

School of Natural Resource Sciences
Queensland University of Technology

MICROSTRUCTURE AND EARLY DIAGENESIS OF RECENT REEF BUILDING
SCLERACTINIAN CORALS, HERON REEF, GREAT BARRIER REEF:
IMPLICATIONS FOR PALAEOCLIMATE ANALYSIS

by

Luke D. Nothdurft

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Supervisor

Dr. Gregory E. Webb

Associate Supervisors

Dr. J. Theo Kloprogge

Assoc. Prof. Malcolm Cox

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ABSTRACT

Scleractinian corals increasingly are studied as geochemical archives of modern- and palaeoclimate, but microsampling for geochemical data is complicated by: 1) the microstructural complexity and spatial variability in skeletal growth in different coral genera; and 2) the rapidity and scale of diagenetic alteration that occurs in living coralla. Geochemical sampling techniques now have spatial resolution into the sub-micrometer to tens of micrometers range, and it is hoped that the spatial resolution can be translated to temporal resolution. This study investigated the effects on geochemical analyses imposed by microstructure and diagenesis in different live-collected coral genera representing somewhat different depositional environments. Suites of samples of four reef-building genera (*Acropora*, *Pocillopora*, *Goniastrea* and *Porites*) were collected from three adjacent environments in intertidal and subtidal positions near the reef edge at Heron Reef, Great Barrier Reef and studied by means of optical and scanning electron microscopy, combined with vibrational and energy dispersive spectroscopy. The first section of this study compares and documents the microstructure of the four coral genera. Each genus was found to have very different three-dimensional arrangements of microstructural elements, and a new general growth model was proposed for *Acropora*, to take into account differences in the timing of precipitation of trabeculae and thickening deposits. The results highlight the complexity and spatial variability of skeletal growth in different coral genera. Because microstructural patterns vary in different genera, direct observation of microstructural elements and growth lines are necessary to allow geochemical microsamples to be placed into series that represent temporal sequences with known degrees of time averaging. Coral growth rates (i.e., rates of extension) are discussed to determine the range of temporal relationships that exist between closely spaced skeletal microstructural elements. Such data are necessary in order for coral skeletogenesis to be understood and are critical for constraining microsampling strategies aimed at developing true time series geochemical data at very fine spatial and temporal scales.

The second part of the study focused on early diagenetic alteration of the corals, which is an equally important concern for geochemical analysis. Early marine diagenesis was

documented in the same live-collected samples of the four common reef-building coral genera. Samples show extensive early marine diagenesis where parts of the coralla less than three years old contain abundant macro- and microborings (sponges, algae, cyanobacteria and fungi) and significant amounts of aragonite, high-Mg calcite, low-Mg calcite and brucite $[\text{Mg}(\text{OH})_2]$ cements. Many of the cements are associated with microendoliths and endobionts that inhabit recently abandoned parts of the skeleton. The cements are problematic for palaeoclimate reconstruction because geochemical proxies used for paleoclimate studies are meant to reflect ambient seawater chemistry and conditions, but the occurrence of brucite and low-Mg calcite demonstrates how far fluid chemistry in microenvironments within the corals has evolved from ambient seawater. Some *Porites lobata* specimens have had as much as 60% of the most recently deposited skeletal aragonite (i.e., the part of the skeleton that projects into the layer of living polyps) bored and replaced by low-Mg calcite cement. The low-Mg calcite cement has significantly different trace element ratios ($\text{Sr}/\text{Ca}_{(\text{mmol}/\text{mol})} = 6.3 \pm 1.4$; $\text{Mg}/\text{Ca}_{(\text{mmol}/\text{mol})} = 12.0 \pm 5.1$) than the host coral skeletal aragonite ($\text{Sr}/\text{Ca}_{(\text{mmol}/\text{mol})} = 9.9 \pm 1.3$; $\text{Mg}/\text{Ca}_{(\text{mmol}/\text{mol})} = 4.5 \pm 2.3$), thus providing a serious challenge for Sr/Ca or Mg/Ca based sea surface temperature calculations.

This study illustrates that many diagenetic changes that can radically alter important geochemical characteristics of coral skeleton occur very early on the sea floor (i.e., while corals are still alive). Documented cements altered trace element inventories (e.g., Sr and Mg), thus, interfering with the use of those elements in palaeotemperature calculations. Hence, significant diagenetic changes that jeopardise palaeoclimate data do not require long-term diagenesis or meteoric exposure. Some of the diagenetic changes (e.g., calcite filled borings) occur at scales that are very difficult to detect short of visual inspection using SEM. Hence, vetting of coral samples with SEM is required before any sample is subjected to geochemical analysis.

LIST OF PUBLICATIONS / SUBMITTED MANUSCRIPTS

- Nothdurft, L. D., Webb, G. E., Buster, N. A., Holmes, C. W., Sorauf, J. E. and Kloprogge, J. T. (2005) Brucite microbialites in living coral skeletons: Indicators of extreme microenvironments in shallow-marine settings. *Geology* **33**, 169-172.
- Nothdurft, L. D. and Webb, G. E. (2007) Microstructure of common reef-building coral genera *Acropora*, *Pocillopora*, *Goniastrea*, and *Porites*: constraints on spatial resolution in geochemical sampling. *Facies* **53**, 1-26.
- Nothdurft, L. D. and Webb, G. E. (2007) 'Shingle' microstructure in scleractinian corals: a possible analogue for lamellar and microlamellar microstructure in Palaeozoic tabulate corals. In *Proceedings of the 9th International Symposium on Fossil Cnidaria and Porifera* (eds. B. Hubmann and W. E. Piller) *Schriftenreihe der Erdwissenschaftlichen Kommissionen* 17 pp. 85-99.
- Nothdurft, L. D., Webb, G. E., Bostrom, T. and Rintoul, L. (2007) Calcite-filled borings in the most recently deposited skeleton in live-collected *Porites* (Scleractinia): Implications for trace element archives. *Geochimica et Cosmochimica Acta* **71**, 5423-5438.
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CONTENTS

INTRODUCTION	1
Research Problem	1
Aims of the Thesis	3
Sampling and Methods	4
Research Progression	6
Thesis Outcomes	8
LITERATURE REVIEW	10
1. Coral skeletogenesis	10
2. Palaeoclimate studies using geochemical archives in coral skeletons	22
3. Scleractinian coral diagenesis	30
<i>Carbonate Diagenesis</i>	30
<i>Cementation</i>	31
<i>Cement Precipitation</i>	31
<i>Cement Facies</i>	34
<i>Cementation in Holocene coral reefs</i>	35
<i>Early Diagenesis in Scleractinian corals</i>	37
<i>Cements</i>	37
<i>Bioerosion</i>	39
<i>Cement Geochemistry</i>	42
PUBLISHED PAPERS / SUBMITTED MANUSCRIPTS	44
<i>Paper 1</i>	44
Nothdurft, L. D. and Webb, G. E. (2007) Microstructure of common reef-building coral genera <i>Acropora</i> , <i>Pocillopora</i> , <i>Goniastrea</i> , and <i>Porites</i> : constraints on spatial resolution in geochemical sampling. <i>Facies</i> 53, 1-26.	
Contribution of authors	44
Abstract	45
Introduction	45

<i>Coral skeletal microstructure</i>	46
Methods and Materials	50
Results	50
<i>Acropora hyacinthus microstructure</i>	50
<i>Pocillopora damicornis microstructure</i>	54
<i>Goniastrea favulus microstructure</i>	60
<i>Porities lobata microstructure</i>	60
Discussion	62
<i>Models of Skeletogenesis</i>	62
<i>Implications for geochemical proxies</i>	66
Conclusions	68
Acknowledgements	68
References	69
Paper 2	71
Nothdurft, L. D. and Webb, G. E. (submitted) Earliest diagenesis in scleractinian coral skeletons: implications for palaeoclimate-sensitive geochemical archives. <i>Facies</i> .	
Contribution of authors	71
Abstract	72
Introduction	72
Early Diagenesis in Scleractinian corals	74
Methods	76
Results	79
<i>Sample pretreatment experiment and interpretation</i>	81
Bioerosion	84
<i>Sponges</i>	84
<i>Microborings</i>	89
Early Cements	97
<i>Aragonite cements</i>	97
<i>Magnesium Calcite Cements</i>	106
<i>Low-Mg calcite cements</i>	112
<i>Brucite cements</i>	112
Discussion	117

