals from corals in the Central and Southern GBR. Ba/Ca displayed a regular 12-month seasonal periodicity in Hummocky Island, Whitsunday Island and South Molle Island with peaks occurring at different months of the year. Other sites also recorded sharp pulsed Ba/Ca peaks, but the seasonal regularity was less significant. The different timing of Ba/Ca peaks and lack of correlation between annual Ba/Ca and river discharge (or luminescent ranges) suggest Ba/Ca signals are not simply related to summer freshwater input. Hook Island is the only site that most likely tracked biological activities; however, we are not able to fully disentangle the contributions from SST-dependence and biological impacts. Spatial disparities of Ba/Ca signals in the Central and Southern GBR highlight the importance of site selection. Regression results show that Ba/Ca peak ratios or annual Ba/Ca ratios cannot provide an accurate estimation of river discharge levels in most sites, indicating that Ba availability was different in individual flood events. Besides, it is still essential but also difficult to separate the coupled influence of river discharge and sediment loads. Replication of coral records was not excellent

in this study, but we still recommend the collection of replicate cores (if possible) to make sure that the trace element variations are reproducible and truly reflect the natural perturbations through time. In conclusion, coral Ba/Ca concentration is strongly related to changes in seawater Ba/Ca concentration, but the quantification of sediment loads or river discharge calculated from coral Ba/Ca peaks should be made with caution. To better understand the Ba signatures in corals, direct measurements of dissolved Ba and Ba-rich particulates in freshwater and estuarine zone remain critical as emphasized in a few other studies (Lewis et al., 2018; Sinclair and McCulloch, 2004; Walther et al., 2013).

Mn/Ca baseline values were relatively stable for all sites throughout the years analyzed. Regular seasonal-timescale variations of Mn/Ca across different sites may be temperature-dependent or associated with regular biological activities. However, coral Mn was also sensitive to abrupt changes in terrestrial Mn inputs which was induced by large environmental perturbations. Seasonal oscillation of skeletal Y/Ca was not quite evident compared to that of Mn/Ca or Ba/Ca, but annual to decadal scale Y/Ca was still coherent with local river discharge. Overall, Mn is a good recorder for seasonal time-scale variations and major environmental disturbances, and Y can be used to validate Ba's linkage to river runoff. Geochemical cycling of Mn and Y in coastal seawater is not well understood so further work needs to fully assess the geochemical assemblages of Mn and Y (in both dissolved and particulate components) in flood plumes.

7.6 Supplementary Information

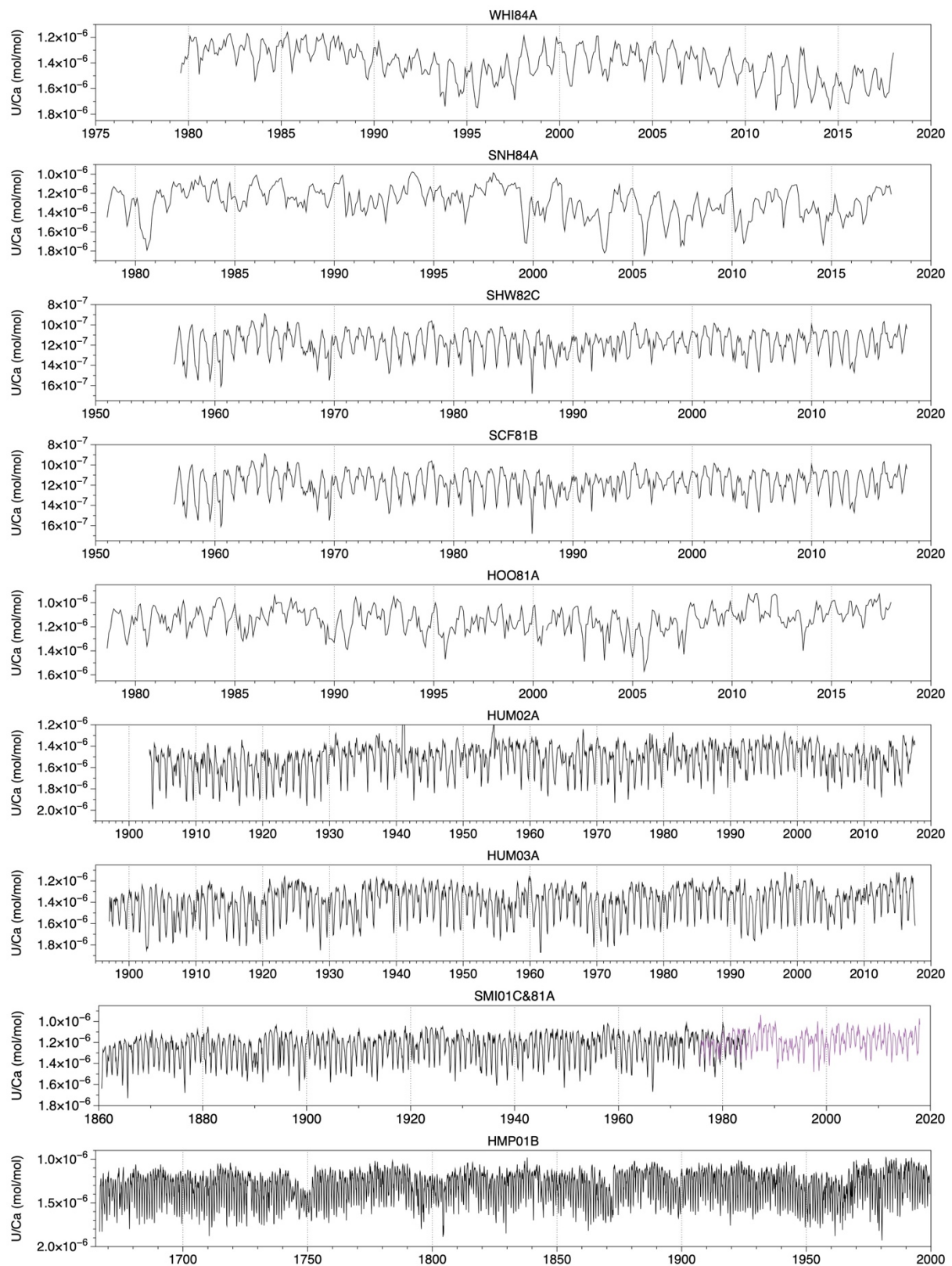


Figure S7.1 Seasonal cycles of U/Ca at HUM02A, HUM03A, HMP01B, SCF81B, SHW82C, WHI84A, SNH84A, HOO81A, SMI01C and SMI81A

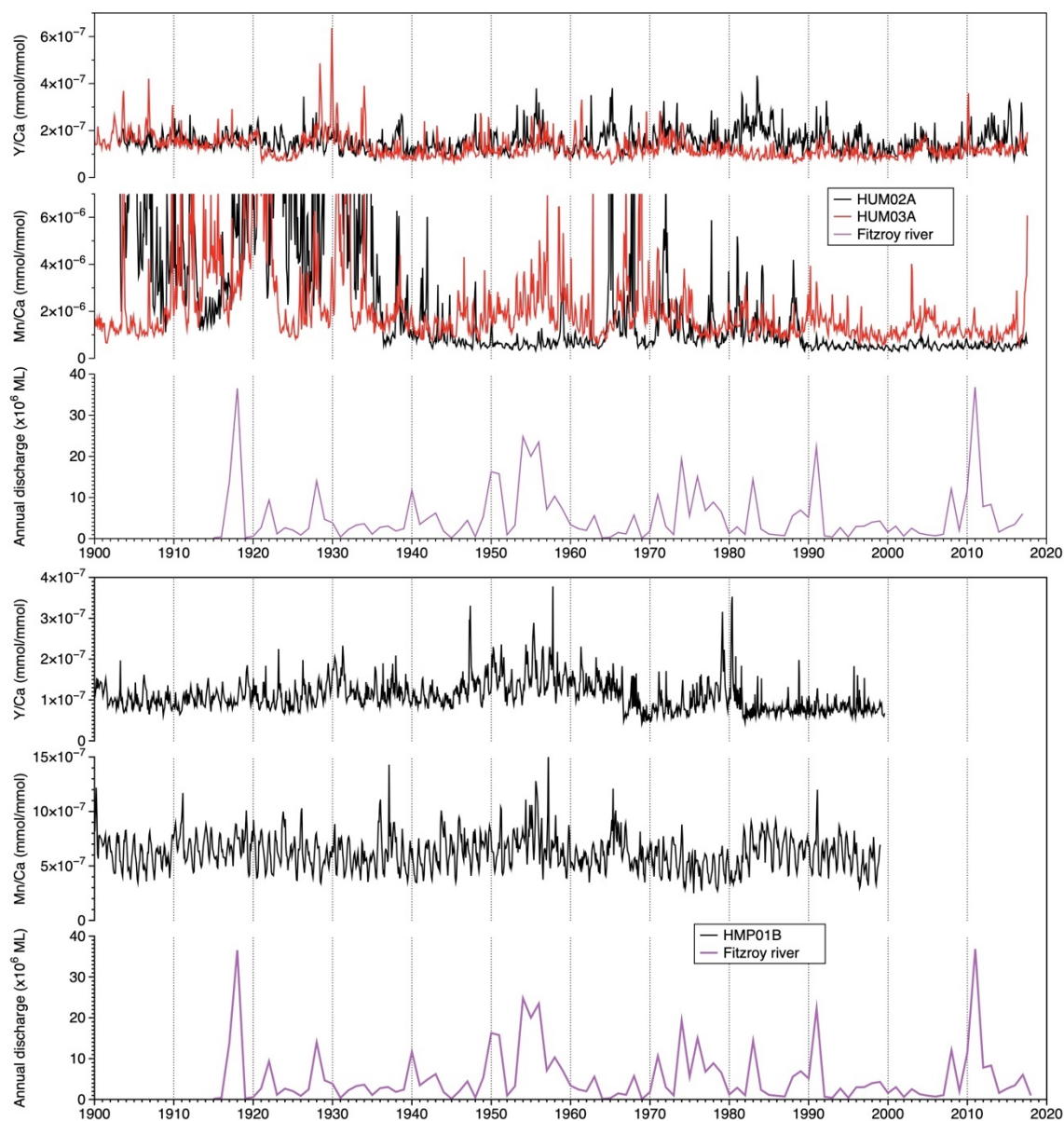


Figure S7.2 Coral Mn/Ca and Y/Ca records from Hummocky Island (HUM02A&03A) and Humpy Island (HMP01B) to the north of Gladstone region

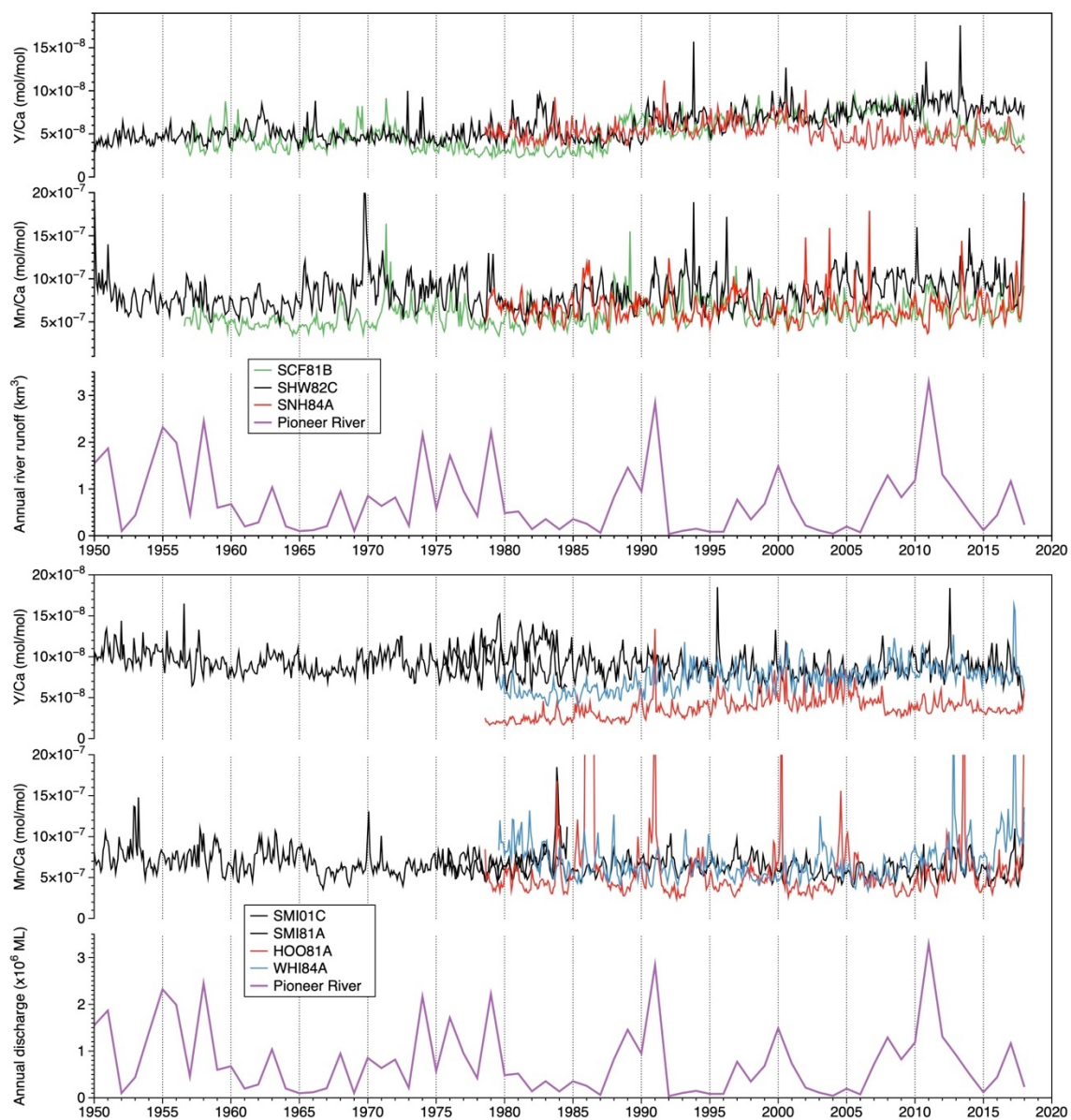


Figure S7.3 Coral Mn/Ca and Y/Ca records from the Whitsunday Islands

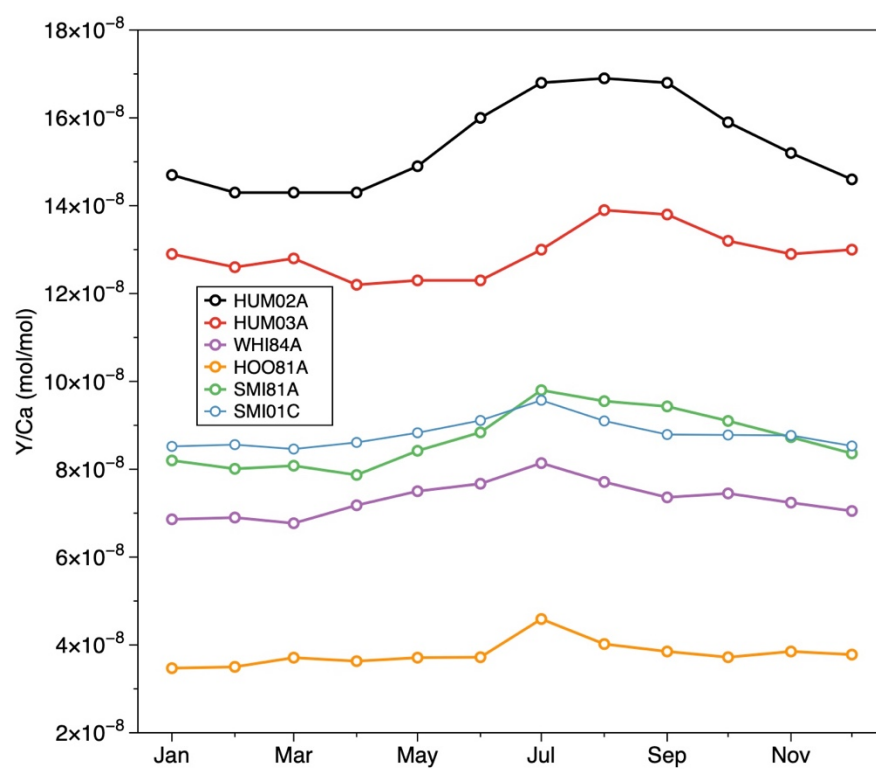


Figure S7.4 Seasonal averages of coral Y/Ca showing the Y/Ca peaks occurred regularly in late winter

Chapter 8: Conclusions and future directions

This thesis examined the isotopic and elemental signatures preserved in *Porites* coral skeletons to provide insights into seasonal-to-centennial timescale paleoclimatic and paleoenvironmental information in the South China Sea and the Great Barrier Reef. This study shows that *Porites* corals are useful as tracers of ocean currents and as biomonitors of the coastal environment. The individual results from each chapter are summarised below. As a whole, this thesis shows the significance of long-term geochemical records in corals and spatial heterogeneity of records. Thus, palaeoenvironment is 4-dimensional in nature - spatial and temporal. These data and results allow that environmental ‘whole’ to be investigated.