Bioerosion	117
<i>Sponges</i>	117
<i>Microborings</i>	118
Cements	120
<i>Aragonite Cement</i>	122
<i>High-Mg calcite (HMC) cement</i>	126
<i>Low-Mg calcite (LMC) cement</i>	128
<i>Brucite cement</i>	129
<i>Cement Distribution</i>	130
<i>Are the present samples representative of older Holocene corals</i> ..	135
<i>Implications for geochemical analysis and palaeoclimate research</i>	136
Acknowledgements	139
References	140
<i>Paper 3</i>	150
Nothdurft, L. D., Webb, G. E., Bostrom, T. and Rintoul, L. (2007) Calcite-filled borings in the most recently deposited skeleton in live- collected <i>Porites</i> (Scleractinia): Implications for trace element archives. <i>Geochimica et Cosmochimica Acta</i> 71, 5423-5438.	
<i>Contribution of authors</i>	150
Abstract	151
Introduction	151
Coral microstructure and endolithic borings	154
Materials and Methods	154
Results	156
Discussion	157
<i>Age of borings and mode of formation</i>	157
<i>Implication for geochemical analysis</i>	159
Conclusions	162
Acknowledgements	163
Appendix	163
References	163

Paper 4	167
Nothdurft, L. D., Webb, G. E., Buster, N. A., Holmes, C. W., Sorauf, J.E., and Kloprogge, J. T. (2005) Brucite microbialites in living coral skeletons: Indicators of extreme microenvironments in shallow-marine settings. <i>Geology</i> 33, 169-172.	
Contribution of authors	167
Abstract	168
Introduction	168
Methods	168
Results	169
Interpretation and Discussion	170
Acknowledgements	171
References Cited	171
GENERAL DISCUSSION	174
Coral Microstructure	174
<i>Constraints on temporal series geochemical data</i>	174
<i>Taxonomy of scleractinian corals</i>	177
Early Diagenesis	178
<i>Implications for palaeoclimate records</i>	178
<i>Microenvironments</i>	179
Implications for future research	180
Summary	183
CONCLUSIONS	184
REFERENCES	187
APPENDICES	217
Appendix 1	217
Nothdurft, L. D. and Webb, G. E. (2007) 'Shingle' microstructure in scleractinian corals: a possible analogue for lamellar and microlamellar microstructure in Palaeozoic tabulate corals – In: Hubmann, B. &	

Piller, W. E. (Eds.): Fossil Corals and Sponges. Proceedings of the 9th International Symposium on Fossil Cnidaria and Porifera. – Osterr. Akad. Wiss., Schriftenr. Edwiss. Komm. 17: 85-99, 2 Figs., 2 Pls., Wien.

Contribution of authors.....217

LIST OF ABBREVIATIONS

COC	Centres of Calcification
CRA	Centres of Rapid Accretion
dCRA	deposits of Centres of Rapid Accretion
DIC	Dissolved Inorganic Carbon
ECZ	Early Calcification Zone
EDS	Energy Dispersive Spectrometry
EMZ	Early Mineralisation Zone
ENSO	El Niño Southern Oscillation system
F	Fibres
GBR	Great Barrier Reef
HMC	High-Magnesian Calcite
LA-ICP-MS	Laser Ablation-Inductively Coupled-Mass Spectrometry
LMC	Low Magnesian Calcite
NOA	North Atlantic Oscillation
PDO	Pacific Decadal Oscillation
RAF	Rapid Accretion Front
dRAF	deposits of Rapid Accretion Front
REE	Rare Earth Elements
SEM	Scanning Electron Microscopy
SIMS	Secondary Ion Mass Spectrometry
SHRIMP RG	Sensitive High Resolution Ion Microprobe Reverse Geometry
SST	Sea Surface Temperature
TD	Thickening deposits
VDPB	Vienna-Peedee Belemnite Standard

STATEMENT OF ORIGINAL AUTHORSHIP

The work contained in this thesis has not been previously submitted for a degree or diploma at any other higher education institution. To the best of my knowledge and belief, the thesis contains no material previously published or written by another person except where due reference has been made.

Signature:

Date:

INTRODUCTION

Research Problem

Scleractinian coral skeletons incorporate elemental and isotopic proxies that reflect environmental conditions of the ambient seawater in which they grow. The age of coral growth can be constrained (i.e. annual, seasonal) by combining density banding with isotopic dating techniques, which makes them useful for studying past environments. Hence, the geochemical proxies contained within scleractinian coral skeletons are commonly applied to the study of palaeoclimate, including such parameters as sea surface temperature (SST) (e.g., Corrège, 2006), coastal run-off (e.g., Lewis et al., 2007), ocean up-welling (e.g., Fallon et al., 1999), and marine productivity (e.g., Wyndham et al., 2004). At the same time, sampling techniques, such as laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) (e.g., Sinclair and McCulloch, 2004), ion microprobe (e.g., Meibom et al., 2007) and Secondary Ion Mass Spectrometry (NanoSIMS) (e.g., Meibom et al., 2004), are allowing geochemical sampling at increasing levels of spatial resolution with the hope for increased, subannual (e.g., Gill et al., 2006) or even sub-daily temporal resolution (e.g., Meibom et al., 2007) of geochemical data. Increasingly finer scales of sampling resolution emphasize the natural microstructural and fine-scale geochemical heterogeneity in the coral skeleton and place a greater responsibility on the researcher to constrain exactly what part of the skeleton is being analysed (e.g., Meibom et al., 2004). Trace element distribution in coral skeletons is intimately related to the organo-mineralization process (e.g., Marshall, 2002; Meibom et al., 2004). Thus, trace element distribution is not homogenous at fine scales, but should be related to the microstructure in a more or less predictable way. Unfortunately, owing to the complex three-dimensional skeletal morphology within corallites and the variety of differing microstructural patterns (e.g., Sorauf, 1972; Jell, 1974; Jell and Hill, 1974; Cuif and Dauphin, 1998; Stolarski, 2003), types of thickening deposits, and sequences of skeletal emplacement in different coral genera, any given linear sequence of microsamples may not correspond to a time series. However, few studies have focused on how individual laser and microprobe sampling strategies relate

to spatio-temporal scales of skeletal emplacement or the degree of time-averaging represented by the data. Such data are critical for developing reliable time series geochemical data for palaeoclimate analysis at very fine temporal scales.

Additionally, the use of coral skeletons as temporal archives for geochemical proxies requires that coral skeletons preserve trace element and isotopic ratios that reflect the ambient conditions of the seawater in which the skeleton was precipitated. Although evidence increasingly suggests that trace element and stable isotope distributions within coral skeletons are affected by poorly understood vital effects (e.g., Sinclair and Risk, 2006), coral skeletons should provide useful palaeoenvironmental proxies where original trace element and stable isotope inventories have not been altered by subsequent diagenesis. Although coral skeletons are routinely vetted prior to analysis to check for diagenetic alteration, especially including recrystallization of skeletal aragonite to calcite during meteoric diagenesis (e.g., Enmar et al., 2000; McGregor and Gagan, 2003; Quinn and Taylor, 2006), it is generally assumed that coral skeleton, especially in live-collected corals, that has not been exposed to freshwater should retain reliable marine trace element inventories. However, early marine cements have been well documented in coral reef settings, and cements that occur within the coral skeleton contain trace element concentrations that differ from those of the coral skeleton (e.g., Enmar et al., 2000, Müller et al., 2001; Ribaud-Laurenti et al., 2001). Thus, attention must be paid to the effects of early marine diagenesis as well, if reliable palaeoclimate data are to be acquired. Endolithic and endobiotic microbes also have long been of concern to geochemists seeking pristine coral skeleton for analysis because some microbes induce and/or localize the precipitation of secondary aragonite and high-Mg calcite (Schroeder, 1972). Additionally, bioeroding sponges are among the most important internal excavating biotas in tropical environments (Rützler, 1975), and sponges may occur in very young parts of coralla (e.g., Schönberg, 2002) where they could alter localised fluid flow or diffusion characteristics (Schroeder, 1972; Scherer, 1974; Land and Moore, 1980). Internal hydrodynamic changes caused by borers in coral skeletons could thus have follow-on effects on diagenesis and preservation.

In summary, for geochemical data obtained from coral skeletons to be useful for palaeoclimate studies they must meet the following criteria. 1) Data must reflect a

known temporal sequence (i.e., time series data). 2) Data should reflect a known degree of time averaging. 3) The normal degree of heterogeneity in data (scatter) must be known for a particular sample resolution. 4) The sampled skeletal aragonite must reflect the seawater in which it was precipitated (i.e., lack of subsequent diagenetic alteration). However, increasing sample resolution has had the following effects.