8.1 Coral radiocarbon

Surface seawater radiocarbon (^{14}C) records have been reconstructed from corals collected in the Palawan Island (eastern SCS) and the Masthead Island (GBR) to examine seasonal to decadal scale ocean circulation and climatic dynamics. Both coral radiocarbon records have been demonstrated to be highly reproducible from parallel tracks and from different sites in the nearby region, showing the coral $\Delta^{14}\text{C}$ record is quite reliable in tracking seawater mass movement and mixing. The SCS coral detected an ‘early radiocarbon bomb peak’ in late 1955 as seen in corals from Ishigaki, Guam and Makassar Straits which is due to the immediate advection of ^{14}C labelled water from nuclear test sites. This indicates that the Pacific water can intrude into the eastern side of the SCS. The diluted ‘early radiocarbon bomb peak’ was also used to provide an estimation of the relative proportion of non-North Equatorial Current waters that have been laterally entrained during transit of the ^{14}C labelled water from Guam to the SCS. This study also suggests that the circulation in the SCS is strongly influenced by the East

Asian Monsoon and the intrusion of Pacific water into the South China Sea may be impacted by the El Niño-Southern Oscillation and the Pacific Decadal Oscillation.

The Masthead coral $\Delta^{14}\text{C}$ record is in good agreement with other published regional coral $\Delta^{14}\text{C}$ records in the GBR, confirming the major influence on GBR seawater $\Delta^{14}\text{C}$ is the East Australian Current (EAC). The seasonal variations recorded in the Masthead $\Delta^{14}\text{C}$ record are likely due to the variable influences of the South Equatorial Current or wind reversals. The southeast trade winds move surface waters towards the northwest and suppress the poleward-flowing EAC. Most El Niño-Southern Oscillation events were found to be observed as low $\Delta^{14}\text{C}$ values in the Masthead coral. The Masthead coral record also extends the currently available surface seawater ^{14}C record to 2017. This extended record has provided new insights into the long-term overturning of the ^{14}C ocean reservoir in the past decades and can act as a ^{14}C reference curve for oceanic bomb pulse dating in the GBR. Since 2010, the main reservoir of bomb ^{14}C has shifted from the atmosphere to surface ocean.

8.2 Coral trace elements (element/calcium ratio)

SST proxies

Two traditional SST proxies (Sr/Ca, U/Ca), a recently developed SST proxy (Li/Mg) and a new potential proxy (B/Mg) have been assessed and used to reconstruct the SST in the GBR. For most corals in this work, U/Ca is the most robust temperature recorder based on its long-term stability in tracking SST variations. Sr/Ca is a close second, and the average performance may be potentially due to its higher sensitivity (% change Sr/Ca per 1 °C). Li/Mg and B/Mg have clearer periodicity and a higher correlation with SST compared to Li/Ca and B/Ca alone. Both Li/Mg and B/Mg are strongly correlated with SST during the calibration interval but exhibit long-term drift. Empirical calibrations established in this study were also applied to

revisit the UMTECS model. Even though the model cannot always reproduce the empirical calibrations, the presence of geometric centroid has been proved to be universal for different temperature proxies.

Environmental perturbations and terrestrial runoff

Metal spikes such as Al/Ca, Ti/Ca, V/Ca, Mn/Ca recorded in the Gladstone corals relative to their baseline values imply that coastal seawater around the Gladstone Harbour has been impacted by industrial activity. The timing of these elevated elemental ratios was highly related to dredging events and industrial activities associated with port development of the Gladstone Harbour. The near harbour corals (i.e., Seal Rocks, Sable Chief) consistently recorded higher metal concentrations in their skeletons than other more distant corals (Hummocky Island, Masthead Island). In general, the trace element concentrations within the Gladstone corals were lower than other industrialised regions from over the world suggesting that contamination is probably lower in this Australian impacted site. For some corals, the co-variation of certain trace elements is quite evident as confirmed by Principal Component Analysis, indicative of a same source or coherent geochemical characteristics.

Coral skeletal Ba/Ca ratios examined in this work are difficult to interpret. Over the long timescale, the increase in the Ba/Ca baseline is consistent with the increasing sediment inputs associated with land use change in the coastal regions. Corals near the Fitzroy river mouth also recorded large Ba/Ca spikes during drought-breaking years as expected. Of note, annual luminescent range in some corals were strongly correlated to the annual discharge but the Ba/Ca ratios were not (e.g., Hummocky Island corals). However, the seasonal Ba/Ca cycles were quite evident for most corals. Despite lacking a quantitative relationship, the summer Ba/Ca peaks were most likely related to summer floods, discharge, and rainfall but the non-summer

Ba/Ca peaks suggest that corals were recording something else entirely such as temperature or the biological activity.

8.3 Future work

^{14}C and trace element in flood plume

Previous studies suggest ^{14}C should be depleted in river plume as the carbon can originate from terrestrial materials. On the other hand, ^{14}C level in river plume may be overprinted by rainwater because the dissolved inorganic carbon of rainwater should have the ^{14}C level similar to atmospheric ^{14}C (water in equilibrium with atmospheric ^{14}C). Therefore, whether such ^{14}C -depleted carbon can be recorded in river runoff and can be further developed as runoff proxy remains inconclusive. That would largely depend if ^{14}C level in the river plumes during flood years is higher or lower than surface ocean ^{14}C level. This hypothesis can be tested from the direct measurement of ^{14}C in flood plume or in the nearby coral skeletons. The luminescent lines in coral skeletons are excellent markers for major river plume because they can be easily located and marked. The high-resolution coral ^{14}C record generated from the offshore Masthead coral can be used as good reference for this purpose. Besides, as suggested in chapter 7, metal concentrations (in both dissolved form and particulates) such as Ba, Mn, Y are also recommended to be measured in flood plumes to decouple the influences of river discharge and sediment loads.

SST proxy

The incorporation mechanisms for trace elements such as Li and U still require further investigation. Recent work shows that U/Ca is not sensitive to temperature but is dependent on Rayleigh fractionation and carbonate ion concentration ($[\text{CO}_3^{2-}]$) in the calcifying fluid (DeCarlo et al., 2016; DeCarlo et al., 2015). This cannot fully explain the good performance of U/Ca in tracking SST from this work. Similarly, B/Ca is also considered to be related to

seawater [CO₃²⁻] and whether B/Mg can become a new temperature proxy requires more solid evidence. The geochemical records for those elemental ratios can also be cross-validated by solution based ICP-MS or ICP-OES especially for Sr/Ca which has relatively higher analytical uncertainty using LA-ICPMS. Besides, for long-term fluctuations in response, ‘vital effects’ could be examined in the future to see if growth rate and/or skeletal microstructure could make a difference in longer term trending.

Aquarium study of metal uptake by corals

Compared to ‘major’ trace elements, the uptake and incorporation mechanism of heavy metals in coral skeletons is poorly understood. Chapter 6 tried to determine the distribution coefficients (*K_d*) for a few heavy metals (e.g., Al, Mn, V, Pb) but those *K_d* values have large variations. Aquarium study can be performed to better understand the metal distribution between ambient seawater and coral skeletons (or coral tissue layers) because the environmental factors such as temperature, salinity, pH, light and trace element concentrations (both dissolved and particulate) can be better constrained. This work is essential to validate the use of corals as biomonitors to reflect major historical marine pollution events. An accurate determination of *K_d* values can also be used to reconstruct the long-term seawater chemistry using metal concentrations recorded in coral skeletons.

References

- Abram, N. J., Wright, N. M., Ellis, B., Dixon, B. C., Wurtzel, J. B., England, M. H., Ummenhofer, C.C., Philibosian, B., Cahyarini, S.Y., Yu, T.L., Shen, C.C., Cheng, H., Edwards, R.L. & Heslop, D. (2020). Coupling of Indo-Pacific climate variability over the last millennium. *Nature*, 579(7799), 385-392. doi:10.1038/s41586-020-2084-4
- Ainsworth, T. D., Heron, S. F., Ortiz, J. C., Mumby, P. J., Grech, A., Ogawa, D., Eakin, C.M. & Leggat, W. (2016). Climate change disables coral bleaching protection on the Great Barrier Reef. *Science*, 352(6283), 338-342. doi:10.1126/science.aac7125
- Akagi, T., Hashimoto, Y., Fu, F. F., Tsuno, H., Tao, H., & Nakano, Y. (2004). Variation of the distribution coefficients of rare earth elements in modern coral-lattices: Species and site dependencies. *Geochimica Et Cosmochimica Acta*, 68(10), 2265-2273. doi:10.1016/j.gca.2003.12.014
- Al-Rousan, S. A., Al-Shioul, R. N., Al-Horani, F. A., & Abu-Hilal, A. H. (2007). Heavy metal contents in growth bands of Porites corals: Record of anthropogenic and human developments from the Jordanian Gulf of Aqaba. *Marine Pollution Bulletin*, 54(12), 1912-1922. doi:10.1016/j.marpolbul.2007.08.014
- Ali, A. H. A. M., Hamed, M. A., & Abd El-Azim, H. (2011). Heavy metals distribution in the coral reef ecosystems of the Northern Red Sea. *Helgoland Marine Research*, 65(1), 67-80. doi:10.1007/s10152-010-0202-7
- Alibert, C., & Kinsley, L. (2008). A 170-year Sr/Ca and Ba/Ca coral record from the western Pacific warm pool: 1. What can we learn from an unusual coral record?. *Journal of Geophysical Research: Oceans*, 113(C4). doi:Artn C0400810.1029/2006jc003979
- Alibert, C., & McCulloch, M. T. (1997). Strontium/calcium ratios in modern Porites corals from the Great Barrier Reef as a proxy for sea surface temperature: Calibration of the thermometer and monitoring of ENSO. *Paleoceanography*, 12(3), 345-363. doi:10.1029/97pa00318
- Alibert, C., Kinsley, L., Fallon, S. J., McCulloch, M. T., Berkelmans, R., & McAllister, F. (2003). Source of trace element variability in Great Barrier Reef corals affected by the Burdekin flood plumes. *Geochimica Et Cosmochimica Acta*, 67(2), 231-246. doi:10.1016/S0016-7037(00)01055-4
- Allison, N. (1996). Geochemical anomalies in coral skeletons and their possible implications for palaeoenvironmental analyses. *Marine Chemistry*, 55(3-4), 367-379. doi:10.1016/S0304-4203(96)00060-6
- Allison, N., & Finch, A. A. (2007). High temporal resolution Mg/Ca and Ba/Ca records in modern Porites lobata corals. *Geochemistry, Geophysics, Geosystems*, 8. doi:Artn Q0500110.1029/2006gc001477
- Alpert, A. E., Cohen, A. L., Oppo, D. W., DeCarlo, T. M., Gove, J. M., & Young, C. W. (2016). Comparison of equatorial Pacific sea surface temperature variability and trends with Sr/Ca records from multiple corals. *Paleoceanography*, 31(2), 252-265. doi:10.1002/2015pa002897
- Amiel, A. J., Friedman, G. M., & Miller, D. S. (1973). Distribution and Nature of Incorporation of Trace-Elements in Modern Aragonitic Corals. *Sedimentology*, 20(1), 47-64. doi:10.1111/j.1365-3091.1973.tb01606.x
- Andrews, A. H., Asami, R., Iryu, Y., Kobayashi, D. R., & Camacho, F. (2016). Bomb-produced radiocarbon in the western tropical Pacific Ocean: Guam coral reveals operation-specific signals from the Pacific Proving Grounds. *Journal of Geophysical Research: Oceans*, 121(8), 6351-6366. doi:10.1002/2016jc012043

- Andrews, A. H., Humphreys, R. L., & Sampaga, J. D. (2018). Blue marlin (*Makaira nigricans*) longevity estimates confirmed with bomb radiocarbon dating. *Canadian Journal of Fisheries and Aquatic Sciences*, 75(1), 17-25. doi:10.1139/cjfas-2017-0031
- Andrews, A. H., Siciliano, D., Potts, D. C., DeMartini, E. E., & Covarrubias, S. (2016). Bomb radiocarbon and the Hawaiian Archipelago: coral, otoliths, and seawater. *Radiocarbon*, 58(3), 531-548. doi:10.1017/Rdc.2016.32
- Andrews, J. C., & Gentien, P. (1982). Upwelling as a source of nutrients for the Great Barrier Reef ecosystems: A solution to Darwin's question?. *Marine Ecology Progress Series*, 8(3), 257-269. doi:10.3354/meps008257
- Antwertinger, Y. J. (2011). Coral Biomonitoring of a Macrotidal Harbour in the Wet/dry Tropics; Darwin, North Australia. Charles Darwin University.
- Armid, A., Asami, R., Fahmiati, T., Sheikh, M. A., Fujimura, H., Higuchi, T., Taira, E., Shinjo, R. & Oomori, T. (2011). Seawater temperature proxies based on D-Sr, D-Mg, and D-U from culture experiments using the branching coral *Porites cylindrica*. *Geochimica Et Cosmochimica Acta*, 75(15), 4273-4285. doi:10.1016/j.gca.2011.05.010
- Barnard, L. A., Macintyre, I. G., & Pierce, J. W. (1974). Possible environmental index in tropical reef corals. *Nature*, 252(5480), 219-220. doi:10.1038/252219a0
- Barnes, D. J., Taylor, R. B., & Lough, J. M. (2003). Measurement of luminescence in coral skeletons. *Journal of Experimental Marine Biology and Ecology*, 295(1), 91-106. doi:10.1016/S0022-0981(03)00274-0
- Bartley, R., Thompson, C., Croke, J., Pietsch, T., Baker, B., Hughes, K., & Kinsey-Henderson, A. (2018). Insights into the history and timing of post-European land use disturbance on sedimentation rates in catchments draining to the Great Barrier Reef. *Marine Pollution Bulletin*, 131, 530-546. doi:10.1016/j.marpolbul.2018.04.070
- Bastidas, C., & Garcia, E. (1999). Metal content on the reef coral *Porites astreoides*: an evaluation of river influence and 35 years of chronology. *Marine Pollution Bulletin*, 38(10), 899-907. doi:10.1016/S0025-326x(99)00089-2
- Beck, J. W., Edwards, R. L., Ito, E., Taylor, F. W., Recy, J., Rougerie, F., Joannot, P. & Henin, C. (1992). Sea-surface temperature from coral skeletal strontium/calcium ratios. *Science*, 257(5070), 644-647. doi:10.1126/science.257.5070.644
- Beck, J. W., Recy, J., Taylor, F., Edwards, R. L., & Cabioch, G. (1997). Abrupt changes in early Holocene tropical sea surface temperature derived from coral records. *Nature*, 385(6618), 705-707. doi:10.1038/385705a0
- Berkelmans, R., Weeks, S. J., & Steinberg, C. R. (2010). Upwelling linked to warm summers and bleaching on the Great Barrier Reef. *Limnology and Oceanography*, 55(6), 2634-2644. doi:10.4319/lo.2010.55.6.2634
- Bin Mokhtar, M., Praveena, S. M., Aris, A. Z., Yong, O. C., & Lim, A. P. (2012). Trace metal (Cd, Cu, Fe, Mn, Ni and Zn) accumulation in Scleractinian corals: A record for Sabah, Borneo. *Marine Pollution Bulletin*, 64(11), 2556-2563. doi:10.1016/j.marpolbul.2012.07.030
- Blois, J. L., Zarnetske, P. L., Fitzpatrick, M. C., & Finnegan, S. (2013). Climate change and the past, present, and future of biotic interactions. *Science*, 341(6145), 499-504. doi:10.1126/science.1237184
- Boer, G. J., Flato, G., Reader, M. C., & Ramsden, D. (2000). A transient climate change simulation with greenhouse gas and aerosol forcing: experimental design and comparison with the instrumental record for the twentieth century. *Climate Dynamics*, 16(6), 405-425. doi:10.1007/s003820050337

- Bolton, A., Goodkin, N. F., Druffel, E. R. M., Griffin, S., & Murty, S. A. (2016). Upwelling of Pacific Intermediate Water in the South China Sea revealed by coral radiocarbon record. *Radiocarbon*, 58(1), 37-53. doi:10.1017/Rdc.2015.4
- Branson, O., Fehrenbacher, J. S., Vetter, L., Sadekov, A. Y., Eggins, S. M., & Spero, H. J. (2019). LAtools: A data analysis package for the reproducible reduction of LA-ICPMS data. *Chemical Geology*, 504, 83-95. doi:10.1016/j.chemgeo.2018.10.029
- Brenner, L. D., Linsley, B. K., & Dunbar, R. B. (2017). Examining the utility of coral Ba/Ca as a proxy for river discharge and hydroclimate variability at Coiba Island, Gulf of Chirquí, Panamá. *Marine pollution bulletin*, 118(1-2), 48-56.
- Brodie, J., & Waterhouse, J. (2012). A critical review of environmental management of the 'not so Great' Barrier Reef. *Estuarine Coastal and Shelf Science*, 104, 1-22. doi:10.1016/j.ecss.2012.03.012
- Brodie, J., Wolanski, E., Lewis, S., & Bainbridge, Z. (2012). An assessment of residence times of land-sourced contaminants in the Great Barrier Reef lagoon and the implications for management and reef recovery. *Marine Pollution Bulletin*, 65(4-9), 267-279. doi:10.1016/j.marpolbul.2011.12.011
- Brown, B. E., Tudhope, A. W., Letissier, M. D. A., & Scoffin, T. P. (1991). A Novel Mechanism for Iron Incorporation into Coral Skeletons. *Coral Reefs*, 10(4), 211-215. doi:10.1007/Bf00336776
- Bryan, S. P., & Marchitto, T. M. (2008). Mg/Ca-temperature proxy in benthic foraminifera: New calibrations from the Florida Straits and a hypothesis regarding Mg/Li. *Paleoceanography*, 23(2). doi:Artn Pa222010.1029/2007pa001553
- Byrd, J. T., & Andreae, M. O. (1982). Tin and methyltin species in seawater: concentrations and fluxes. *Science*, 218(4572), 565-569. doi:10.1126/science.218.4572.565
- Byrne, R. H., & Liu, X. W. (1996). Metal speciation assessments in natural waters: Comment on "Rare earth element complexation behavior in circumneutral pH ground waters: Assessing the role of carbonate and phosphate ions". *Earth and Planetary Science Letters*, 145(1-4), 135-137. doi:10.1016/S0012-821x(96)00198-7
- Byrne, R. H., Liu, X. W., & Schijf, J. (1996). The influence of phosphate coprecipitation on rare earth distributions in natural waters. *Geochimica Et Cosmochimica Acta*, 60(17), 3341-3346. doi:10.1016/0016-7037(96)00197-4
- Cantin, N. E., Fallon, S. J., Wu, Y., & Lough, J. M. (2018). Project ISP019: Calcification and geochemical signatures of industrial development of the Gladstone Harbour from century old coral skeletons. *Report prepared for Gladstone Healthy Harbour Partnership*. Australian Institute of Marine Science, Townsville, Qld. (40 pp).
- Cantin, N., Wu, Y., Fallon, S., & Lough, J. (2019a). Historical records of terrestrial sediment and flood plume inputs to the Whitsunday Island region from coral skeletons: 1861-2017. Australian Institute of Marine Science, Townsville, Qld. (30pp)
- Cantin, N. E., & Lough, J. M. (2019b). Coral luminescence records freshwater impacts from the Fitzroy River Basin. *Report prepared for BHP Billiton*. Australian Institute of Marine Science, Townsville, Qld. (20 pp + appendices)
- Cardinal, D., Hamelin, B., Bard, E., & Patzold, J. (2001). Sr/Ca, U/Ca and delta O-18 records in recent massive corals from Bermuda: relationships with sea surface temperature. *Chemical Geology*, 176(1-4), 213-233. doi:10.1016/S0009-2541(00)00396-X
- Carilli, J. E., Prouty, N. G., Hughen, K. A., & Norris, R. D. (2009). Century-scale records of land-based activities recorded in Mesoamerican coral cores. *Marine Pollution Bulletin*, 58(12), 1835-1842. doi:10.1016/j.marpolbul.2009.07.024
- Carroll, J., Falkner, K. K., Brown, E. T., & Moore, W. S. (1993). The role of the Ganges-Brahmaputra mixing zone in supplying barium and ²²⁶Ra to the Bay of Bengal.

- Geochimica Et Cosmochimica Acta*, 57(13), 2981-2990. doi:10.1016/0016-7037(93)90287-7
- Case, D. H., Robinson, L. F., Auro, M. E., & Gagnon, A. C. (2010). Environmental and biological controls on Mg and Li in deep-sea scleractinian corals. *Earth and Planetary Science Letters*, 300(3-4), 215-225. doi:10.1016/j.epsl.2010.09.029
- Chalker, B. E., & Barnes, D. J. (1990). Gamma-Densitometry for the Measurement of Skeletal Density. *Coral Reefs*, 9(1), 11-23. doi:10.1007/Bf00686717
- Chao, Y., Ghil, M., & McWilliams, J. C. (2000). Pacific interdecadal variability in this century's sea surface temperatures. *Geophysical Research Letters*, 27(15), 2261-2264. doi:10.1029/1999gl011324
- Chave, K. E. (1954). Aspects of the biogeochemistry of magnesium 1. Calcareous marine organisms. *Journal of Geology*, 62(3), 266-283. doi:10.1086/626162
- Chen T. R., Yu, K. F., Li S., Chen, T. G., & Shi, Q. (2011). Anomalous Ba/Ca signals associated with low temperature stresses in Porites corals from Daya Bay, northern South China Sea. *Journal of Environmental Sciences*, 23(9), 1452-1459. doi:10.1016/s1001-0742(10)60606-7
- Chen, F. H., Bloemendal, J., Wang, J. M., Li, J. J., & Oldfield, F. (1997). High-resolution multi-proxy climate records from Chinese loess, evidence for rapid climatic changes over the last 75 kyr. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 130(1-4), 323-335. doi:10.1016/S0031-0182(96)00149-6
- Chen, M. L., Goodkin, N. F., Boyle, E. A., Switzer, A. D., & Bolton, A. (2016). Lead in the western South China Sea: Evidence of atmospheric deposition and upwelling. *Geophysical Research Letters*, 43(9), 4490-4499. doi:10.1002/2016gl068697
- Chen, T. R., Yu, K. F., Li, S., Price, G. J., Shi, Q., & Wei, G. J. (2010). Heavy metal pollution recorded in Porites corals from Daya Bay, northern South China Sea. *Marine Environmental Research*, 70(3-4), 318-326. doi:10.1016/j.marenvres.2010.06.004
- Chen, T. R., Yu, K. F., Zhao, J. X., Yan, H. Q., Song, Y. X., Feng, Y. X., & Chen, T. G. (2015). Testing coral paleothermometers (B/Ca, Mg/Ca, Sr/Ca, U/Ca and delta O-18) under impacts of large riverine runoff. *Acta Oceanologica Sinica*, 34(8), 20-26. doi:10.1007/s13131-015-0705-9
- Chen, X. F., D'Olivo, J. P., Wei, G. J., & McCulloch, M. (2019). Anthropogenic ocean warming and acidification recorded by Sr/Ca, Li/Mg, $\delta^{11}\text{B}$ and B/Ca in Porites coral from the Kimberley region of northwestern Australia. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 528, 50-59. doi:10.1016/j.palaeo.2019.04.033
- Chen, X. F., Wei, G. J., Deng, W. F., Liu, Y., Sun, Y. L., Zeng, T., & Xie, L. H. (2015). Decadal variations in trace metal concentrations on a coral reef: Evidence from a 159 year record of Mn, Cu, and V in a Porites coral from the northern South China Sea. *Journal of Geophysical Research: Oceans*, 120(1), 405-416. doi:10.1002/2014jc010390
- Chu, P. C., Edmons, N. L., & Fan, C. W. (1999). Dynamical mechanisms for the South China Sea seasonal circulation and thermohaline variabilities. *Journal of Physical Oceanography*, 29(11), 2971-2989. doi:10.1175/1520-0485(1999)029<2971:Dmftsc>2.0.Co;2
- Cohen, A. L., Owens, K. E., Layne, G. D., & Shimizu, N. (2002). The effect of algal symbionts on the accuracy of Sr/Ca paleotemperatures from coral. *Science*, 296(5566), 331-333. doi:10.1126/science.1069330
- Comeau, S., Cornwall, C. E., & McCulloch, M. T. (2017). Decoupling between the response of coral calcifying fluid pH and calcification to ocean acidification. *Scientific Reports*, 7. doi:ARTN 757310.1038/s41598-017-08003-z

- Cooper, T. F., Gilmour, J. P., & Fabricius, K. E. (2009). Bioindicators of changes in water quality on coral reefs: review and recommendations for monitoring programmes. *Coral Reefs*, 28(3), 589-606. doi:10.1007/s00338-009-0512-x
- Coplen, T. B. (1994). Reporting of Stable Hydrogen, Carbon, and Oxygen Isotopic Abundances. *Pure and Applied Chemistry*, 66(2), 273-276. doi:10.1351/pac199466020273
- Coplen, T. B., Brand, W. A., Gehre, M., Groning, M., Meijer, H. A. J., Toman, B., & Verkouteren, R. M. (2006). After two decades a second anchor for the VPDB $\delta^{13}\text{C}$ scale. *Rapid Communications in Mass Spectrometry*, 20(21), 3165-3166. doi:10.1002/rcm.2727
- Correge, T. (2006). Sea surface temperature and salinity reconstruction from coral geochemical tracers. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 232(2-4), 408-428. doi:10.1016/j.palaeo.2005.10.014
- Crabbe, M. J. C. (2008). Climate change, global warming and coral reefs: Modelling the effects of temperature. *Computational Biology and Chemistry*, 32(5), 311-314. doi:10.1016/j.compbiolchem.2008.04.001
- Cross, T. S., & Cross, B. W. (1984). U, Sr and Mg in Holocene and Pleistocene Corals A. Palmata and M. Annularis: Reply. *Journal of Sedimentary Petrology*, 54(1), 328-329. Doi:10.1306/212f8413-2b24-11d7-8648000102c1865d
- Crowley, T. J. (2000). Causes of climate change over the past 1000 years. *Science*, 289(5477), 270-277. doi:10.1126/science.289.5477.270
- Cuny-Guirriec, K., Douville, E., Reynaud, S., Allemand, D., Bordier, L., Canesi, M., Mazzoli, C., Taviani, M., Canese, S., McCulloch, M., Trotter, J., Rico-Esenaro, S.D., Sanchez-Cabeza, J.A., Ruiz-Fernandez, A.C., Carricart-Ganivet, J.P., Scott, P.M., Sadekov, A. & Montagna, P. (2019). Coral Li/Mg thermometry: Caveats and constraints. *Chemical Geology*, 523, 162-178. doi:10.1016/j.chemgeo.2019.03.038
- D'Olive, J. P., & McCulloch, M. T. (2017). Response of coral calcification and calcifying fluid composition to thermally induced bleaching stress. *Scientific Reports*, 7. doi:ARTN 220710.1038/s41598-017-02306-x
- D'Olive, J. P., Georgiou, L., Falter, J., DeCarlo, T. M., Irigoien, X., Voolstra, C. R., Roder, C., Trotter, J. & McCulloch, M.T. (2019). Long-term impacts of the 1997-1998 bleaching event on the growth and resilience of massive Porites corals from the central Red Sea. *Geochemistry, Geophysics, Geosystems*, 20(6), 2936-2954. doi:10.1029/2019gc008312
- D'Olive, J. P., Sinclair, D. J., Rankenburg, K., & McCulloch, M. T. (2018). A universal multi-trace element calibration for reconstructing sea surface temperatures from long-lived Porites corals: Removing 'vital-effects'. *Geochimica Et Cosmochimica Acta*, 239, 109-135. doi:10.1016/j.gca.2018.07.035
- David, C. P. (2003). Heavy metal concentrations in growth bands of corals: a record of mine tailings input through time (Marinduque Island, Philippines). *Marine Pollution Bulletin*, 46(2), 187-196. doi:Pii S0025-326x(02)00315-6
- De'ath, G., & Fabricius, K. (2010). Water quality as a regional driver of coral biodiversity and macroalgae on the Great Barrier Reef. *Ecological Applications*, 20(3), 840-850. doi:10.1890/08-2023.1
- De'ath, G., Fabricius, K. E., Sweatman, H., & Puotinen, M. (2012). The 27-year decline of coral cover on the Great Barrier Reef and its causes. *Proceedings of the National Academy of Sciences of the United States of America*, 109(44), 17995-17999. doi:10.1073/pnas.1208909109

- DeCarlo, T. M., Gaetani, G. A., Cohen, A. L., Foster, G. L., Alpert, A. E., & Stewart, J. A. (2016). Coral Sr-U thermometry. *Paleoceanography*, 31(6), 626-638. doi:10.1002/2015pa002908
- DeCarlo, T. M., Gaetani, G. A., Holcomb, M., & Cohen, A. L. (2015). Experimental determination of factors controlling U/Ca of aragonite precipitated from seawater: Implications for interpreting coral skeleton. *Geochimica Et Cosmochimica Acta*, 162, 151-165. doi:10.1016/j.gca.2015.04.016
- Delaney, M. L., Linn, L. J., & Druffel, E. R. M. (1993). Seasonal Cycles of Manganese and Cadmium in Coral from the Galapagos-Islands. *Geochimica Et Cosmochimica Acta*, 57(2), 347-354. doi:10.1016/0016-7037(93)90436-Z
- DeLong, K. L., Flannery, J. A., Poore, R. Z., Quinn, T. M., Maupin, C. R., Lin, K., & Shen, C. C. (2014). A reconstruction of sea surface temperature variability in the southeastern Gulf of Mexico from 1734 to 2008 CE using cross-dated Sr/Ca records from the coral *Siderastrea siderea*. *Paleoceanography*, 29(5), 403-422. doi:10.1002/2013pa002524
- DeLong, K. L., Quinn, T. M., & Taylor, F. W. (2007). Reconstructing twentieth-century sea surface temperature variability in the southwest Pacific: A replication study using multiple coral Sr/Ca records from New Caledonia. *Paleoceanography*, 22(4). doi:Artn Pa421210.1029/2007pa001444
- DeLong, K. L., Quinn, T. M., Taylor, F. W., Shen, C. C., & Lin, K. (2013). Improving coral-base paleoclimate reconstructions by replicating 350 years of coral Sr/Ca variations. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 373, 6-24. doi:10.1016/j.palaeo.2012.08.019
- Deng, W. F., Wei, G. J., McCulloch, M., Xie, L. H., Liu, Y., & Zeng, T. (2014). Evaluation of annual resolution coral geochemical records as climate proxies in the Great Barrier Reef of Australia. *Coral Reefs*, 33(4), 965-977. doi:10.1007/s00338-014-1203-9
- Deser, C., Alexander, M. A., Xie, S. P., & Phillips, A. S. (2010). Sea surface temperature variability: Patterns and mechanisms. *Annual Review of Marine Science*, 2, 115-143. doi:10.1146/annurev-marine-120408-151453
- Devilliers, S., Shen, G. T., & Nelson, B. K. (1994). The Sr/Ca-temperature relationship in coralline aragonite: Influence of variability in (Sr/Ca) seawater and skeletal growth parameters. *Geochimica Et Cosmochimica Acta*, 58(1), 197-208. doi:10.1016/0016-7037(94)90457-X
- Dietzel, M., Gussone, N., & Eisenhauer, A. (2004). Co-precipitation of Sr^{2+} and Ba^{2+} with aragonite by membrane diffusion of CO_2 between 10 and 50 °C. *Chemical Geology*, 203(1-2), 139-151. doi:10.1016/j.chemgeo.2003.09.008
- Djogic, R., Sipos, L., & Branica, M. (1986). Characterization of uranium(VI) in seawater 1. *Limnology and Oceanography*, 31(5), 1122-1131. doi:10.4319/lo.1986.31.5.1122
- Dodge, R. E., & Vaisnys, J. R. (1975). Hermatypic coral growth banding as environmental recorder. *Nature*, 258(5537), 706-708. doi:10.1038/258706a0
- Dong, W. M., & Brooks, S. C. (2006). Determination of the formation constants of ternary complexes of uranyl and carbonate with alkaline earth metals (Mg^{2+} , Ca^{2+} , Sr^{2+} , and Ba^{2+}) using anion exchange method. *Environmental Science & Technology*, 40(15), 4689-4695. doi:10.1021/es0606327
- Druffel, E. (2002). Radiocarbon in corals: records of the carbon cycle, surface circulation and climate. *Oceanography*, 15(1), 122-127. doi:10.5670/oceanog.2002.43
- Druffel, E. R. M. (1987). Bomb radiocarbon in the Pacific: Annual and seasonal timescale variations. *Journal of Marine Research*, 45(3), 667-698. doi:10.1357/002224087788326876