1) The finest spatial resolution of geochemical sampling now intersects with the natural fine-scale heterogeneity and fine-scale (microstructural) patterns of spatio-temporal distribution of trace elements and organic matter inherent in coral skeletons.

2) Geochemical sample sizes are now so small that even very minor diagenetic alteration in coral skeletons may severely affect analyses, but vetting strategies have lagged behind the increasingly sophisticated sampling technology.

Aims of the Thesis

The aim of this thesis research is to investigate the spatio-temporal relationships of different coral microstructures and the effects of early marine diagenesis (bioerosion and cementation) on the preservation of temporally constrained geochemical records in coral skeletons at scales relevant to high resolution sampling techniques. Specifically, the research tests the following hypotheses. 1) Different microstructures in different scleractinian coral genera will have different patterns of fine-scale temporal relationships between adjacent areas of skeleton. 2) Very early marine diagenesis (i.e., that which occurs during the life of the coral) may compromise geochemical proxies contained within coral skeletons. 3) The nature and degree of early diagenetic alteration of coral skeletons depends on minor differences in the local depositional environment. 4) The nature and degree of early diagenetic alteration in coral skeletons partially depends on the growth form and/or microstructure of the coral.

Sampling and Methods

Samples chosen for study include sections of live-collected scleractinian coral skeletons from Heron Reef (Fig.1). A set of fifteen ~5 cm samples were collected from small coralla of each of four different species representing four different common reef-building genera (*Acropora hyacinthus*, *Pocillopora damicornis*, *Porites lobata* and *Goniastrea favulus*) within 10 m of the reef margin (Fig. 2). Five samples each were collected from: 1) the reef flat within 10 m of the reef edge in positions that were exposed completely at low tide; 2) the reef flat within 10 m of the edge that remained continuously submerged in 10-30 cm of ponded reef flat water at low tide; and 3) a protected pool over the reef edge in ~2-3 m water depth at low tide. Additional specimens of *Acropora cuneata* also were collected, but a full survey of the three environments was not carried out on those samples. Specimens were collected in October of 2003 and September of 2004. The oldest specimen was dated back to 1993 (11 years - *Goniastrea favulus* -04-9-06) with annual density bands. However, most specimens grew between 2000 and 2003 (2 to 3 years old). Skeletal microstructure was documented and compared among the four genera using a range of optical microscopy and scanning electron microscopy (SEM) techniques. Early diagenesis was assessed for all samples and local diagenetic environments (i.e., the three sample settings) using SEM and vibrational spectroscopy techniques. More detailed methodologies are outlined in each chapter where relevant. In each case, implications for high resolution geochemical analysis were highlighted.

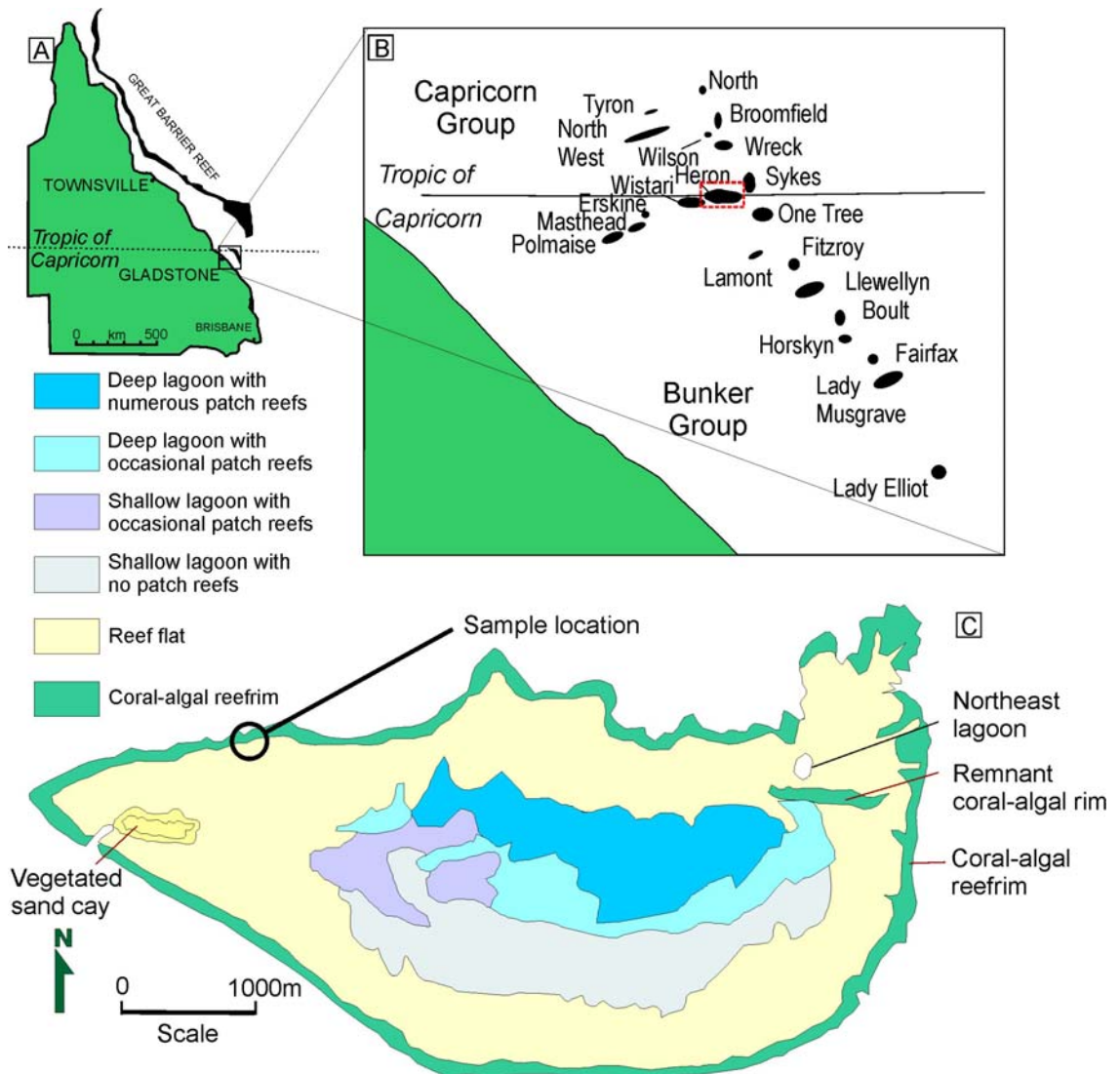


Fig. 1. Maps of A) the Great Barrier Reef, B) Capricorn – Bunker Groups in the Southern Great Barrier Reef, and C) Heron Reef showing reef zone distribution and site where specimens were collected for this study (modified from Smith et al., 1998).

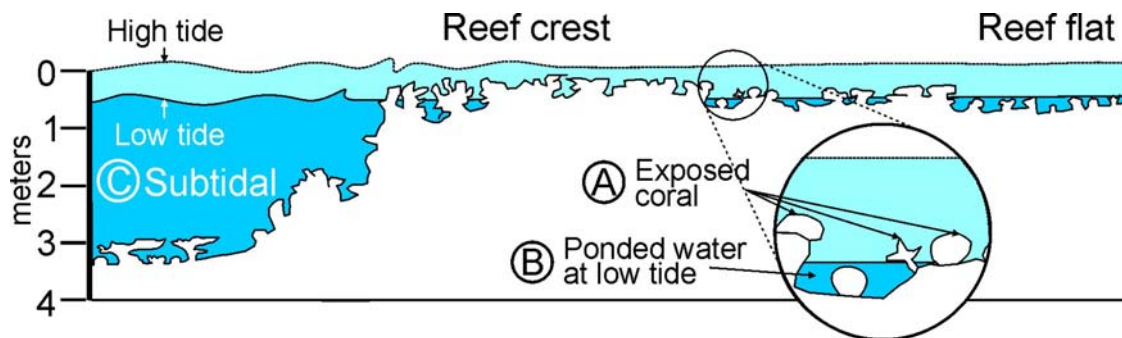


Fig. 2 Schematic cross-section of the three environments from which corals were sampled.