- Druffel, E. R. M. (1989). Decade time scale variability of ventilation in the North-Atlantic: High-precision measurements of bomb radiocarbon in banded corals. *Journal of Geophysical Research: Oceans*, 94(C3), 3271-3285. doi:10.1029/JC094iC03p03271
- Druffel, E. R. M. (1997a). Geochemistry of corals: Proxies of past ocean chemistry, ocean circulation, and climate. *Proceedings of the National Academy of Sciences of the United States of America*, 94(16), 8354-8361. doi:10.1073/pnas.94.16.8354
- Druffel, E. R. M. (1997b). Pulses of rapid ventilation in the North Atlantic surface ocean during the past century. *Science*, 275(5305), 1454-1457. doi:10.1126/science.275.5305.1454
- Druffel, E. R. M., & Griffin, S. (1993). Large variations of surface ocean radiocarbon: Evidence of circulation changes in the Southwestern Pacific. *Journal of Geophysical Research: Oceans*, 98(C11), 20249-20259. doi:10.1029/93jc02113
- Druffel, E. R. M., & Griffin, S. (1995). Regional variability of surface ocean radiocarbon from southern great barrier reef corals. *Radiocarbon*, 37(2), 517-524. doi:10.1017/s0033822200031003
- Druffel, E. R. M., & Griffin, S. (1999). Variability of surface ocean radiocarbon and stable isotopes in the southwestern Pacific. *Journal of Geophysical Research: Oceans*, 104(C10), 23607-23613. doi:10.1029/1999jc900212
- Druffel, E. R. M., Griffin, S., Beaufre, S. R., & Dunbar, R. B. (2007). Oceanic climate and circulation changes during the past four centuries from radiocarbon in corals. *Geophysical Research Letters*, 34(9). doi:Artn L0960110.1029/2006gl028681
- Druffel, E. R. M., Griffin, S., Guilderson, T. P., Kashgarian, M., Southon, J., & Schrag, D. P. (2001). Changes of subtropical North Pacific radiocarbon and correlation with climate variability. *Radiocarbon*, 43(1), 15-25. doi:10.1017/s0033822200031593
- Dunbar, R. B., Wellington, G. M., Colgan, M. W., & Glynn, P. W. (1994). Eastern Pacific sea surface temperature since 1600 AD: The $\delta^{18}\text{O}$ record of climate variability in Galápagos corals. *Paleoceanography*, 9(2), 291-315. doi:10.1029/93pa03501
- Edmond, J. M., Spivack, A., Grant, B. C., Hu, M. H., Chen, Z. X., Chen, S., & Zeng, X. S. (1985). Chemical dynamics of the Changjiang estuary. *Continental Shelf Research*, 4(1-2), 17-36. doi:10.1016/0278-4343(85)90019-6
- Eggins, S. M., Kinsley, L. P. J., & Shelley, J. M. G. (1998). Deposition and element fractionation processes during atmospheric pressure laser sampling for analysis by ICP-MS. *Applied Surface Science*, 127, 278-286. doi:10.1016/S0169-4332(97)00643-0
- Elderfield, H., Upstillgoddard, R., & Sholkovitz, E. R. (1990). The rare earth elements in rivers, estuaries, and coastal seas and their significance to the composition of ocean waters. *Geochimica Et Cosmochimica Acta*, 54(4), 971-991. doi:10.1016/0016-7037(90)90432-K
- Endrizzi, F., & Rao, L. F. (2014). Chemical speciation of uranium (VI) in marine environments: complexation of calcium and magnesium Ions with $[(\text{UO}_2)(\text{CO}_3)_3]^{4-}$ and the effect on the extraction of uranium from seawater. *Chemistry-a European Journal*, 20(44), 14499-14506. doi:10.1002/chem.201403262
- Esslemont, G. (2000). Heavy metals in seawater, marine sediments and corals from the Townsville section, Great Barrier Reef Marine Park, Queensland. *Marine Chemistry*, 71(3-4), 215-231. doi:10.1016/S0304-4203(00)00050-5
- Esslemont, G., Russell, R. A., & Maher, W. A. (2004). Coral record of harbour dredging: Townsville, Australia. *Journal of Marine Systems*, 52(1-4), 51-64. doi:10.1016/j.jmarsys.2004.01.005
- Fabricius, K., De'ath, G., McCook, L., Turak, E., & Williams, D. M. (2005). Changes in algal, coral and fish assemblages along water quality gradients on the inshore Great Barrier

- Reef. *Marine Pollution Bulletin*, 51(1-4), 384-398. doi:10.1016/j.marpolbul.2004.10.041
- Fallon, S. J., & Guilderson, T. P. (2005). Extracting growth rates from the nonlaminated coralline sponge *Astrosclera willeyana* using bomb radiocarbon. *Limnology and Oceanography: Methods*, 3, 455-461. doi:10.4319/lom.2005.3.455
- Fallon, S. J., & Guilderson, T. P. (2008). Surface water processes in the Indonesian throughflow as documented by a high-resolution coral $\Delta^{14}\text{C}$ record. *Journal of Geophysical Research*, 113(C9). doi:10.1029/2008jc004722
- Fallon, S. J., Fifield, L. K., & Chappell, J. M. (2010). The next chapter in radiocarbon dating at the Australian National University: Status report on the single stage AMS. *Nuclear Instruments & Methods in Physics Research Section B-Beam Interactions with Materials and Atoms*, 268(7-8), 898-901. doi:10.1016/j.nimb.2009.10.059
- Fallon, S. J., Guilderson, T. P., & Caldeira, K. (2003). Carbon isotope constraints on vertical mixing and air-sea CO_2 exchange. *Geophysical Research Letters*, 30(24). doi:Artn 228910.1029/2003gl018049
- Fallon, S. J., McCulloch, M. T., & Alibert, C. (2003). Examining water temperature proxies in Porites corals from the Great Barrier Reef: a cross-shelf comparison. *Coral Reefs*, 22(4), 389-404. doi:10.1007/s00338-003-0322-5
- Fallon, S. J., McCulloch, M. T., van Woesik, R., & Sinclair, D. J. (1999). Corals at their latitudinal limits: laser ablation trace element systematics in Porites from Shirigai Bay, Japan. *Earth and Planetary Science Letters*, 172(3-4), 221-238. doi:10.1016/S0012-821x(99)00200-9
- Fallon, S. J., White, J. C., & McCulloch, M. T. (2002). Porites corals as recorders of mining and environmental impacts: Misima Island, Papua New Guinea. *Geochimica Et Cosmochimica Acta*, 66(1), 45-62. doi:10.1016/S0016-7037(01)00715-3
- Felis, T., Suzuki, A., Kuhnert, H., Dima, M., Lohmann, G., & Kawahata, H. (2009). Subtropical coral reveals abrupt early-twentieth-century freshening in the western North Pacific Ocean. *Geology*, 37(6), 527-530. doi:10.1130/G25581a.1
- Ferrier-Pages, C., Boisson, F., Allemand, D., & Tambutte, E. (2002). Kinetics of strontium uptake in the scleractinian coral *Stylophora pistillata*. *Marine Ecology Progress Series*, 245, 93-100. doi:10.3354/meps245093
- Finch, A. A., & Allison, N. (2008). Mg structural state in coral aragonite and implications for the paleoenvironmental proxy. *Geophysical Research Letters*, 35(8). doi:Artn L0870410.1029/2008gl033543
- Fleitmann, D., Dunbar, R. B., McCulloch, M., Mudelsee, M., Vuille, M., McClanahan, T. R., Cole, J. E., & Eggins, S. (2007). East African soil erosion recorded in a 300 year old coral colony from Kenya. *Geophysical Research Letters*. 34(4). doi:10.1029/2006gl028525
- Fowell, S. E., Sandford, K., Stewart, J. A., Castillo, K. D., Ries, J. B., & Foster, G. L. (2016). Intrareef variations in Li/Mg and Sr/Ca sea surface temperature proxies in the Caribbean reef-building coral *Siderastrea siderea*. *Paleoceanography*, 31(10), 1315-1329. doi:10.1002/2016pa002968
- Froelich, P. N., Kaul, L. W., Byrd, J. T., Andreae, M. O., & Roe, K. K. (1985). Arsenic, barium, germanium, tin, dimethylsulfide and nutrient biogeochemistry in Charlotte Harbor, Florida, a phosphorus-enriched estuary. *Estuarine Coastal and Shelf Science*, 20(3), 239-264. doi:10.1016/0272-7714(85)90041-1
- Gabitov, R. I., Gaetani, G. A., Watson, E. B., Cohen, A. L., & Ehrlich, H. L. (2008). Experimental determination of growth rate effect on U^{6+} and Mg^{2+} partitioning between

- aragonite and fluid at elevated U^{6+} concentration. *Geochimica Et Cosmochimica Acta*, 72(16), 4058-4068. doi:10.1016/j.gca.2008.05.047
- Gaetani, G. A., & Cohen, A. L. (2006). Element partitioning during precipitation of aragonite from seawater: A framework for understanding paleoproxies. *Geochimica Et Cosmochimica Acta*, 70(18), 4617-4634. doi:10.1016/j.gca.2006.07.008
- Gaetani, G. A., Cohen, A. L., Wang, Z. R., & Crusius, J. (2011). Rayleigh-based, multi-element coral thermometry: A biomineralization approach to developing climate proxies. *Geochimica Et Cosmochimica Acta*, 75(7), 1920-1932. doi:10.1016/j.gca.2011.01.010
- Gagan, M. K., Ayliffe, L. K., Beck, J. W., Cole, J. E., Druffel, E. R. M., Dunbar, R. B., & Schrag, D. P. (2000). New views of tropical paleoclimates from corals. *Quaternary Science Reviews*, 19(1-5), 45-64. doi:10.1016/S0277-3791(99)00054-2
- Gagan, M. K., Dunbar, G. B., & Suzuki, A. (2012). The effect of skeletal mass accumulation in Porites on coral Sr/Ca and $\delta^{18}O$ paleothermometry. *Paleoceanography*, 27. doi:Artn Pa120310.1029/2011pa002215
- Ganachaud, A., & Wunsch, C. (2000). Improved estimates of global ocean circulation, heat transport and mixing from hydrographic data. *Nature*, 408(6811), 453-457. doi:10.1038/35044048
- Ganachaud, A., & Wunsch, C. (2003). Large-scale ocean heat and freshwater transports during the World Ocean Circulation Experiment. *Journal of Climate*, 16(4), 696-705. doi:10.1175/1520-0442(2003)016<0696:Lsohaf>2.0.Co;2
- Giokas, D. L., Salvador, A., & Chisvert, A. (2007). UV filters: From sunscreens to human body and the environment. *Trac-Trends in Analytical Chemistry*, 26(5), 360-374. doi:10.1016/j.trac.2007.02.012
- Gissi, F., Reichelt-Brushett, A. J., Chariton, A. A., Stauber, J. L., Greenfield, P., Humphrey, C., Salmon, M., Stephenson, S.A., Cresswell, T. & Jolley, D.F. (2019). The effect of dissolved nickel and copper on the adult coral *Acropora muricata* and its microbiome. *Environmental Pollution*, 250, 792-806. doi:10.1016/j.envpol.2019.04.030
- Glynn, D., Druffel, E., Griffin, S., Dunbar, R., Osborne, M., & Sanchez-Cabeza, J. A. (2013). Early bomb radiocarbon detected in Palau Archipelago corals. *Radiocarbon*, 55(2-3), 1659-1664. doi:10.1017/S0033822200048578
- Godfrey, J. S., Cresswell, G. R., Golding, T. J., & Pearce, A. F. (1980). The separation of the east Australian current. *Journal of Physical Oceanography*, 10(3), 430-440. doi:10.1175/1520-0485(1980)010<0430:Tsofea>2.0.Co;2
- Godwin, H. (1962). Half-life of radiocarbon. *Nature*, 195(4845), 984. doi:10.1038/195984a0
- Gonneea, M. E., Cohen, A. L., DeCarlo, T. M., & Charette, M. A. (2017). Relationship between water and aragonite barium concentrations in aquaria reared juvenile corals. *Geochimica Et Cosmochimica Acta*, 209, 123-134. doi:10.1016/j.gca.2017.04.006
- Graven, H. D. (2015). Impact of fossil fuel emissions on atmospheric radiocarbon and various applications of radiocarbon over this century. *Proceedings of the National Academy of Sciences of the United States of America*, 112(31), 9542-9545. doi:10.1073/pnas.1504467112
- Grottoli, A. G., & Eakin, C. M. (2007). A review of modern coral $\delta^{18}O$ and $\Delta^{14}C$ proxy records. *Earth-Science Reviews*, 81(1-2), 67-91. doi:10.1016/j.earscirev.2006.10.001
- Grove, C. A., Zinke, J., Peeters, F., Park, W., Scheufen, T., Kasper, S., . Randriamanantsoa, B., McCulloch, M.T. & Brummer, G.J.A. (2013). Madagascar corals reveal a multidecadal signature of rainfall and river runoff since 1708. *Climate of the Past*, 9(2), 641-656. doi:10.5194/cp-9-641-2013
- Grove, C. A., Zinke, J., Scheufen, T., Maina, J., Epping, E., Boer, W., Randriamanantsoa, B. & Brummer, G.J.A. (2012). Spatial linkages between coral proxies of terrestrial runoff