Research progression

This thesis follows ‘thesis by publication’ guidelines set out by the Queensland University of Technology and is organized so as to provide a clear and coherent guide to the research progression. The literature review provides the general context for the research, detailing current hypotheses on coral skeletogenesis and microstructural models, as well as background on early diagenesis in modern coral reefs with a focus on scleractinian corals. The literature review, of necessity, replicates some literature cited in subsequent chapters, and as some papers generated from this research have already reached publication, some of the literature has come out subsequent to completion of parts of the research. For completeness sake, the papers that have reached publication are listed in the literature review, but of course, those published results were not known upon initiation of the research project.

Four major papers are presented as individual chapters. The first major paper (Nothdurft and Webb, 2007) documents the microstructure of four important reef-building coral genera, *Acropora*, *Pocillopora*, *Goniastrea* and *Porites*, the latter of which is widely analysed as a geochemical archive. This paper tests the hypothesis that the internal organization and microstructure of coral skeleton differs significantly in different coral genera, thus providing important constraints on the geometry of microsamples required for generating time series data. Coral growth rates (i.e., rates of extension) are discussed in terms of specific skeletal microstructures in order to

determine the range of temporal relationships that exist between closely spaced skeletal elements. Such data are critical for understanding the degree of time-averaging inherent in geochemical samples of various sizes and spatial relationships. Apart from the intended goal of the study, better differentiation of microstructural patterns in scleractinian corals has important implications for phylogenetic analysis within the Scleractinia.

The second major paper describes the products of earliest diagenesis in live-collected scleractinian coral skeletons, including cementation and bioerosion that could potentially influence geochemical data collected for palaeoclimate analysis. The paper documents a range of cavity-filling early marine cements, including several different mineral species, which precipitate in intra-skeletal cavities located beneath the living coral polyp. The paper also documents the relationship between some endobionts and cementation within coralla.

The third major paper focuses on a particular type of early diagenetic calcite cement that completely occludes microbial borings in live-collected samples of *Porites lobata*. The borings occur within the most recently formed parts of the coral skeletons, i.e., those parts that are contained within the uppermost part of the corallum that is still occupied by living coral polyps. Skeleton in this region of living polyps is theoretically the most pristine skeleton possible, because it is still in direct contact with living coral tissue, and its surfaces are still potentially undergoing active biomineralization beneath the calicoblastic epithelium of the coral. Although the cement-filled borings are too small and scattered to affect X-ray diffraction data where they are not very abundant, they could significantly contaminate microsamples used for laser ablation or microprobe analyses, thus providing erroneous data for sea surface temperature calculations. To investigate the effects of the borings on geochemical analyses, selected trace element (Mg, Sr) concentrations were measured using X-ray microanalysis.

The final paper documents abundant brucite cement in the skeletons of live-collected, shallow-marine, scleractinian corals. The occurrence of brucite in corals is significant because it is not expected to precipitate in marine settings owing to the relatively low pH and high $p\text{CO}_2$ of seawater (Morse and Mackenzie, 1990). Smith and DeLong (1978) previously suggested that brucite in coral skeletons resulted from

microbial activity in abandoned intracorallum spaces. The present work tests their hypothesis. Although brucite is undersaturated in seawater, its precipitation was apparently induced in the corals by lowered $p\text{CO}_2$ and increased pH within microenvironments protected by microbial biofilms. The occurrence of brucite in shallow-marine settings highlights the importance of such microenvironments for the formation and early diagenesis of marine carbonates with the important implication that some cements within coral skeletons do not reflect the chemistry of ambient seawater.

The final section of the thesis summarises the results of the four papers and includes discussion of their implications for current palaeoclimate studies and directions for future work. The reference section includes all resources used in the thesis, including those cited in the published and prepared manuscripts. References cited in individual manuscripts accompany them for completeness. The appendix section contains an additional published manuscript that is related to the work, but did not contribute to the main aims of the thesis.

Thesis Outcomes

The outcomes of the research have significant implications for wide-ranging studies that involve scleractinian corals. Firstly, palaeoclimate studies that utilise geochemical proxies in corals require that the data: 1) are temporally constrained; and 2) reflect the ambient conditions of the seawater in which the corals grew. Documentation of the fine-scale spatio-temporal relationships of coral microstructure in different genera allow for better devised geochemical microsampling strategies in those genera, thus enabling production of true time-series data with known degrees of time-averaging. Such records are especially necessary as studies seek to understand secular changes in subannual (e.g., seasonal) trends in parameters such as SST (e.g., Meibom et al., 2003). Additionally, detailed knowledge of microstructure is required to account for, and possibly predict or constrain, the natural heterogeneity in trace element incorporation in coral skeletons (e.g., Meibom et al., 2004). Increasingly smaller sample sizes have led to increases in the measured natural scatter of geochemical data (e.g., Cohen et al., 2001; Allison and Finch, 2004), and some of that heterogeneity appears to be related to skeletal microstructure in predictable ways (e.g., Meibom et al., 2007). Finally, better

knowledge of the taxonomic distribution of different coral microstructures in light of recent advances in understanding skeletogenesis in corals in general (e.g., Stolarski, 2003) has implications for phylogeny and systematics in the Scleractinia. Attempts to link skeletal microstructure with molecular phylogenetic techniques (Cuif et al., 2003b; Stolarski, 2003; Fukami et al., 2004) have given only partial support for microstructure-based phylogenetic relationships within the Scleractinia, but Cuif and Perrin (1999) suggested that this is partly the result of numerous uncertainties concerning the exact microstructural patterns of the species upon which major taxa are based.

The other critical outcomes of the present research for palaeoclimate studies focus on understanding and recognizing the effects of early diagenesis. Corals are generally vetted prior to geochemical analysis, but that vetting generally involves X-ray diffraction (XRD) or thin section petrography aimed at recognising alteration of skeletal aragonite to calcite during meteoric diagenesis (e.g., McGregor and Gagan, 2003). It is commonly assumed that corals that have not been exposed to meteoric diagenesis should contain pristine skeletal records of their ambient environments. Documentation of the spatial distribution and abundance of early diagenetic alteration within coral skeletons allows better vetting strategies to be devised, and those strategies apply not only to palaeoclimate studies, but to other studies utilizing coral geochemistry, such as the dating of coral skeletons to establish the positions of palaeo-sea levels (e.g., Lazar et al., 2004; Quinn and Taylor, 2006).

Additional outcomes of the study include a better understanding of the controls on early diagenetic processes themselves. This has implications for recognizing ancient depositional environments and possibly for understanding how early diagenesis may affect subsequent, longer-term diagenesis, which controls porosity and permeability evolution in limestones that are reservoirs for hydrocarbons or fresh water.

LITERATURE REVIEW

This literature review is divided into three sections that provide context for the subsequent chapters of this thesis. The three sections are:

1. Coral skeletogenesis
2. Palaeoclimate studies using geochemical archives in coral skeletons
3. Scleractinian coral diagenesis

1. Coral skeletogenesis

The microstructure of coral skeletons has been studied for well over a century, but our understanding of coral biomineralisation processes has improved particularly over the last 30 years. For much of the previous century the ‘spherulitic’ hypothesis, or physio-chemical model, of skeletal precipitation was favoured based mostly on the work of Bryan and Hill (1941). However, recent models have highlighted the biological control of skeletogenesis by the coral polyp (e.g., Cuif et al., 1997; Stolarski, 2003). A historical review of the evolution of scleractinian coral skeletogenesis models is shown in Table 1. Additionally, recent reviews were provided by Cuif and Sorauf, (2001), Stolarski (2003), Cuif and Dauphin, (2005a) and Stolarski and Mazur (2005).

Bryan and Hill’s (1941) “spherulitic” hypothesis provided the first comprehensive model explaining the underlying processes of skeletal formation. Their model stacked cone-shaped trabeculae (Table 2) to form vertical skeletal elements and proposed that the skeletal aragonite precipitates as a result of abiotic processes. Although Bryan and Hill (1941) considered skeletal growth to be primarily physico-chemical in nature, they noted the coexistence of organic and mineral phases in the skeleton, and several other researchers also suggested some biological factors in skeletal formation (e.g., Goreau, 1959; Wainwright, 1964; Young, 1971; Constantz and Weiner, 1988; Gautret et al., 1997). The advent of SEM to investigate coral skeletons highlighted the complexity and taxonomic value of microstructure and microarchitecture (e.g.,

Sorauf, 1972; Jell, 1974; Jell and Hill, 1974). Despite this, several similar models perpetuated the hypothesis that coral skeletogenesis was fundamentally an inorganic process (Barnes, 1970; Constantz, 1986a).

Table. 1 History of important contributions to models for the skeletogenesis of Scleractinian corals.