- across a large embayment in Madagascar. *Biogeosciences*, 9(8), 3063-3081. doi:10.5194/bg-9-3063-2012
- Grumet, N. S., Abram, N. J., Beck, J. W., Dunbar, R. B., Gagan, M. K., Guilderson, T. P., Hantoro, W.S. & Suwargadi, B.W. (2004). Coral radiocarbon records of Indian Ocean water mass mixing and wind-induced upwelling along the coast of Sumatra, Indonesia. *Journal of Geophysical Research-Oceans*, 109(C5). doi:Artn C0500310.1029/2003jc002087
- Guilderson, T. P., & Schrag, D. P. (1998). Abrupt shift in subsurface temperatures in the Tropical Pacific associated with changes in El Nino. *Science*, 281(5374), 240-243. doi:10.1126/science.281.5374.240
- Guilderson, T. P., Fallon, S., Moore, M. D., Schrag, D. P., & Charles, C. D. (2009). Seasonally resolved surface water $\Delta^{14}\text{C}$ variability in the Lombok Strait: A coralline perspective. *Journal of Geophysical Research*, 114(C7). doi:10.1029/2008jc004876
- Guilderson, T. P., Schrag, D. P., & Cane, M. A. (2004). Surface water mixing in the Solomon Sea as documented by a high-resolution coral ^{14}C record. *Journal of Climate*, 17(5), 1147-1156. doi:10.1175/1520-0442(2004)017<1147:Swmits>2.0.Co;2
- Guilderson, T. P., Schrag, D. P., Goddard, E., Kashgarian, M., Wellington, G. M., & Linsley, B. K. (2000). Southwest subtropical pacific surface water radiocarbon in a high-resolution coral record. *Radiocarbon*, 42(2), 249-256. doi:10.1017/s0033822200059051
- Guilderson, T. P., Schrag, D. P., Kashgarian, M., & Southon, J. (1998). Radiocarbon variability in the western equatorial Pacific inferred from a high-resolution coral record from Nauru Island. *Journal of Geophysical Research: Oceans*, 103(C11), 24641-24650. doi:10.1029/98jc02271
- Guzman, H. M., & Jarvis, K. E. (1996). Vanadium century record from Caribbean reef corals: A tracer of oil pollution in Panama. *Ambio*, 25(8), 523-526.
- Hammer, Ø., Harper, D. A., & Ryan, P. D. (2001). Past: Paleontological statistics software package for education and data analysis. *Palaeontologia Electronica*, 4(1), 9.
- Hart, S. R., & Cohen, A. L. (1996). An ion probe study of annual cycles of Sr/Ca and other trace elements in corals. *Geochimica Et Cosmochimica Acta*, 60(16), 3075-3084. doi:10.1016/0016-7037(96)00154-8
- Hathorne, E. C., Felis, T., James, R. H., & Thomas, A. (2011). Laser ablation ICP-MS screening of corals for diagenetically affected areas applied to Tahiti corals from the last deglaciation. *Geochimica Et Cosmochimica Acta*, 75(6), 1490-1506. doi:10.1016/j.gca.2010.12.011
- Hathorne, E. C., Felis, T., Suzuki, A., Kawahata, H., & Cabioch, G. (2013). Lithium in the aragonite skeletons of massive Porites corals: A new tool to reconstruct tropical sea surface temperatures. *Paleoceanography*, 28(1). doi:10.1029/2012pa002311
- Haynes, D., Brodie, J., Waterhouse, J., Bainbridge, Z., Bass, D., & Hart, B. (2007). Assessment of the water quality and ecosystem health of the Great Barrier Reef (Australia): Conceptual models. *Environmental Management*, 40(6), 993-1003. doi:10.1007/s00267-007-9009-y
- Hemming, N. G., & Hanson, G. N. (1992). Boron isotopic composition and concentration in modern marine carbonates. *Geochimica Et Cosmochimica Acta*, 56(1), 537-543. doi:10.1016/0016-7037(92)90151-8
- Hemming, N. G., Reeder, R. J., & Hanson, G. N. (1995). Mineral-fluid partitioning and isotopic fractionation of boron in synthetic calcium carbonate. *Geochimica Et Cosmochimica Acta*, 59(2), 371-379. doi:10.1016/0016-7037(95)00288-B

- Highsmith, R. C. (1979). Coral growth rates and environmental control of density banding. *Journal of Experimental Marine Biology and Ecology*, 37(2), 105-125. doi:10.1016/0022-0981(79)90089-3
- Hirabayashi, S., Yokoyama, Y., Suzuki, A., Miyairi, Y., & Aze, T. (2017a). Multidecadal oceanographic changes in the western Pacific detected through high-resolution bomb-derived radiocarbon measurements on corals. *Geochemistry, Geophysics, Geosystems*, 18(4), 1608-1617. doi:10.1002/2017gc006854
- Hirabayashi, S., Yokoyama, Y., Suzuki, A., Miyairi, Y., Aze, T., Siringan, F., & Maeda, Y. (2019). Insight into Western Pacific Circulation from South China Sea coral skeletal radiocarbon. *Radiocarbon*, 61(6), 1923-1937. doi:10.1017/Rdc.2019.145
- Hirabayashi, S., Yokoyama, Y., Suzuki, A., Miyairi, Y., Aze, T., Siringan, F. & Maeda, Y. (2017b). Radiocarbon variability recorded in coral skeletons from the northwest of Luzon Island, Philippines. *Geoscience Letters*, 4(1), 15. doi:10.1186/s40562-017-0081-8
- Hodell, D. A., Curtis, J. H., Jones, G. A., Higuera-Gundy, A., Brenner, M., Binford, M. W., & Dorsey, K. T. (1991). Reconstruction of Caribbean climate change over the past 10,500 years. *Nature*, 352(6338), 790-793. doi:10.1038/352790a0
- Hoegh-Guldberg, O. (1999). Climate change, coral bleaching and the future of the world's coral reefs. *Marine and Freshwater Research*, 50(8), 839-866. doi:10.1071/Mf99078
- Holcomb, M., DeCarlo, T. M., Gaetani, G. A., & McCulloch, M. (2016). Factors affecting B/Ca ratios in synthetic aragonite. *Chemical Geology*, 437, 67-76. doi:10.1016/j.chemgeo.2016.05.007
- Hook, M., & Tang, X. (2013). Depletion of fossil fuels and anthropogenic climate change: A review. *Energy Policy*, 52, 797-809. doi:10.1016/j.enpol.2012.10.046
- Hopkins, Z. R., & Blaney, L. (2016). An aggregate analysis of personal care products in the environment: Identifying the distribution of environmentally-relevant concentrations. *Environment International*, 92-93, 301-316. doi:10.1016/j.envint.2016.04.026
- Horn, I., Hinton, R. W., Jackson, S. E., & Longerich, H. P. (1997). Ultra-trace element analysis of NIST SRM 616 and 614 using laser ablation microprobe inductively coupled plasma mass spectrometry (LAM-ICP-MS): a comparison with secondary ion mass spectrometry (SIMS). *Geostandards Newsletter-the Journal of Geostandards and Geoanalysis*, 21(2), 191-203. doi:10.1111/j.1751-908X.1997.tb00670.x
- Houghton, R. A. (1999). The annual net flux of carbon to the atmosphere from changes in land use 1850-1990. *Tellus Series B-Chemical and Physical Meteorology*, 51(2), 298-313. doi:10.1034/j.1600-0889.1999.00013.x
- Houghton, R. A. (2003). Revised estimates of the annual net flux of carbon to the atmosphere from changes in land use and land management 1850-2000. *Tellus Series B-Chemical and Physical Meteorology*, 55(2), 378-390. doi:10.1034/j.1600-0889.2003.01450.x
- Howard, L. S., & Brown, B. E. (1984). Heavy-metals and reef corals. *Oceanography and Marine Biology*, 22, 195-210.
- Hsin, Y. C., Wu, C. R., & Chao, S. Y. (2012). An updated examination of the Luzon Strait transport. *Journal of Geophysical Research: Oceans*, 117. doi:ArtID C0302210.1029/2011jc007714
- Hu, J., Kawamura, H., Hong, H. J., & Qi, Y. (2000). A review on the currents in the South China Sea: seasonal circulation, South China Sea warm current and Kuroshio intrusion. *Journal of Oceanography*, 56(6), 607-624.
- Hu, J., Emile-Geay, J., Partin, J. (2017). Correlation-based interpretations of paleoclimatedata-where statistics meet past climates. *Earth Planet. Sci. Lett.* 459, 362-371. doi:10.1016/j.epsl.2016.11.048

- Hua, Q., & Barbetti, M. (2004). Review of tropospheric bomb ^{14}C data for carbon cycle modeling and age calibration purposes. *Radiocarbon*, 46(3), 1273-1298. doi:10.1017/s0033822200033142
- Hua, Q., Barbetti, M., & Rakowski, A. Z. (2013). Atmospheric radiocarbon for the period 1950-2010. *Radiocarbon*, 55(4), 2059-2072. doi:10.2458/azu_js_rc.v55i2.16177
- Huang, B. Y., Angel, W., Boyer, T., Cheng, L. J., Chepurin, G., Freeman, E., Liu, C.Y. & Zhang, H.M. (2018). Evaluating SST analyses with independent ocean profile observations. *Journal of Climate*, 31(13), 5015-5030. doi:10.1175/Jcli-D-17-0824.1
- Huh, Y., Chan, L. H., Zhang, L., & Edmond, J. M. (1998). Lithium and its isotopes in major world rivers: Implications for weathering and the oceanic budget. *Geochimica Et Cosmochimica Acta*, 62(12), 2039-2051. doi:10.1016/S0016-7037(98)00126-4
- Hunt, C. D. (1983). Variability in the benthic Mn flux in coastal marine ecosystems resulting from temperature and primary production 1. *Limnology and Oceanography*, 28(5), 913-923. doi:10.4319/lo.1983.28.5.0913
- Inoue, M., Hata, A., Suzuki, A., Nohara, M., Shikazono, N., Yim, W. W. S., Hantoro, W.S., Sun, D.H. & Kawahata, H. (2006). Distribution and temporal changes of lead in the surface seawater in the western Pacific and adjacent seas derived from coral skeletons. *Environmental Pollution*, 144(3), 1045-1052. doi:10.1016/j.envpol.2005.11.048
- Inoue, M., Ishikawa, D., Miyaji, T., Yamazaki, A., Suzuki, A., Yamano, H., Kawahata, H. & Watanabe, T. (2014). Evaluation of Mn and Fe in coral skeletons (*Porites* spp.) as proxies for sediment loading and reconstruction of 50 yrs of land use on Ishigaki Island, Japan. *Coral Reefs*, 33(2), 363-373. doi:10.1007/s00338-014-1128-3
- Inoue, M., Suwa, R., Suzuki, A., Sakai, K., & Kawahata, H. (2011). Effects of seawater pH on growth and skeletal U/Ca ratios of *Acropora digitifera* coral polyps. *Geophysical Research Letters*, 38. doi:ArtN L1280910.1029/2011gl047786
- Inoue, M., Suzuki, A., Nohara, M., Hibino, K., & Kawahata, H. (2007). Empirical assessment of coral Sr/Ca and Mg/Ca ratios as climate proxies using colonies grown at different temperatures. *Geophysical Research Letters*, 34(12). doi:ArtN L1261110.1029/2007gl029628
- Inoue, M., Suzuki, A., Nohara, M., Kan, H., Edward, A., & Kawahata, H. (2004). Coral skeletal tin and copper concentrations at Pohnpei, Micronesia: possible index for marine pollution by toxic anti-biofouling paints. *Environmental Pollution*, 129(3), 399-407. doi:10.1016/j.envpol.2003.11.009
- Jiang, Q. W., Cao, Z. M., Wang, D. R., Li, Y. C., Wu, Z. J., & Ni, J. Y. (2017). Coral Ba/Ca and Mn/Ca ratios as proxies of precipitation and terrestrial input at the eastern offshore area of Hainan Island. *Journal of Ocean University of China*, 16(6), 1072-1080. doi:10.1007/s11802-017-3265-0
- Jiang, W., Yu, K. F., Song, Y. X., Zhao, J. X., Feng, Y. X., Wang, Y. H., & Xu, S. D. (2017). Coral trace metal of natural and anthropogenic influences in the northern South China Sea. *Science of the Total Environment*, 607, 195-203. doi:10.1016/j.scitotenv.2017.06.105
- Jiang, W., Yu, K. F., Wang, N., Yang, H., Yang, H. D., Xu, S. D., Wei, C.S., Wang, S.P. & Wang, Y.H. (2020). Distribution coefficients of trace metals between modern coral-lattices and seawater in the northern South China Sea: Species and SST dependencies. *Journal of Asian Earth Sciences*, 187. doi:ARTN 10408210.1016/j.jseaes.2019.104082
- Johnson, F. (1965). Half-life of radiocarbon. *Science*, 149(3690), 1326. doi:10.1126/science.149.3690.1326

- Jones, R., Fisher, R., Stark, C., & Ridd, P. (2015). Temporal patterns in seawater quality from dredging in tropical environments. *Plos One*, 10(10). doi:ARTN e0137112/10.1371/journal.pone.0137112
- Jovanovic, B., & Guzman, H. M. (2014). Effects of titanium dioxide (TiO₂) nanoparticles on caribbean reef-building coral (*Montastraea faveolata*). *Environmental toxicology and chemistry*, 33(6), 1346-1353. doi:10.1002/etc.2560
- Jupiter, S., Roff, G., Marion, G., Henderson, M., Schrameyer, V., McCulloch, M., & Hoegh-Guldberg, O. (2008). Linkages between coral assemblages and coral proxies of terrestrial exposure along a cross-shelf gradient on the southern Great Barrier Reef. *Coral Reefs*, 27(4), 887-903. doi:10.1007/s00338-008-0422-3
- Kalin, M., Wheeler, W. N., & Meinrath, G. (2005). The removal of uranium from mining waste water using algal/microbial biomass. *Journal of Environmental Radioactivity*, 78(2), 151-177. doi:10.1016/j.jenvrad.2004.05.002
- Kawakubo, Y., Alibert, C., & Yokoyama, Y. (2017). A reconstruction of subtropical western North Pacific SST variability back to 1578, based on a Porites Coral Sr/Ca record from the northern Ryukyus, Japan. *Paleoceanography*, 32(12), 1352-1370. doi:10.1002/2017pa003203
- Kawakubo, Y., Yokoyama, Y., Suzuki, A., Okai, T., Alibert, C., Kinsley, L., & Eggins, S. (2014). Precise determination of Sr/Ca by laser ablation ICP-MS compared to ICP-AES and application to multi-century temperate corals. *Geochemical Journal*, 48(2), 145-152. doi:10.2343/geochemj.2.0295
- Kelly, A. E., Reuer, M. K., Goodkin, N. F., & Boyle, E. A. (2009). Lead concentrations and isotopes in corals and water near Bermuda, 1780-2000. *Earth and Planetary Science Letters*, 283(1-4), 93-100. doi:10.1016/j.epsl.2009.03.045
- Key, R. M. (1996). WOCE Pacific Ocean radiocarbon program. *Radiocarbon*, 38(3), 415-423. doi:10.1017/S003382220003006x
- Key, R. M., Quay, P. D., Jones, G. A., McNichol, A. P., vonReden, K. F., & Schneider, R. J. (1996). WOCE AMS radiocarbon 1: Pacific Ocean results (P6, P16 and P17). *Radiocarbon*, 38(3), 425-518. doi:10.1017/S0033822200030071
- Key, R. M., Quay, P. D., Schlosser, P., McNichol, A. P., von Reden, K. F., Schneider, R. J., Elder, K.L., Stuiver, M. & Ostlund, H.G. (2002). WOCE radiocarbon IV: Pacific Ocean results; P10, P13N, P14C, P18, P19 & S4P. *Radiocarbon*, 44(1), 239-392. doi:10.1017/S0033822200064845
- Kim, S. T., Mucci, A., & Taylor, B. E. (2007). Phosphoric acid fractionation factors for calcite and aragonite between 25 and 75 °C: Revisited. *Chemical Geology*, 246(3-4), 135-146. doi:10.1016/j.chemgeo.2007.08.005
- Kilbourne, K. H., Quinn, T. M., Guilderson, T. P., Webb, R. S., & Taylor, F. W. (2007). Decadal-to interannual-scale source water variations in the Caribbean Sea recorded by Puerto Rican coral radiocarbon. *Climate Dynamics*, 29(1), 51-62. doi:10.1007/s00382-007-0224-2
- Knutson, D. W., Smith, S. V., & Buddemeier, R. W. (1972). Coral chronometers: seasonal growth bands in reef corals. *Science*, 177(4045), 270-272. doi:10.1126/science.177.4045.270
- Konishi, K., Tanaka, T., & Sakanoue, M. (1981). Secular variation of radiocarbon concentrations in seawater: Sclerochronological approach. *Proceedings of the Fourth International Coral Reef Symposium*, 1, 181-185.
- Kroon, F. J., Berry, K. L. E., Brinkman, D. L., Kookana, R., Leusch, F. D. L., Melvin, S. D., Neale, P.A., Negri, A.P., Puotinen, M., Tsang, J.J., van de Merwe, J.P. & Williams, M. (2020). Sources, presence and potential effects of contaminants of emerging concern in