Reference	Model control*	Comments
Bryan and Hill, 1941	A	The first comprehensive model to explain the underlying processes of coral skeleton formation. They proposed a spherulitic hypothesis, wherein fibres fan out from the "centres of calcification" by abiotic chemical precipitation governed by supersaturation. An individual fibre was described as "a single orthorhombic crystal of aragonite".
Goreau, 1959	B	Histochemically characterised the mucopolysaccharide layer directly underlying the basal ectoderm. This paper is considered by Cuif and Sorauf (2001) as the starting point for research emphasizing biologically driven crystallisation in corals.
Wainwright, 1964	B	Demonstrated that the fibres that were considered individual crystal units in Bryan and Hill's model are actually polycrystalline aggregates with ordered c-axis and randomly distributed a and b axes.
Barnes, 1970	A	Proposed a model where the fastest growing fibres formed in spaces where the calciblastic ectoderm lifted away from the skeletal surface, and the fibre morphologies can be explained by abiotic crystal growth.
Johnston, 1980	B	Published the first evidence of a possible relationship between organic and mineral materials at a submicrometer scale by illustrating the organic network in the uppermost 3 µm of a coral fibre. Pointed out that previous skeletogenesis models were made in ignorance of the organic material's spatial distribution within the skeleton.
Constantz, 1986a	A	Stated that the growth of skeletal aragonite fibres and their organisation into bundles was entirely predictable by factors controlling abiotic, physico-chemical crystal growth.
Cuif and co-authors (e.g., Cuif et al., 1997; Gautret et al., 1997; Cuif et al., 1999; Cuif et al., 2003a)	B	Introduced the 'two-step' model, with the first phase of growth occurring in organic-rich centres of calcification. The centres then served as scaffolding for successive growth of a distinctly separate, second phase of layered aragonite fibres. This model emphasized that microstructural organisation of the mineral phase is strictly controlled by a spatial arrangement of the organic compounds that are incorporated into the skeletal structure.
Stolarski, 2003	B	Proposed the 'layered' model where alternating layers of aragonite fibres and organic-rich zones pass through centers of rapid accretion and thickening deposits, so that centres of calcification are not fundamentally distinct from layers of fibres that cause skeletal thickening. This paper also introduced new nomenclature.
Cuif and Dauphin, 2005	B	The original 'two step' model of Cuif et al. (1997) evolved to encompass the cyclic alternation of organic-rich and mineral phases both in individual fibres and in early mineralising zones.

* Abiotic (A) or biologically (B) controlled model.

Table 2. Compilation of important microstructural units of scleractinian coral skeleton including their abbreviation, description of their appearance and short history of the meaning and use of terms with current usage. Scanning electron microscope images of microstructural units referred to this thesis are shown in Fig. 3.

Unit	Description	Notes
Centres of Calcification (COC)	In thin-section COC appear as darkened areas at the centre of trabeculae composed of tiny crystals, densely packed, randomly oriented and embedded in an organic component (i.e., organic rich compare to fibres) (Cuif and Dauphin, 1998).	Originally defined by Ogilvie (1896) as the zones from which fibres originate. This notion was essentially supported by Bryan and Hill (1941) in the 'spherulitic hypothesis' and by Wells (1956), although with some trepidation as he used quotation marks whenever he wrote the term because of a paucity of histological evidence to support the conclusion. Cuif et al. (1999) stated that the use of this term was inaccurate because COC do not act as nucleation sites of fibre growth. Cuif et al. (2003) later replaced COC with the EMZ to better describe the growing process. Stolarski (2003) recommended the term should be replaced by CRA.
Fibres (F)	Polycyclic crystals built of composite growth increments ~3 µm thick resulting in growth lines that can be revealed with both light enzymatic and acidic etching techniques (Cuif and Sorauf, 2001).	Fibrous organisation of coral skeletons first observed by Pratz (1882) and described by Ogilvie (1896). Bryan and Hill (1941) described the fibre as a single orthorhombic crystal of aragonite. It was later shown by Wainwright (1964) as a polycrystalline aggregate. New model from Cuif and Dauphin (2005a) describe a fibre as a multiple of superimposed smaller units that independantly record physiological and environmental signatures to the time equivalent of one day. Mineral phases of fibers are known to consist of nm-scale aragonite granules and organic matter (Stolarski and Mazur, 2005).
Trabeculae	Composed of upwardly directed fibres diverging from COC. Decribed by Bryan and Hill (1941) as a cylinder tapering convexly at the top.	Used as the basis of the 'spherulitic model' of Bryan and Hill (1941) was decribed as 'Tabelekn' of Pratz (1982). Stolarski correctly pointed out that boundary between trabeculae and skeletal fibres is commonly difficult to distinguish and suggests that the trabecular concept is vague and not applicable to his models. However, whilst many, if not all microstructures previously decribed as trabeculae can be re-evaluated to fit the layered model, some microstructures can still be decribed as true trabeculae (e.g., Nothdurft and Webb, 2007).
Sclerodermite	Typically refered to in abiotic models of skeletogenesis. Generally described as COC together with clusters of fibres that when arranged vertically produce trabecula.	Generally, the concept of sclerodermites has been abandoned (e.g., Gill, 1967), and Stolarski (2003) states that the term is no longer applicable because they do not form stucturally limited regions.
Early Mineralisation Zone (EMZ)	See COC. Additionally, defined as the trace of the distal growth edge within the septum. EMZ have been characterised as biochemically distinct from skeletal fibers using both microprobe and staining techniques (e.g., Cuif and Dauphin, 1998; Cuif et al., 2004; Cuif and Dauphin, 2005; Meibom et al., 2007).	Term introduced by Cuif et al. (2003a) to replace COC to account for the physico-chemical connotations associated with COC. Describes the same structure as CRA and RAF of Stolarski (2003). EMZ is a modified version of term Early Calcification Zone (ECZ) of Cuif et al. (2003b).

Table 2. continued.

Unit	Description	Notes
(deposits) Centres of Rapid Accretion [(d)CRA]	Well differentiated regions of skeletal rapid accretion with alternations of organic and mineral components (Stolarski, 2003). Organic components significantly higher than TD. CRA can be recognised in etched longitudinal and transverse sections.	Term introduced for the layered model by Stolarski (2003) to replace COC to account for the connotations associated with COC. Describes the same structure as EMZ of Cuif and co-authors.
(deposits) Rapid Accretion Front [(d)RAF]	More or less continuous zone of rapid accretion (e.g., crest of septum, pali, paliformal lobe, wall, columella) (Stolarski, 2003).	Term introduced for the layered model by Stolarski (2003) to replace COC to account for the connotations associated with COC. Describes the same structure as EMZ of Cuif and co-authors. However, because continuity between dRAF and TD, Stolarski defines the difference between the two regions as resulting purely from differential growth dynamics, and not necessarily different timing as suggested by Cuif and co-authors in the two-step mode with EMZ and fiber units.
Thickening deposits (TD)	Microstructures deposited outside the RAF and CRA, although components may be continuous structures from one the other. Generally contains less organic component than CRA and RAF. It is essentially fibrous growth.	TD is a form of fibrous growth, therefore the notes on fibres applies here. The term was introduced by Stolarski (2003) for the layered model to replace informal terms previously used to describe fibrous deposits [e.g., stereome (Sorauf, 1972); tectura (Stolarski, 1995).
Shingles or Bundles	Microstructure composed of clusters of aragonite fibres (typically 4 to 50 um in width) arranged into low-relief, overlapping, shingle-like pattern arranged roughly parallel to the growth surface.	Sorauf (1972) used the term 'shingles' to describe such clusters of fibers in <i>Fungia</i> and described them as resembling overlapping 'fish scales'. The term 'fish scales' was again used to describe <i>Flabellum</i> by Sorauf and Podoff (1977), and subsequent variations have included 'scale-like' as used by Gautret et al. (2000) in <i>Acropora</i> and by Stolarski (2003) in <i>Flabellum</i> and <i>Galaxea</i> . Cuif et al. (1997) called the bundles in <i>Acropora</i> 'elongate sclerodermites' to distinguish them from other microstructural elements. However, these units should not be confused with sclerodermites of other authors.

➡ **Fig. 3 Scanning electron microscope images of the microstructural units of scleractinian coral skeletons described in Table 2. A) Longitudinal section through a septum etched with mild formic acid showing centres of calcification (COC), early mineralisation zones (EMZ) and deposits of centres of rapid accretion (CRA), all of which represent the dark, organic rich zone in the centre of the septum. The rapid accretion front (RAF) is at tip of the septum and the thickening deposits (TD) are fibrous crystals with growth lines on the margins of the septum. B) Longitudinal section of trabecula (T) with crystals diverging from COC, EMZ or CRA. C) “Shingles” on the outer surface of septa in *Acropora*. D) Longitudinal section through CRA. E) Transverse section through CRA. F) Fibres (F) in formic acid-etched TD showing polycyclic crystals. One cycle represents one days growth.**

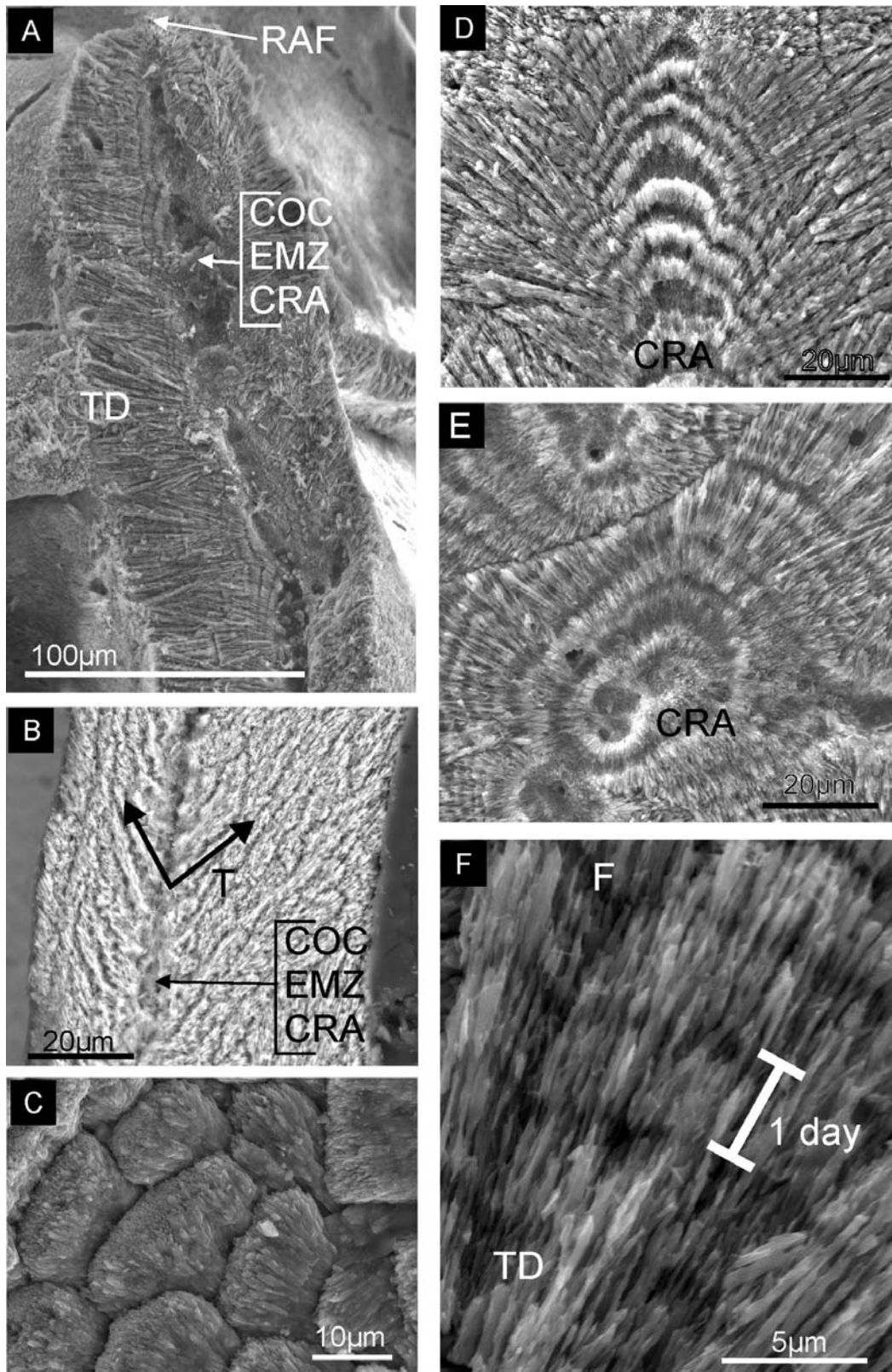


Fig. 3. *Caption on previous page.*

Studies of other calcareous skeletons (e.g., Mollusca) and the association of skeletal units with organic compounds led to the development of the “skeletal matrix” concept of Towe (1972). In coral skeletons, the swing toward biomineralisation models was highlighted by Johnston (1980) who pointed out that previous skeletogenesis models were made in ignorance of the spatial distribution of organic material within the skeleton. He noted evidence of a possible relationship between organic and mineral materials at a submicrometer scale by illustrating the organic network in the uppermost 3µm of a coral fibre. However, the work of Cuif and co-authors represents a major shift toward a hypothesis of biomineralisation in scleractinian skeletons by applying the organic matrix concept (Cuif et al., 1997; Cuif et al., 1999; Cuif and Sorauf, 2001; Cuif et al., 2003). Hence, over the past decade, the physico-chemical model has been replaced by more complex models wherein biomineralisation is intimately controlled by organic matrices (e.g., Goreau, 1959; Johnston, 1980; Constantz and Weiner, 1988; Gautret et al., 1997; Cuif et al., 1997; Cuif and Sorauf, 2001; Cuif et al., 2003a; Cuif and Dauphin, 2005b). Barnes (1970) hypothesized that an ectodermal “uplift” at the crystallisation front created free space available for abiotic aragonite growth. However, no mechanism was proposed for this ectoderm “uplift”. In contrast, the secretion of a hydro-organic gel (Cuif et al., 2004) by the basal ectoderm creates the space and environment for crystallisation without requiring the formation of a void predating mineralisation itself.

Johnston’s (1980) study dealt only with skeletal fibres and gave no insight into the nucleation of these fibres (Cuif and Sorauf, 2001). Centres of calcification (COC) (Table 2) were differentiated as discrete structures by both microstructural and biochemical techniques (e.g., Bryan and Hill, 1941; Gautret et al., 1997). These centres were originally interpreted to contain micrometer-size, randomly orientated crystals at the centres of trabeculae and were generally regarded as areas where many individual fibres nucleated (e.g., Bryan and Hill, 1941). However, in some cases, centres appear to consist primarily of organic matter with few preserved biocrystals (Stolarski, 2003). The differences between COC and radiating fibres led to the development of the ‘two-step model’ of coral skeleton growth (Cuif et al., 1997), with the first phase of growth occurring in the organic-rich centres of calcification. The centres then served as scaffolding for successive growth of a distinctly separate, second phase of layers of

aragonite fibres. The two steps highlight temporal differences in the formation of distinct microstructural and biochemical units. The model was subsequently adjusted with calcification centres replaced by the 'Early Mineralisation Zone' (EMZ) (Cuif et al., 2003a) to reference the temporal relationship.

Stolarski (2003) introduced a new 'layered model' with new nomenclature to contrast with the traditional 'two-step model'. In the layered model, centres of calcification are not fundamentally distinct from layers of fibres that cause skeletal thickening. Whilst similar to Cuif's 'two-step model', the 'layered model' explains the difference between COC or early mineralizing zones and fibres in terms of differential growth dynamics (e.g., rates) between the two units and not necessarily different timing of emplacement. Alternating layers of aragonite fibres and organic-rich zones pass through the COC, suggesting simultaneous formation of centres of calcification and lateral fibrous layers. However, Stolarski (2003) suggested two extreme end members. One depicts continuous growth of organic and mineral zones between 'Centres of Rapid Accretion' (dCRA) (or EMZ *sensu* Cuif et al., 2003a) and 'thickening deposits' (TD) (or fibrous growth) with no disjunction between the two zones (see Figure 17 from Stolarski, 2003, p. 519). The second end member has a discontinuity between dCRA and TD due to an increased rate of growth at dCRA, which is similar to the original two step model of Cuif et al. (1997). Stolarski suggested that this boost in growth is mainly due to increased production of organic matrix and not to the mineral phases within the dCRA. As distribution of organic and mineral phases in the EMZ and in individual fibres has been better documented, the original two step model of Cuif et al. (1997) has evolved to encompass the cyclic alternation of organic-rich and mineral phases both in individual fibres and in the EMZ (Cuif and Dauphin, 2005b).