- the marine environments of the Great Barrier Reef and Torres Strait, Australia. *Science of the Total Environment*, 719. doi:ARTN 13514010.1016/j.scitotenv.2019.135140
- Kroon, F. J., Thorburn, P., Schaffelke, B., & Whitten, S. (2016). Towards protecting the Great Barrier Reef from land-based pollution. *Global Change Biology*, 22(6), 1985-2002. doi:10.1111/gcb.13262
- Kuffner, I. B., Jokiel, P. L., Rodgers, K. S., Andersson, A. J., & Mackenzie, F. T. (2012). An apparent "vital effect" of calcification rate on the Sr/Ca temperature proxy in the reef coral *Montipora capitata*. *Geochemistry, Geophysics, Geosystems*, 13. doi:Artn Q0800410.1029/2012gc004128
- Kumamoto, Y., Murata, A., Kawano, T., Watanabe, S., & Fukasawa, M. (2013). Decadal changes in the bomb-produced radiocarbon in the Pacific Ocean from the 1990s to 2000s. *Radiocarbon*, 55(2-3), 1641-1650. doi:10.1017/S0033822200048554
- Labille, J., Slomberg, D., Catalano, R., Robert, S., Apers-Tremelo, M. L., Boudenne, J. L., Manasfi, T. & Radakovitch, O. (2020). Assessing UV filter inputs into beach waters during recreational activity: A field study of three French Mediterranean beaches from consumer survey to water analysis. *Science of the Total Environment*, 706. doi:ARTN 13601010.1016/j.scitotenv.2019.136010
- Lashof, D. A., & Ahuja, D. R. (1990). Relative contributions of greenhouse gas emissions to global warming. *Nature*, 344(6266), 529-531. doi:10.1038/344529a0
- Lau, K. M. W. (1978). Experiment with a simple ocean-atmosphere climate model: The role of the ocean in the global climate. *Journal of the Atmospheric Sciences*, 35(7), 1144-1163. doi:10.1175/1520-0469(1978)035<1144:Ewasoa>2.0.Co;2
- LaVigne, M., Grotoli, A. G., Palardy, J. E., & Sherrell, R. M. (2016). Multi-colony calibrations of coral Ba/Ca with a contemporaneous in situ seawater barium record. *Geochimica et Cosmochimica Acta*, 179, 203-216. Doi:10.1016/j.gca.2015.12.038
- Lea, D. W., Shen, G. T., & Boyle, E. A. (1989). Coralline barium records temporal variability in equatorial Pacific upwelling. *Nature*, 340(6232), 373-376. doi:10.1038/340373a0
- Lee, K., Kim, T. W., Byrne, R. H., Millero, F. J., Feely, R. A., & Liu, Y. M. (2010). The universal ratio of boron to chlorinity for the North Pacific and North Atlantic oceans. *Geochimica Et Cosmochimica Acta*, 74(6), 1801-1811. doi:10.1016/j.gca.2009.12.027
- Leonard, N. D., Welsh, K. J., Nguyen, A. D., Sadler, J., Pandolfi, J. M., Clark, T. R., Zhao, J.X., Feng, Y.X. & Webb, G.E. (2019). High resolution geochemical analysis of massive *Porites* spp. corals from the Wet Tropics, Great Barrier Reef: rare earth elements, yttrium and barium as indicators of terrigenous input. *Marine Pollution Bulletin*, 149. doi:UNSP 11063410.1016/j.marpolbul.2019.110634
- Levin, I., Kromer, B., Schochfischer, H., Bruns, M., Munnich, M., Berdau, D., Vogel, J. C. & Munnich, K. O. (1985). 25 years of tropospheric ¹⁴C observations in central-Europe. *Radiocarbon*, 27(1), 1-19. doi:10.1017/s0033822200006895
- Lewis, S. E., Brodie, J. E., McCulloch, M. T., Mallela, J., Jupiter, S. D., Williams, H. S., Lough, J.M. & Matson, E.G. (2012). An assessment of an environmental gradient using coral geochemical records, Whitsunday Islands, Great Barrier Reef, Australia. *Marine Pollution Bulletin*, 65(4-9), 306-319. doi:10.1016/j.marpolbul.2011.09.030
- Lewis, S. E., Lough, J. M., Cantin, N. E., Matson, E. G., Kinsley, L., Bainbridge, Z. T., & Brodie, J. E. (2018). A critical evaluation of coral Ba/Ca, Mn/Ca and Y/Ca ratios as indicators of terrestrial input: New data from the Great Barrier Reef, Australia. *Geochimica Et Cosmochimica Acta*, 237, 131-154. doi:10.1016/j.gca.2018.06.017
- Lewis, S. E., Shields, G. A., Kamber, B. S., & Lough, J. M. (2007). A multi-trace element coral record of land-use changes in the Burdekin River catchment, NE Australia.

- Palaeogeography, Palaeoclimatology, Palaeoecology*, 246(2-4), 471-487. doi:10.1016/j.palaeo.2006.10.021
- Li, Y. H., & Chan, L. H. (1979). Desorption of Ba and ^{226}Ra from river-borne sediments in the Hudson estuary. *Earth and Planetary Science Letters*, 43(3), 343-350. doi:10.1016/0012-821x(79)90089-X
- Linn, L. J., Delaney, M. L., & Druffel, E. R. M. (1990). Trace metals in contemporary and seventeenth-century Galapagos coral: Records of seasonal and annual variations. *Geochimica Et Cosmochimica Acta*, 54(2), 387-394. doi:10.1016/0016-7037(90)90327-H
- Liu, Y., Li, X. H., Zeng, Z., Yu, H. M., Huang, F., Felis, T., & Shen, C. C. (2019). Annually-resolved coral skeletal $\delta^{138/134}\text{Ba}$ records: A new proxy for oceanic Ba cycling. *Geochimica Et Cosmochimica Acta*, 247, 27-39. doi:10.1016/j.gca.2018.12.022
- Livingston, H. D. (1971). Trace element concentrations in some modern corals. *Limnology and Oceanography*, 16(5), 786-796. doi:10.4319/lo.1971.16.5.0786
- Lough, J. M. (2007). Tropical river flow and rainfall reconstructions from coral luminescence: Great Barrier Reef, Australia. *Paleoceanography*, 22(2). doi:Artn Pa221810.1029/2006pa001377
- Lough, J. M. (2010). Climate records from corals. *Wiley Interdisciplinary Reviews-Climate Change*, 1(3), 318-331. doi:10.1002/wcc.39
- Lough, J. M., & Barnes, D. J. (1990a). Intra-annual timing of density band formation of Porites coral from the central Great Barrier Reef. *Journal of Experimental Marine Biology and Ecology*, 135(1), 35-57. doi:10.1016/0022-0981(90)90197-K
- Lough, J. M., & Barnes, D. J. (1990b). Measurement of density in slices of coral skeleton: effect of densitometer beam diameter. *Journal of Experimental Marine Biology and Ecology*, 143(1-2), 91-99. doi:10.1016/0022-0981(90)90113-Q
- Lough, J. M., Anderson, K. D., & Hughes, T. P. (2018). Increasing thermal stress for tropical coral reefs: 1871-2017. *Scientific Reports*, 8. doi:ARTN 607910.1038/s41598-018-24530-9
- Lough, J. M., Barnes, D. J., & McAllister, F. A. (2002). Luminescent lines in corals from the Great Barrier Reef provide spatial and temporal records of reefs affected by land runoff. *Coral Reefs*, 21(4), 333-343. doi:10.1007/s00338-002-0253-6
- Lough, J. M., Cantin, N. E., Fallon, S., & Wu, Y. (2020). Summary Report: Potential of coral geochemical Tracers to record environmental histories within the Fitzroy River Basin. *Report prepared for BHP Billiton*. Australian Institute of Marine Science, Townsville, Qld. (163 pp)
- Lough, J. M., Lewis, S. E., & Cantin, N. E. (2015). Freshwater impacts in the central Great Barrier Reef: 1648-2011. *Coral Reefs*, 34(3), 739-751. doi:10.1007/s00338-015-1297-8
- Luo, Y. R., & Byrne, R. H. (2004). Carbonate complexation of yttrium and the rare earth elements in natural waters. *Geochimica Et Cosmochimica Acta*, 68(4), 691-699. doi:10.1016/S0016-7037(03)00495-2
- Macdonald, A. M., & Wunsch, C. (1996). An estimate of global ocean circulation and heat fluxes. *Nature*, 382(6590), 436-439. doi:10.1038/382436a0
- Marchitto, T. M., Bryan, S. P., Doss, W., McCulloch, M. T., & Montagna, P. (2018). A simple biomineralization model to explain Li, Mg, and Sr incorporation into aragonitic foraminifera and corals. *Earth and Planetary Science Letters*, 481, 20-29. doi:10.1016/j.epsl.2017.10.022

- Marland, G., Rotty, R. M., & Treat, N. L. (1985). CO₂ from fossil fuel burning: Global distribution of emissions. *Tellus Series B-Chemical and Physical Meteorology*, 37(4-5), 243-258. doi:10.3402/tellusb.v37i4-5.15028
- Marriott, C. S., Henderson, G. M., Belshaw, N. S., & Tudhope, A. W. (2004). Temperature dependence of $\delta^7\text{Li}$, $\delta^{44}\text{Ca}$ and Li/Ca during growth of calcium carbonate. *Earth and Planetary Science Letters*, 222(2), 615-624. doi:10.1016/j.epsl.2004.02.031
- Marriott, C. S., Henderson, G. M., Crompton, R., Staubwasser, M., & Shaw, S. (2004). Effect of mineralogy, salinity, and temperature on Li/Ca and Li isotope composition of calcium carbonate. *Chemical Geology*, 212(1-2), 5-15. doi:10.1016/j.chemgeo.2004.08.002
- Marshall, J. F., & McCulloch, M. T. (2002). An assessment of the Sr/Ca ratio in shallow water hermatypic corals as a proxy for sea surface temperature. *Geochimica Et Cosmochimica Acta*, 66(18), 3263-3280. doi:Pii S0016-7037(02)00926-2
- Mavromatis, V., Montouillout, V., Noireaux, J., Gaillardet, J., & Schott, J. (2015). Characterization of boron incorporation and speciation in calcite and aragonite from co-precipitation experiments under controlled pH, temperature and precipitation rate. *Geochimica Et Cosmochimica Acta*, 150, 299-313. doi:10.1016/j.gca.2014.10.024
- McConnaughey, T. (1989). ¹³C and ¹⁸O isotopic disequilibrium in biological carbonates: II. In vitro simulation of kinetic isotope effects. *Geochimica Et Cosmochimica Acta*, 53(1), 163-171. doi:10.1016/0016-7037(89)90283-4
- McCulloch, M. T., D'Olivo, J. P., Falter, J., Holcomb, M., & Trotter, J. A. (2017). Coral calcification in a changing World and the interactive dynamics of pH and DIC upregulation. *Nature Communications*, 8. doi:ARTN 1568610.1038/ncomms15686
- McCulloch, M. T., Fallon, S., & Wyndham, T. (2002). Geochemical tracing of human impacts on coral reefs. *Geochimica Et Cosmochimica Acta*, 66(15a), A499-A499.
- McCulloch, M. T., Gagan, M. K., Mortimer, G. E., Chivas, A. R., & Isdale, P. J. (1994). A high-resolution Sr/Ca and $\delta^{18}\text{O}$ coral record from the Great Barrier Reef, Australia, and the 1982-1983 El Niño. *Geochimica Et Cosmochimica Acta*, 58(12), 2747-2754. doi:10.1016/0016-7037(94)90142-2
- McCulloch, M. T., Tudhope, A. W., Esat, T. M., Mortimer, G. E., Chappell, J., Pillans, B., Chivas, A.R. & Omura, A. (1999). Coral record of equatorial sea-surface temperatures during the penultimate deglaciation at Huon Peninsula. *Science*, 283(5399), 202-204. doi:10.1126/science.283.5399.202
- McCulloch, M., Fallon, S., Wyndham, T., Hendy, E., Lough, J., & Barnes, D. (2003). Coral record of increased sediment flux to the inner Great Barrier Reef since European settlement. *Nature*, 421(6924), 727-730. doi:10.1038/nature01361
- Meibom, A., Cuif, J. P., Hillion, F. O., Constantz, B. R., Juillet-Leclerc, A., Dauphin, Y., Watanabe, T. & Dunbar, R.B. (2004). Distribution of magnesium in coral skeleton. *Geophysical Research Letters*, 31(23). doi:Artn L2330610.1029/2004gl021313
- Meinshausen, M., Meinshausen, N., Hare, W., Raper, S. C. B., Frieler, K., Knutti, R., . Frame, D.J. & Allen, M.R. (2009). Greenhouse-gas emission targets for limiting global warming to 2 °C. *Nature*, 458(7242), 1158-U1196. doi:10.1038/nature08017
- Min, G. R., Edwards, R. L., Taylor, F. W., Recy, J., Gallup, C. D., & Beck, J. W. (1995). Annual cycles of U/Ca in coral skeletons and U/Ca thermometry. *Geochimica Et Cosmochimica Acta*, 59(10), 2025-2042.
- Mitsuguchi, T., Dang, P. X., Kitagawa, H., Yoneda, M., & Shibata, Y. (2007). Tropical South China Sea surface ¹⁴C record in an annually-banded coral. *Radiocarbon*, 49(2), 905-914. doi:10.1017/s0033822200042776

- Mitsuguchi, T., Matsumoto, E., & Uchida, T. (2003). Mg/Ca and Sr/Ca ratios of Porites coral skeleton: Evaluation of the effect of skeletal growth rate. *Coral Reefs*, 22(4), 381-388. doi:10.1007/s00338-003-0326-1
- Mitsuguchi, T., Matsumoto, E., Abe, O., Uchida, T., & Isdale, P. J. (1996). Mg/Ca thermometry in coral-skeletons. *Science*, 274(5289), 961-963. doi:10.1126/science.274.5289.961
- Moller, P., Morteani, G., & Dulski, P. (2003). Anomalous gadolinium, cerium, and yttrium contents in the adige and isarco river waters and in the water of their tributaries (Provinces Trento and Bolzano/Bozen, NE Italy). *Acta Hydrochimica Et Hydrobiologica*, 31(3), 225-239. doi:10.1002/aheh.200300492
- Montaggioni, L. F., Le Cornec, F., Corregge, T., & Cabioch, G. (2006). Coral barium/calcium record of mid-Holocene upwelling activity in New Caledonia, South-West Pacific. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 237(2-4), 436-455. doi:10.1016/j.palaeo.2005.12.018
- Montaggioni, L. F., Le Cornec, F., Corregge, T., & Cabioch, G. (2006). Coral barium/calcium record of mid-Holocene upwelling activity in New Caledonia, South-West Pacific. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 237(2-4), 436-455. doi:10.1016/j.palaeo.2005.12.018
- Montagna, P., McCulloch, M., Douville, E., Lopez Correa, M., Trotter, J., Rodolfo-Metalpa, R., Dissard, D., Ferrier-Pages, C., Frank, N., Freiwald, A., Goldstein, S., Mazzoli, C., Reynaud, S., Ruggeberg, A., Russo, S. & Taviani, M. (2014). Li/Mg systematics in scleractinian corals: Calibration of the thermometer. *Geochimica Et Cosmochimica Acta*, 132, 288-310. doi:10.1016/j.gca.2014.02.005
- Morris, A. W. (1974). Seasonal variation of dissolved metals in inshore waters of the Menai Straits. *Marine Pollution Bulletin*, 5(4), 54-59. doi:10.1016/0025-326x(74)90113-1
- Moyer, R. P., Grottoli, A. G., & Olesik, J. W. (2012). A multiproxy record of terrestrial inputs to the coastal ocean using minor and trace elements (Ba/Ca, Mn/Ca, Y/Ca) and carbon isotopes ($\delta^{13}\text{C}$, $\Delta^{14}\text{C}$) in a nearshore coral from Puerto Rico. *Paleoceanography*, 27. doi:10.1029/2011pa002249
- Nan, F., Xue, H. J., & Yu, F. (2015). Kuroshio intrusion into the South China Sea: A review. *Progress in Oceanography*, 137, 314-333. doi:10.1016/j.pocean.2014.05.012
- Neelin, J. D., Battisti, D. S., Hirst, A. C., Jin, F. F., Wakata, Y., Yamagata, T., & Zebiak, S. E. (1998). ENSO theory. *Journal of Geophysical Research: Oceans*, 103(C7), 14261-14290. doi:10.1029/97jc03424
- Neil, D. T., Orpin, A. R., Ridd, E. V., & Yu, B. F. (2002). Sediment yield and impacts from river catchments to the Great Barrier Reef lagoon. *Marine and Freshwater Research*, 53(4), 733-752. doi:10.1071/Mf00151
- Newman, M., Alexander, M. A., Ault, T. R., Cobb, K. M., Deser, C., Di Lorenzo, E., Mantua, N.J., Miller, A.J., Minobe, S., Nakamura, H., Schneider, N., Vimont, D.J., Phillips, A.S., Scott, J.D. & Smith, C.A. (2016). The Pacific decadal oscillation, revisited. *Journal of Climate*, 29(12), 4399-4427. doi:10.1175/Jcli-D-15-0508.1
- Nguyen, A. D., Zhao, J. X., Feng, Y. X., Hu, W. P., Yu, K. F., Gasparon, M., Pham, T.B. & Clark, T.R. (2013). Impact of recent coastal development and human activities on Nha Trang Bay, Vietnam: evidence from a Porites lutea geochemical record. *Coral Reefs*, 32(1), 181-193. doi:10.1007/s00338-012-0962-4
- Nydal, R., & Lovseth, K. (1983). Tracing bomb ^{14}C in the atmosphere 1962-1980. *Journal of Geophysical Research: Oceans*, 88(C6), 3621-3642. doi:10.1029/JC088iC06p03621
- Oke, P. R., Roughan, M., Cetina-Heredia, P., Pilo, G. S., Ridgway, K. R., Rykova, T., Archer, M.R., Coleman, R.C., Kerry, C.G., Rocha, C., Schaeffer, A. & Vitarelli, E. (2019). Revisiting the circulation of the East Australian Current: Its path, separation, and eddy