The shift towards matrix-mediated skeletogenesis models has placed a greater emphasis on understanding the transport, accumulation and storage of the mineralizing ions in the coral polyp and the eventual transfer of the ions into the mineral and organic phase of the skeleton (see Gattuso et al., 1999; Marshall, 2002; Allemand et al., 2004, for reviews). Many previous investigations of the geochemistry of coral skeletons have been made under the simplified assumption that biological activity is limited to the transport of Ca^{2+} that creates the required conditions of supersaturation for aragonite

precipitation (e.g., McConnaughey, 1989; Sinclair and McCulloch, 2004). The biomineralisation process is controversial. Pathways of various chemical elements are believed to involve several steps and to be carrier mediated (e.g., Tambutte et al., 1996; Clode and Marshall, 2002; Ferrier-Pages et al., 2002; Al-Horani et al., 2003). Cuif and Dauphin (2005a) pointed out that little attention had been paid to soluble and insoluble organic compounds and to possible roles of the crystallisation process in previous investigations of the geochemistry of coral skeletons. Recent studies have revealed that organic and mineral components are not separated on the micro-scale and that seemingly monocrystalline fibres are actually composed of densely packed grains, tens of nanometers in diameter, embedded in a thin layer of organic material (Dauphin, 2001; Clode and Marshall, 2003a; Cuif et al., 2004; Cuif and Dauphin, 2005a, b; Rousseau et al., 2005; Stolarski and Mazur, 2005; Przenioslo et al., 2008). These papers have built on previous research (Isa, 1986; Clode and Marshall, 2003b) that described spherule crystals in subepithelial spaces as $\sim 1 \mu\text{m}$ in diameter and consisting of many finely granulated substructures of about 50 nm diameter. The mineral phases are controlled by the distribution of the ectoderm and organic molecules at various scales of interaction down to nanometer-scale organization within individual 'crystals' (e.g., Przenioslo et al., 2008). The organic components have been known to exist since Bryan and Hill (1941) and have been biochemically characterized and imaged in many studies of live corals since. They have also been shown to be preserved in fossil coral skeletons (e.g., Cuif et al., 2003a; Sorauf, 2003; Cuif and Dauphin, 2005b; Puvarel et al., 2005). Additionally, the effect of skeletal organic matter has been shown to influence the trace element and stable isotope ratios within the skeleton (Meibom et al., 2004; Muscatine et al., 2005), which has particularly important implications for the use of coral skeletons as recorders of palaeoclimate.

The current state of knowledge can be summarized as follows. Scleractinian coral polyps build exoskeletons of aragonite (CaCO_3) crystals formed beneath a layer of organic material secreted by cells in the basal ectoderm of the polyp (Sorauf, 1972). Individual aragonite 'crystals' are precipitated in a 'hydro-organic gel' (Cuif et al., 2004; Cuif and Dauphin, 2005b) and are arranged into macroscopic skeletal elements such as walls, septa and dissepiments (see Diagram 5 of Veron, 1986, p. 55) as controlled by the

distribution of the ectoderm and organic matrix molecules at nanometer scales of organisation (Cuif and Sorauf, 2001; Cuif and Dauphin, 2005a, b; Stolarski and Mazur, 2005). Etching techniques have revealed the remains of a cyclic biomineralisation process characterized by the presence of micrometer scale zonation or growth lines perpendicular to the direction of growth that are thought to correspond to successive positions of the secretory ectoderm (e.g., Ogilvie, 1896; Cuif and Sorauf, 2001). Cuif and Dauphin (2005a) showed that the growth lines correlate across adjacent microstructural elements, interpreting them as daily growth increments. Fluorescent staining techniques and atomic force microscopy suggest that the growth layers include intra-fibrous organic components (Gautret et al., 2000; Cuif and Dauphin, 2005a, b). Thus, skeletal fibres with lengths of tens of micrometers consist of composite growth increments of aragonite approximately 3 to 5 μm long separated by thin organic rich layers (Cuif and Sorauf, 2001), and even the mineral-rich phases consist of smaller units of aragonite contained within organic matter (e.g., Stolarski and Mazur, 2005). Cuif and Dauphin (2005a) showed that the increments are coordinated between adjacent microstructural elements, highlighting the biological control on mineralisation.

Irrespective of the models of skeletogenesis that produce the specific micro- and nanostructures, it is the three-dimensional spatial-temporal interplay between different microstructural elements that provides specific microstructural patterns in coral skeletons. The fundamental units of coral microstructure (i.e., fibres and centres of calcification and subsequent terms) have been well established for many years. Ogilvie (1896) developed a classification scheme of scleractinian corals based on the distribution of septal trabeculae using recent and fossil representatives. These observations were largely ignored until revision by Vaughan and Wells (1943) and Wells (1956). Subsequent classification schemes attempted to assimilate new data from Mesozoic and Cenozoic faunas (Alloiteau, 1952; Chevalier and Beauvais, 1987; see review by Stolarski and Roniewicz, 2001).

Different coral microstructures have been described in detail in some scleractinian genera since the advent of scanning electron microscopy, and the works of Sorauf (1972), Jell (1974), and Jell and Hill (1974) remain some of the best descriptions of microstructural relationships in coral skeletons. A seminal paper by Sorauf (1972)

noted that fibres and centres of calcification are arranged differently in different scleractinian genera resulting in a variety of distinct three-dimensional microstructural patterns. The implications of those different patterns are still being elucidated (e.g., Sorauf, 1970; Sorauf and Jell, 1977; Roniewicz, 1996; Cuif et al., 1997; Cuif and Perrin, 1999; Perrin, 2003; Stolarski, 2003). Sorauf (1972) and Roniewicz (1996) pointed out that fibres in corals occur in discrete geometric associations, and these associations combine in three dimensions to form macroscopic skeletal structures such as septa. The microstructural associations include: 1) columns of radiating fibres (trabeculae), 2) layers wherein parallel or palisaded fibres are perpendicular to the ectoderm (fibronormal microstructure), and 3) bundles of sub-parallel to radiating fibres that may lie at low angles to the overall surfaces on which they are secreted. The surface expression (i.e., microarchitecture) of these microstructural elements varies with fibronormal layers typically resulting in smooth surfaces, trabeculae resulting in spines or spinules, and bundles resulting in smaller bumps commonly referred to as fasciculi (Wise, 1970), tufts (Jell, 1974), scales or shingles (Sorauf, 1972). Much variability in microstructure between different coral genera is caused by differences in the occurrence and/or disposition of these microstructural fibre associations. The focus of different researchers on genera that have different combinations of associations has contributed to some of the difficulties in interpreting scleractinian coral skeletogenesis. Additionally, recent attention has been focused away from gross microstructure towards more nanostructural studies (i.e., of structure within individual fibres) (e.g., Cuif and Dauphin, 2005a, b; Stolarski and Mazur, 2005; Przenioslo et al., 2008), and there has been a rapid evolution of microstructural concepts and terminology. Recent attempts to link skeletal microstructure with molecular phylogenetic techniques (Cuif et al., 2003b; Stolarski, 2003; Fukami et al., 2004) have given only partial support for microstructure-based phylogenetic relationships within Scleractinia, but Cuif and Perrin (1999) suggested that this may partly result from the numerous uncertainties concerning the exact microstructural patterns of the species upon which major taxa have been based.

2. Palaeoclimate studies using geochemical archives in coral skeletons

Stable isotopes and trace elements in the aragonite skeletons of scleractinian corals have been widely studied because of their potential as recorders of temporally constrained palaeoclimatic data and pollution events (Table 3) (*see reviews by* Druffel, 1997; Bradley, 1999; Gagan et al., 2000; Felis and Patzold, 2003; Swart and Grottoli, 2003; Lough, 2004; Corrège, 2006; Eakin and Grottoli, 2007; Grottoli and Eakin, 2007). Palaeoclimate information recorded in coral skeletons includes sea surface temperature (SST) and climatic cycles defined on that basis, salinity, coastal run-off versus drought, ocean up-welling, wind anomalies and marine productivity (see Table 3 for specific references). Instrumental climate records are too short to resolve long term natural climate variability. Hence, knowledge of these proxies allows coral skeletons to be used to reconstruct records of intra-annual, inter-annual, inter-decadal, and centennial scale climate variability. Coral based geochemical proxies are most commonly used for records of seasonal variability and pre-instrumental records of oceanographic systems such as the El Niño Southern Oscillation system (ENSO) (e.g., Cole et al., 1992; Lough, 1994; Linsley et al., 1999; Corrège et al., 2000), the Pacific Decadal Oscillation (PDO) (e.g., Cobb et al., 2001; Linsley et al., 2004), Indo-Pacific Warm Pool (IPWP) (e.g., Gagan et al., 2004), North Atlantic Oscillation (NAO) (e.g., Felis et al., 2000) and pre-versus post-industrial climate events. The most important of these palaeoclimate records are recovered from large, massive corals growing in warm tropical waters that are centuries-old (e.g., Quinn et al., 1996; Lewis et al., 2007). Some individual coralla record growth spanning up to 350 years (Dunbar et al., 1994), dated with annual banding visible in cross-sections of coral skeleton by X-ray radiography (Knutson et al., 1972). Additionally, because coral skeletons are datable using ^{14}C and U/Th techniques, fossil corals have revealed important climate cycles lasting decades at known intervals throughout the Holocene (e.g., Beck et al., 1997; Gagan et al., 1998; Corrège et al., 2000; Moustafa et al., 2000), and coral skeletons have recorded the last interglacial warm period in the Late Pleistocene (e.g., Aharon and Chappell, 1986; McCulloch et al., 1996; Hughen et al., 1999). Such climate records are important because natural climate variables, such as ENSO, have socio-economic implications owing to their large scale