- field. *Progress in Oceanography*, 176. doi:ARTN 10213910.1016/j.pocean.2019.102139
- Okumura, M., & Kitano, Y. (1986). Coprecipitation of alkali-metal Ions with calcium carbonate. *Geochimica Et Cosmochimica Acta*, 50(1), 49-58. doi:10.1016/0016-7037(86)90047-5
- Ourbak, T., Correge, T., Malaize, B., Le Cornec, F., Charlier, K., & Peypouquet, J. P. (2006). A high-resolution investigation of temperature, salinity, and upwelling activity proxies in corals. *Geochemistry Geophysics Geosystems*, 7. doi:Artn Q0301310.1029/2005gc001064
- Paillard, D., Labeyrie, L., & Yiou, P. (1996). Macintosh program performs time-series analysis. *Eos, Transactions American Geophysical Union*, 77(39), 379-379. doi:10.1029/96eo00259
- Parker, D. E., Basnett, T. A., Brown, S. J., Gordon, M., Horton, E. B., & Rayner, N. A. (2000). Climate observations-the instrumental record. *Space Science Reviews*, 94(1-2), 309-320. doi:10.1023/A:1026787727530
- Pearce, N. J. G., Perkins, W. T., Westgate, J. A., Gorton, M. P., Jackson, S. E., Neal, C. R., & Chenery, S. P. (1997). A compilation of new and published major and trace element data for NIST SRM 610 and NIST SRM 612 glass reference materials. *Geostandards Newsletter-the Journal of Geostandards and Geoanalysis*, 21(1), 115-144. doi:10.1111/j.1751-908X.1997.tb00538.x
- Peng, Z., Liu, J., Zhou, C., Nie, B., & Chen, T. (2006). Temporal variations of heavy metals in coral *Porites lutea* from Guangdong Province, China: Influences from industrial pollution, climate and economic factors. *Chinese Journal of Geochemistry*, 25(2), 132-138. doi:10.1007/bf02872172
- Pfeiffer, M., Dullo, W. C., Zinke, J., & Garbe-Schonberg, D. (2009). Three monthly coral Sr/Ca records from the Chagos Archipelago covering the period of 1950-1995 AD: reproducibility and implications for quantitative reconstructions of sea surface temperature variations. *International Journal of Earth Sciences*, 98(1), 53-66. doi:10.1007/s00531-008-0326-z
- Pierce, D. W., Barnett, T. P., Schneider, N., Saravanan, R., Dommenges, D., & Latif, M. (2001). The role of ocean dynamics in producing decadal climate variability in the North Pacific. *Climate Dynamics*, 18(1-2), 51-70. doi:10.1007/s003820100158
- Politi, Y., Batchelor, D. R., Zaslansky, P., Chmelka, B. F., Weaver, J. C., Sagi, I., Weiner, S., & Addadi, L. (2010). Role of magnesium ion in the stabilization of biogenic amorphous calcium carbonate: A structure-function investigation. *Chemistry of Materials*, 22(1), 161-166. doi:10.1021/cm902674h
- Pravalié, R. (2014). Nuclear weapons tests and environmental consequences: A global perspective. *Ambio*, 43(6), 729-744. doi:10.1007/s13280-014-0491-1
- Prouty, N. G., Field, M. E., Stock, J. D., Jupiter, S. D., & McCulloch, M. (2010). Coral Ba/Ca records of sediment input to the fringing reef of the southshore of Moloka'i, Hawai'i over the last several decades. *Marine Pollution Bulletin*, 60(10), 1822-1835. doi:10.1016/j.marpolbul.2010.05.024
- Qiu, B., & Lukas, R. (1996). Seasonal and interannual variability of the North Equatorial Current, the Mindanao Current, and the Kuroshio along the Pacific western boundary. *Journal of Geophysical Research-Oceans*, 101(C5), 12315-12330. doi:10.1029/95jc03204
- Qu, T. D., Du, Y., & Sasaki, H. (2006). South China Sea throughflow: A heat and freshwater conveyor. *Geophysical Research Letters*, 33(23). doi:Artn L2361710.1029/2006gl028350

- Qu, T. D., Song, Y. T., & Yamagata, T. (2009). An introduction to the South China Sea throughflow: Its dynamics, variability, and application for climate. *Dynamics of Atmospheres and Oceans*, 47(1-3), 3-14. doi:10.1016/j.dynatmoce.2008.05.001
- Quinn, T. M., & Sampson, D. E. (2002). A multiproxy approach to reconstructing sea surface conditions using coral skeleton geochemistry. *Paleoceanography*, 17(4). doi:Artn 106210.1029/2000pa000528
- Raddatz, J., Liebetrau, V., Ruggeberg, A., Hathorne, E., Krabbenhoft, A., Eisenhauer, A., Eisenhauer, A., Bohm, F., Vollstaedt, H., Fietzke, J., Lopez Correa, M., Freiwald, A. & Dullo, W.C. (2013). Stable Sr-isotope, Sr/Ca, Mg/Ca, Li/Ca and Mg/Li ratios in the scleractinian cold-water coral *Lophelia pertusa*. *Chemical Geology*, 352, 143-152. doi:10.1016/j.chemgeo.2013.06.013
- Raddatz, J., Ruggeberg, A., Fogel, S., Hathorne, E. C., Liebetrau, V., Eisenhauer, A., & Dullo, W. C. (2014). The influence of seawater pH on U/Ca ratios in the scleractinian cold-water coral *Lophelia pertusa* (vol 11, pg 1863, 2014). *Biogeosciences*, 11(8), 2373-2373. doi:10.5194/bg-11-2373-2014
- Rahmstorf, S. (2002). Ocean circulation and climate during the past 120,000 years. *Nature*, 419(6903), 207-214. doi:10.1038/nature01090
- Ramos, R. D., Goodkin, N. F., Druffel, E. R. M., Fan, T. Y., & Siringan, F. P. (2019). Interannual coral $\Delta^{14}\text{C}$ records of surface water exchange across the Luzon Strait. *Journal of Geophysical Research: Oceans*, 124(1), 491-505. doi:10.1029/2018jc014735
- Ramos, R. D., Goodkin, N. F., Siringan, F. P., & Hughen, K. A. (2019). Coral records of temperature and salinity in the Tropical Western Pacific reveal influence of the Pacific Decadal Oscillation since the late nineteenth century. *Paleoceanography and Paleoclimatology*, 34(8), 1344-1358. doi:10.1029/2019pa003684
- Raval, A., & Ramanathan, V. (1989). Observational determination of the greenhouse effect. *Nature*, 342(6251), 758-761. doi:10.1038/342758a0
- Rayner, N. A., Parker, D. E., Horton, E. B., Folland, C. K., Alexander, L. V., Rowell, D. P., Kent, E.C. & Kaplan, A. (2003). Global analyses of sea surface temperature, sea ice, and night marine air temperature since the late nineteenth century. *Journal of Geophysical Research-Atmospheres*, 108(D14). doi:Artn 440710.1029/2002jd002670
- Reeder, R. J., Nugent, M., Lamble, G. M., Tait, C. D., & Morris, D. E. (2000). Uranyl incorporation into calcite and aragonite: XAFS and luminescence studies. *Environmental Science & Technology*, 34(4), 638-644. doi:10.1021/es990981j
- Reynaud, S., Ferrier-Pages, C., Meibom, A., Mostefaoui, S., Mortlock, R., Fairbanks, R., & Allemand, D. (2007). Light and temperature effects on Sr/Ca and Mg/Ca ratios in the scleractinian coral *Acropora* sp. *Geochimica Et Cosmochimica Acta*, 71(2), 354-362. doi:10.1016/j.gca.2006.09.009
- Reynolds, R. W., Smith, T. M., Liu, C., Chelton, D. B., Casey, K. S., & Schlax, M. G. (2007). Daily high-resolution-blended analyses for sea surface temperature. *Journal of Climate*, 20(22), 5473-5496. doi:10.1175/2007jcli1824.1
- Rodriguez-Ramirez, A., Grove, C. A., Zinke, J., Pandolfi, J. M., & Zhao, J. X. (2014). Coral luminescence identifies the Pacific Decadal Oscillation as a primary driver of river runoff variability impacting the southern Great Barrier Reef. *Plos One*, 9(1). doi:ARTN e8430510.1371/journal.pone.0084305
- Ross, C. L., DeCarlo, T. M., & McCulloch, M. T. (2019). Calibration of Sr/Ca, Li/Mg and Sr-U paleothermometry in branching and foliose corals. *Paleoceanography and Paleoclimatology*, 34(8), 1271-1291. doi:10.1029/2018pa003426

- Rossoll, D., Bermudez, R., Hauss, H., Schulz, K. G., Riebesell, U., Sommer, U., & Winder, M. (2012). Ocean acidification-induced food quality deterioration constrains trophic transfer. *Plos One*, 7(4). doi:ARTN e3473710.1371/journal.pone.0034737
- Rotmann, S., & Thomas, S. (2012). Coral tissue thickness as a bioindicator of mine-related turbidity stress on coral reefs at Lihir Island, Papua New Guinea. *Oceanography*, 25(4), 52-63. doi:10.5670/oceanog.2012.67
- Saenger, C., Cohen, A. L., Oppo, D. W., & Hubbard, D. (2008). Interpreting sea surface temperature from strontium/calcium ratios in *Montastrea* corals: Link with growth rate and implications for proxy reconstructions. *Paleoceanography*, 23(3). doi:Artn Pa310210.1029/2007pa001572
- Saha, N., Rodriguez-Ramirez, A., Nguyen, A. D., Clark, T. R., Zhao, J. X., & Webb, G. E. (2018). Seasonal to decadal scale influence of environmental drivers on Ba/Ca and Y/Ca in coral aragonite from the southern Great Barrier Reef. *Science of the Total Environment*, 639, 1099-1109. doi:10.1016/j.scitotenv.2018.05.156
- Saha, N., Webb, G. E., & Zhao, J. X. (2016). Coral skeletal geochemistry as a monitor of inshore water quality. *Science of the Total Environment*, 566, 652-684. doi:10.1016/j.scitotenv.2016.05.066
- Saha, N., Webb, G. E., Christy, A. G., & Zhao, J. X. (2019). Vanadium in the massive coral *Porites*: A potential proxy for historical wood clearing and burning. *Earth and Planetary Science Letters*, 527. doi:ARTN 11579310.1016/j.epsl.2019.115793
- Saha, N., Webb, G. E., Zhao, J. X., Leonard, N. D., & Nguyen, A. D. (2018). Influence of marine biochemical cycles on seasonal variation of Ba/Ca in the near-shore coral *Cyphastrea*, Rat Island, southern Great Barrier Reef. *Chemical Geology*, 499, 71-83. doi:10.1016/j.chemgeo.2018.09.005
- Saha, N., Webb, G. E., Zhao, J. X., Nguyen, A. D., Lewis, S. E., & Lough, J. M. (2019). Coral-based high-resolution rare earth element proxy for terrestrial sediment discharge affecting coastal seawater quality, Great Barrier Reef. *Geochimica Et Cosmochimica Acta*, 254, 173-191. doi:10.1016/j.gca.2019.04.004
- Sadler, J., Webb, G.E., Nothdurft, L.D. and Dechnik, B., 2014. Geochemistry-based coral palaeoclimate studies and the potential of 'non-traditional'(non-massive *Porites*) corals: Recent developments and future progression. *Earth-Science Reviews*, 139, pp.291-316. doi:10.1016/j.earscirev.2014.10.002
- Sayani, H. R., Cobb, K. M., DeLong, K., Hitt, N. T., & Druffel, E. R. M. (2019). Intercolony $\delta^{18}\text{O}$ and Sr/Ca variability among *Porites* spp. corals at Palmyra Atoll: Toward more robust coral-based estimates of climate. *Geochemistry, Geophysics, Geosystems*, 20(11), 5270-5284. doi:10.1029/2019gc008420
- Schneider, N. (1998). The Indonesian Throughflow and the global climate system. *Journal of Climate*, 11(4), 676-689. doi:10.1175/1520-0442(1998)011<0676:Titatg>2.0.Co;2
- Schneider, N., & Cornuelle, B. D. (2005). The forcing of the Pacific decadal oscillation. *Journal of Climate*, 18(21), 4355-4373. doi:10.1175/Jcli3527.1
- Schneider, S. H. (1989). The greenhouse-effect: science and policy. *Science*, 243(4892), 771-781. doi:10.1126/science.243.4892.771
- Schoemann, V., de Baar, H. J. W., de Jong, J. T. M., & Lancelot, C. (1998). Effects of phytoplankton blooms on the cycling of manganese and iron in coastal waters. *Limnology and Oceanography*, 43(7), 1427-1441. doi:10.4319/lo.1998.43.7.1427
- Schrag, D. P. (1999). Rapid analysis of high-precision Sr/Ca ratios in corals and other marine carbonates. *Paleoceanography*, 14(2), 97-102. doi:10.1029/1998pa900025

- Shannon, R. D. (1976). Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallographica Section A*, 32(5), 751-767. doi:10.1107/S0567739476001551
- Shen, G. T. (1986). Lead and cadmium geochemistry of corals: reconstruction of historic perturbations in the upper ocean (Doctoral dissertation, Massachusetts Institute of Technology).
- Shen, G. T., & Boyle, E. A. (1988). Determination of lead, cadmium and other trace-metals in annually-banded corals. *Chemical Geology*, 67(1-2), 47-62. doi:10.1016/0009-2541(88)90005-8
- Shen, G. T., & Dunbar, R. B. (1995). Environmental controls on uranium in reef corals. *Geochimica Et Cosmochimica Acta*, 59(10), 2009-2024. doi:10.1016/0016-7037(95)00123-9
- Shen, G. T., Campbell, T. M., Dunbar, R. B., Wellington, G. M., Colgan, M. W., & Glynn, P. W. (1991). Paleochemistry of manganese in corals from the Galapagos Islands. *Coral Reefs*, 10(2), 91-100. doi:10.1007/Bf00571827
- Shen, G. T., Cole, J. E., Lea, D. W., Linn, L. J., McConnaughey, T. A., & Fairbanks, R. G. (1992). Surface ocean variability at Galapagos from 1936-1982: calibration of geochemical tracers in corals. *Paleoceanography*, 7(5), 563-588. doi:10.1029/92pa01825
- Shi, Q., Yu, K. F., Chen, T. R., Zhang, H. L., Zhao, M. X., & Yan, H. Q. (2012). Two centuries-long records of skeletal calcification in massive Porites colonies from Meiji Reef in the southern South China Sea and its responses to atmospheric CO₂ and seawater temperature. *Science China-Earth Sciences*, 55(1), 1-12. doi:10.1007/s11430-011-4320-0
- Sholkovitz, E. R., & Elderfield, H. (1988). Cycling of dissolved rare earth elements in Chesapeake Bay. *Global Biogeochemical Cycles*, 2(2), 157-176. doi:10.1029/GB002i002p00157
- Sholkovitz, E., & Shen, G. T. (1995). The incorporation of rare earth elements in modern coral. *Geochimica Et Cosmochimica Acta*, 59(13), 2749-2756. doi:10.1016/0016-7037(95)00170-5
- Sinclair, D. J. (2005a). Correlated trace element "vital effects" in tropical corals: A new geochemical tool for probing biomineralization. *Geochimica Et Cosmochimica Acta*, 69(13), 3265-3284. doi:10.1016/j.gca.2005.02.030
- Sinclair, D. J. (2005b). Non-river flood barium signals in the skeletons of corals from coastal Queensland, Australia. *Earth and Planetary Science Letters*, 237(3-4), 354-369. doi:10.1016/j.epsl.2005.06.039
- Sinclair, D. J. (2015). RBME coral temperature reconstruction: An evaluation, modifications, and recommendations. *Geochimica Et Cosmochimica Acta*, 154, 66-80. doi:10.1016/j.gca.2015.01.006
- Sinclair, D. J., & McCulloch, M. T. (2004). Corals record low mobile barium concentrations in the Burdekin River during the 1974 flood: evidence for limited Ba supply to rivers?. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 214(1-2), 155-174. doi:10.1016/j.palaeo.2004.07.028
- Sinclair, D. J., Kinsley, L. P. J., & McCulloch, M. T. (1998). High resolution analysis of trace elements in corals by laser ablation ICP-MS. *Geochimica Et Cosmochimica Acta*, 62(11), 1889-1901. doi:10.1016/S0016-7037(98)00112-4
- Sinclair, D. J., Williams, B., & Risk, M. (2006). A biological origin for climate signals in corals- Trace element "vital effects" are ubiquitous in Scleractinian coral skeletons. *Geophysical Research Letters*, 33(17). doi:ArtId1770710.1029/2006gl027183

- Smith, J. E., Risk, M. J., Schwarcz, H. P., & McConnaughey, T. A. (1997). Rapid climate change in the North Atlantic during the Younger Dryas recorded by deep-sea corals. *Nature*, 386(6627), 818-820. doi:10.1038/386818a0
- Smith, S. V., Buddemeier, R. W., Redalje, R. C., & Houck, J. E. (1979). Strontium-calcium thermometry in coral skeletons. *Science*, 204(4391), 404-407. doi:10.1126/science.204.4391.404
- Soeyanto, E., Guo, X. Y., Ono, J., & Miyazawa, Y. (2014). Interannual variations of Kuroshio transport in the East China Sea and its relation to the Pacific Decadal Oscillation and mesoscale eddies. *Journal of Geophysical Research: Oceans*, 119(6), 3595-3616. doi:10.1002/2013jc009529
- Song, S. H., Peng, Z. C., Zhou, W. J., Liu, W. G., Liu, Y., & Chen, T. G. (2012). Variation of the winter monsoon in South China Sea over the past 183 years: Evidence from oxygen isotopes in coral. *Global and Planetary Change*, 98-99, 131-138. doi:10.1016/j.gloplacha.2012.08.013
- Song, Y. X., Yu, K. F., Zhao, J. X., Feng, Y. X., Shi, Q., Zhang, H. L., Ayoko, G.A. & Frost, R.L. (2014). Past 140-year environmental record in the northern South China Sea: Evidence from coral skeletal trace metal variations. *Environmental Pollution*, 185, 97-106. doi:10.1016/j.envpol.2013.10.024
- Sowers, T., & Bender, M. (1995). Climate records covering the last deglaciation. *Science*, 269(5221), 210-214. doi:10.1126/science.269.5221.210
- Spivack, A. J., You, C. F., & Smith, H. J. (1993). Foraminiferal boron isotope ratios as a proxy for surface ocean pH over the past 21 Myr. *Nature*, 363(6425), 149-151. doi:10.1038/363149a0
- Steinberg, C. (2007). Impacts of climate change on the physical oceanography of the Great Barrier Reef.
- Stolpe, B., & Hasselov, M. (2007). Changes in size distribution of fresh water nanoscale colloidal matter and associated elements on mixing with seawater. *Geochimica Et Cosmochimica Acta*, 71(13), 3292-3301. doi:10.1016/j.gca.2007.04.025
- Stuiver, M., & Braziunas, T. F. (1993). Modeling atmospheric ^{14}C influences and ^{14}C ages of marine samples to 10,000 BC. *Radiocarbon*, 35(1), 137-189. doi:10.1017/s0033822200013874
- Stuiver, M., & Polach, H. A. (1977). Discussion reporting of ^{14}C data. *Radiocarbon*, 19(3), 355-363. doi:10.1017/S0033822200003672
- Stuiver, M., & Quay, P. D. (1981). Atmospheric ^{14}C changes resulting from fossil fuel CO_2 release and cosmic ray flux variability. *Earth and Planetary Science Letters*, 53(3), 349-362. doi:10.1016/0012-821x(81)90040-6
- Stuiver, M., Pearson, G. W., & Braziunas, T. (1986). Radiocarbon age calibration of marine samples back to 9000 cal yr BP. *Radiocarbon*, 28(2b), 980-1021. doi:10.1017/S0033822200060264
- Suess, H. E. (1953). Natural radiocarbon and the rate of exchange of carbon dioxide between the atmosphere and the sea. *Nuclear processes in geologic settings*, 43, 52-56.
- Sunda, W. G., & Huntsman, S. A. (1994). Photoreduction of manganese oxides in seawater. *Marine Chemistry*, 46(1-2), 133-152. doi:10.1016/0304-4203(94)90051-5
- Sunda, W. G., Huntsman, S. A., & Harvey, G. R. (1983). Photoreduction of manganese oxides in seawater and its geochemical and biological implications. *Nature*, 301(5897), 234-236. doi:10.1038/301234a0
- Tanaka, K., Holcomb, M., Takahashi, A., Kurihara, H., Asami, R., Shinjo, R., Shinjo, R., Sowa, K., Rankenburg, K., Watanabe, T. & McCulloch, M. (2015). Response of *Acropora digitifera* to ocean acidification: constraints from $\delta^{11}\text{B}$, Sr, Mg, and Ba compositions of

- aragonitic skeletons cultured under variable seawater pH. *Coral Reefs*, 34(4), 1139-1149. doi:10.1007/s00338-015-1319-6
- Tanaka, K., Ohde, S., Cohen, M. D., Snidvongs, A., Ganmanee, M., & McLeod, C. W. (2013). Metal contents of Porites corals from Khang Khao Island, Gulf of Thailand: Anthropogenic input of river runoff into a coral reef from urbanized areas, Bangkok. *Applied Geochemistry*, 37, 79-86. doi:10.1016/j.apgeochem.2013.07.005
- Tans, P. P., Dejong, A. F. M., & Mook, W. G. (1979). Natural atmospheric ^{14}C variation and the Suess effect. *Nature*, 280(5725), 826-827. doi:10.1038/280048a0
- Taylor, R. B., Barnes, D. J., & Lough, J. M. (1995). On the inclusion of trace materials into massive coral skeletons. 1. Materials occurring in the environment in short pulses. *Journal of Experimental Marine Biology and Ecology*, 185(2), 255-278. doi:10.1016/0022-0981(94)00155-7
- Thompson, L. G., Mosley-Thompson, E., Brecher, H., Davis, M., Leon, B., Les, D., Lin, P.N., Mashiotto, T. & Mountain, K. (2006). Abrupt tropical climate change: Past and present. *Proceedings of the National Academy of Sciences of the United States of America*, 103(28), 10536-10543. doi:10.1073/pnas.0603900103
- Thompson, D. M., Cole, J. E., Shen, G. T., Tudhope, A. W., & Meehl, G. A. (2015). Early twentieth-century warming linked to tropical Pacific wind strength. *Nature Geoscience*, 8(2), 117-121.
- Toggweiler, J. R., Dixon, K., & Broecker, W. S. (1991). The Peru upwelling and the ventilation of the South Pacific thermocline. *Journal of Geophysical Research-Oceans*, 96(C11), 20467-20497. doi:10.1029/91jc02063
- Treble, P., Shelley, J. M. G., & Chappell, J. (2003). Comparison of high resolution sub-annual records of trace elements in a modern (1911-1992) speleothem with instrumental climate data from southwest Australia. *Earth and Planetary Science Letters*, 216(1-2), 141-153. doi:10.1016/S0012-821x(03)00504-1
- Tudhope, A. W., Lea, D. W., Shimmield, G. B., Chilcott, C. P., & Head, S. (1996). Monsoon climate and Arabian Sea coastal upwelling recorded in massive corals from southern Oman. *Palaios*, 11(4), 347-361. doi:10.2307/3515245
- Urban, F. E., Cole, J. E., & Overpeck, J. T. (2000). Influence of mean climate change on climate variability from a 155-year tropical Pacific coral record. *Nature*, 407(6807), 989-993. doi:10.1038/35039597
- Vogel, J. S., Southon, J. R., Nelson, D. E., & Brown, T. A. (1984). Performance of catalytically condensed carbon for use in accelerator mass spectrometry. *Nuclear Instruments & Methods in Physics Research Section B-Beam Interactions with Materials and Atoms*, 5(2), 289-293. doi:10.1016/0168-583x(84)90529-9
- Walther, B. D., Kingsford, M. J., & McCulloch, M. T. (2013). Environmental records from Great Barrier Reef corals: inshore versus offshore drivers. *Plos One*, 8(10). doi:ARTN e7709110.1371/journal.pone.0077091
- Wagner, A. J., Guilderson, T. P., Slowey, N. C., & Cole, J. E. (2009). Pre-bomb surface water radiocarbon of the Gulf of Mexico and Caribbean as recorded in hermatypic corals. *Radiocarbon*, 51(3), 947-954.
- Wang, C. Z. (2018). A review of ENSO theories. *National Science Review*, 5(6), 813-825. doi:10.1093/nsr/nwy104
- Wara, M. W., Delaney, M. L., Bullen, T. D., & Ravelo, A. C. (2003). Possible roles of pH, temperature, and partial dissolution in determining boron concentration and isotopic composition in planktonic foraminifera. *Paleoceanography*, 18(4). doi:Artn 110010.1029/2002pa000797

- Watanabe, T. K., Watanabe, T., Ohmori, K., & Yamazaki, A. (2020). Improving analytical method of Sr/Ca ratios in coral skeletons for paleo-SST reconstructions using ICP-OES. *Limnology and Oceanography-Methods*, 18(6), 297-310. doi:10.1002/lom3.10357
- Watanabe, T., Minagawa, M., Oba, T., & Winter, A. (2001). Pretreatment of coral aragonite for Mg and Sr analysis: Implications for coral thermometers. *Geochemical Journal*, 35(4), 265-269. doi:10.2343/geochemj.35.265
- Weber, J.N. (1973). Incorporation of strontium into reef coral skeletal carbonate. *Geochimica et Cosmochimica Acta*, 37(9), pp.2173-2190.
- Weber, J. N. (1974). Skeletal chemistry of scleractinian reef corals; uptake of magnesium from seawater. *American Journal of Science*, 274(1), 84-93. doi:10.2475/ajs.274.1.84
- Wei, G. J., Sun, M., Li, X. H., & Nie, B. F. (2000). Mg/Ca, Sr/Ca and U/Ca ratios of a porites coral from Sanya Bay, Hainan Island, South China Sea and their relationships to sea surface temperature. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 162(1-2), 59-74. doi:10.1016/S0031-0182(00)00105-X
- Wei, Z. X., Fang, G. H., Xu, T. F., Wang, Y. G., & Lian, Z. (2016). Seasonal variability of the isopycnal surface circulation in the South China Sea derived from a variable-grid global ocean circulation model. *Acta Oceanologica Sinica*, 35(1), 11-20. doi:10.1007/s13131-016-0791-3
- Wijeratne, S., Pattiaratchi, C., & Proctor, R. (2018). Estimates of surface and subsurface boundary current transport around Australia. *Journal of Geophysical Research: Oceans*, 123(5), 3444-3466. doi:10.1029/2017jc013221
- Wolanski, E., & Pickard, G. L. (1983). Upwelling by internal tides and Kelvin waves at the continental shelf break on the Great Barrier Reef. *Australian Journal of Marine and Freshwater Research*, 34(1), 65-80. doi:10.1071/mf9830065
- Wooldridge, S. A. (2009). Water quality and coral bleaching thresholds: Formalising the linkage for the inshore reefs of the Great Barrier Reef, Australia. *Marine Pollution Bulletin*, 58(5), 745-751. doi:10.1016/j.marpolbul.2008.12.013
- Wooldridge, S. A., & Done, T. J. (2009). Improved water quality can ameliorate effects of climate change on corals. *Ecological Applications*, 19(6), 1492-1499. doi:10.1890/08-0963.1
- Wooldridge, S., Brodie, J., & Furnas, M. (2006). Exposure of inner-shelf reefs to nutrient enriched runoff entering the Great Barrier Reef Lagoon: Post-European changes and the design of water quality targets. *Marine Pollution Bulletin*, 52(11), 1467-1479. doi:10.1016/j.marpolbul.2006.05.009
- Wyndham, T., McCulloch, M., Fallon, S., & Alibert, C. (2003). High resolution coral records of rare earth elements in coastal corals: A new environmental proxy?. *Geochimica Et Cosmochimica Acta*, 67(18), A537-A537. doi:10.1016/j.gca.2003.11.004
- Wyndham, T., McCulloch, M., Fallon, S., & Alibert, C. (2004). High-resolution coral records of rare earth elements in coastal seawater: Biogeochemical cycling and a new environmental proxy. *Geochimica Et Cosmochimica Acta*, 68(9), 2067-2080. doi:10.1016/j.gca.2003.11.004
- Xyla, A. G., Sulzberger, B., Luther, G. W., Hering, J. G., Vancappellen, P., & Stumm, W. (1992). Reductive dissolution of manganese (III, IV)(hydr) oxides by oxalate: The effect of pH and light. *Langmuir*, 8(1), 95-103. doi:10.1021/la00037a019
- Yu, J. M., & Elderfield, H. (2007). Benthic foraminiferal B/Ca ratios reflect deep water carbonate saturation state. *Earth and Planetary Science Letters*, 258(1-2), 73-86. doi:10.1016/j.epsl.2007.03.025

- Yuan, D. L., Han, W. Q., & Hu, D. X. (2006). Surface Kuroshio path in the Luzon Strait area derived from satellite remote sensing data. *Journal of Geophysical Research-Oceans*, 111(C11). doi:Artn C1100710.1029/2005jc003412
- Yuan, Y. C., Liao, G. H., Yang, C. H., Liu, Z. H., Chen, H., & Wang, Z. G. (2014). Summer Kuroshio Intrusion through the Luzon Strait confirmed from observations and a diagnostic model in summer 2009. *Progress in Oceanography*, 121, 44-59. doi:10.1016/j.pocean.2013.10.003
- Zaunbrecher, L. K., Cobb, K. M., Beck, J. W., Charles, C. D., Druffel, E. R., Fairbanks, R. G., Griffin, S. & Sayani, H. R. (2010). Coral records of central tropical Pacific radiocarbon variability during the last millennium. *Paleoceanography*, 25(4).
- Zhai, F. G., Hu, D. X., Wang, Q. Y., & Wang, F. J. (2014). Long-term trend of Pacific South Equatorial Current bifurcation over 1950-2010. *Geophysical Research Letters*, 41(9), 3172-3180. doi:10.1002/2014gl059934
- Zhao, J., Li, Y. L., & Wang, F. (2013). The role of mindanao dome in the variability of the Pacific North equatorial current bifurcation. *Journal of Oceanography*, 69(3), 313-327. doi:10.1007/s10872-013-0175-7
- Zhong, Q. (1990). An ENSO theory: theoretical analysis of a nonlinear atmosphere-ocean coupled characteristic system and its relation with ENSO events. *Annales Geophysicae-Atmospheres Hydrospheres and Space Sciences*, 8(12), 845-858.
- Zhong, S. J., & Mucci, A. (1989). Calcite and aragonite precipitation from seawater solutions of various salinities: Precipitation rates and overgrowth compositions. *Chemical Geology*, 78(3-4), 283-299. doi:10.1016/0009-2541(89)90064-8
- Zinke, J., D'Olivo, J. P., Gey, C. J., McCulloch, M. T., Bruggemann, J. H., Lough, J. M., & Guillaume, M. M. M. (2019). Multi-trace-element sea surface temperature coral reconstruction for the southern Mozambique Channel reveals teleconnections with the tropical Atlantic. *Biogeosciences*, 16(3), 695-712. doi:10.5194/bg-16-695-2019