modulation of droughts, floods, cyclones, or fish-stocks at time scales relevant to society (Felis and Patzold, 2003). Hence, coral skeleton geochemistry provides a better understanding of past climate variability that is critical for interpreting and/or predicting present and future global climate.

Recent advances in technology have led to sampling techniques, such as laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) (e.g., Sinclair and McCulloch, 2004), ion microprobe (e.g., Meibom et al., 2007) and Secondary Ion Mass Spectrometry (NanoSIMS) (e.g., Meibom et al., 2004) that allow geochemical sampling at increasing levels of spatial resolution with the hope for subannual (e.g., Gill et al., 2006) or even sub-daily temporal resolution (e.g., Meibom et al., 2007). Table 4 contains a summary of high resolution geochemical analytical techniques that have been used on coral skeletons. However, as resolution has increased, these techniques have shown various discrepancies between measured expected values (Allison et al., 2001; Finch et al., 2003). In part, this variation, or heterogeneity in values, has been linked to the biomineralisation process itself (Cuif and Dauphin, 2005a). For example, Meibom et al. (2004) illustrated alternating Mg concentrations that correlate to the daily growth bands of polycyclic biocrystals using NanoSIMS mapping techniques (Secondary Ion Mass Spectrometry) with an analysis area of 50 nm, suggesting a role for Mg in regulation of the crystallisation process (Cuif and Dauphin, 2005a). Additionally, the concentrations of Sr and Mg and stable isotope ratios have been reported to vary between fibres of the TD and the EMZ (e.g., Cohen and McConnaughey, 2003; Rollion-Bard et al., 2003a; Meibom et al., 2004; Allison et al., 2005). Furthermore, ion microprobe analysis of the distribution of Mg, Rb, Sr, Ba and U in coral aragonite showed significant heterogeneity corresponding to monthly growth (~30 µm) (Allison, 1996a, b). The evidence increasingly suggests that trace element and stable isotope distributions within coral skeletons are affected by vital effects (e.g., Sinclair and Risk, 2006), thus, highlighting the importance of scale in the analysis of Scleractinian coral geochemistry for palaeoclimate archives (summarized by Cuif and Dauphin, 2005a; their Fig. 15). The finer the sample resolution, the greater the geochemical heterogeneity appears to be, both in spatial and quantitative terms.

Table 3. Environmental variables that have been reconstructed from the geochemistry of coral skeletons (modified from Table 1 in Grottoli and Eakin, 2007, p. 68).

Proxy	Environmental Variable	Selected Reference
Isotopes		
$\delta^{18}\text{O}$	Sea surface temperature	Epstein et al., 1953; Weber and Woodhead, 1972; Kim and O'Neil, 1997
	Sea surface salinity	Cole et al., 1993; Linsley et al., 1994; Le Bec et al., 2000; Urban et al., 2000
$\delta^{13}\text{C}$	Light (e.g., seasonal cloud cover)	Fairbanks and Dodge, 1979; Shen et al., 1992a; Quinn et al., 1993
	Plankton intake	McConnaughey, 1989
$\delta^{14}\text{C}$	Ocean ventilation, water mass circulation	Druffel and Griffin, 1993; Guilderson et al., 1998; Guilderson et al., 2000
$\delta^{11}\text{B}$	pH	Vengosh et al., 1991; Gaillardet and Allegre, 1995; Honisch et al., 2004; Reynaud et al., 2004; Pelejero et al., 2005
$\delta^{15}\text{N}$	Water quality (fertilizer)	Marion et al., 2005
	Symbiosis	Muscantine et al., 2005
^{10}Be , ^{26}Al , ^{36}Cl	Cosmic ray intensity	Lal et al., 2005
Trace elements		
Sr/Ca	Sea surface temperature	Weber, 1973; Beck et al., 1992; McCulloch et al., 1994; Correge, 2006
U/Ca	Sea surface temperature	Min et al., 1995; Shen and Dunbar, 1995
Mg/Ca	Sea surface temperature	Mitsuguchi et al., 1996; Schrag, 1999; Fallon et al., 2003
B/Ca	Sea surface temperature	Hart and Cohen, 1996; Fallon et al., 1999, 2003
Mn/Ca	Wind anomalies	Shen et al., 1992a, b
	Upwelling	Delaney et al., 1993
	Land use	Lewis et al., 2007
Cd/Ca	Upwelling, contamination	Shen et al., 1987, 1992a; Delaney et al., 1993
Ba/Ca	Upwelling	Lea et al., 1989
	River outflow	Alibert et al., 2003; McCulloch et al., 2003; Sinclair and McCulloch, 2004; Lewis et al., 2007
Pb/Ca	Gasoline burning	Shen and Boyle, 1987; Fallon et al., 2002; Medina-Elizalde et al., 2002
REE	Biological activity, river outflow	Naqvi et al., 1996; Fallon et al., 2002; Wyndham et al., 2004;
Y	River outflow	Lewis et al., 2007
Skeletal characteristics		
Skeletal growth bands	Light (seasonal changes), stress, water motion, sedimentation, sea surface temperature	Dodge and Thompson, 1974; Hudson et al., 1976; Scoffin et al., 1989; Eakin et al., 1993, 1994; Lough, 2004
Luminescence	River outflow, precipitation, ocean productivity	Isdale, 1984; Tudhope et al., 1996; Wild et al., 2000; Lough et al., 2002

Table 4. Summary of high resolution techniques used to measure coral geochemistry, including selected references, the area of a single chemical analysis and comments on observed variability.

Technique	Selected References	Analysis area	Proxy	Env. Variable	Comments
Electron Microprobe	Gill et al., 2006	1 to 2 μm	Sr conc.	—	Sr concentration correlates to daily growth bands
Ion Microprobe	Hart and Cohen, 1996; Cohen et al., 2002	50 to 80 μm	Sr/Ca	SST	Weekly resolution
	Rollion-Bard et al., 2003a	30 to 50 μm	$\delta^{18}\text{O}$, $\delta^{11}\text{B}$, $\delta^{14}\text{C}$	pH	Variability due to vital effects
	Cohen and Sohn, 2004	20 μm	Sr/Ca	SST	Bi-weekly variability
	Allison and Finch, 2004	~10 μm	Sr/Ca	SST	Difference between COC and skeletal fibres
NanoSIMS ¹	Meibom et al., 2004; Meibom et al., 2007	~0.4 μm	Mg/Ca, Sr/Ca	SST	Large heterogeneity, Mg conc. correlates with daily growth bands
SHRIMP RG ²	Meibom et al., 2006	<50 μm	Sr/Ca, Mg/Ca, B/Ca, S/Ca, Ba/Ca, $\delta^{18}\text{O}$, $\delta^{13}\text{C}$	SST	Difference between COC and skeletal fibres
LA-ICP-MS ³	Fallon et al., 2002	100 x 500 μm	Multiple elements	Pollution	—
	Buster and Holmes, 2006	50 μm	Mg/Ca	Diagenetic alteration	—
	Sinclair, 2005	33 to 17 μm	B/Ca, Mg/Ca, Sr/Ca, U/Ca	SST	—
	Runnals and Coleman, 2003	20 μm	Multiple elements	Pollution	—

¹ Secondary Ion Mass Spectrometry

² Sensitive high resolution ion microprobe reverse geometry

³ Laser ablation-inductively coupled plasma-mass spectrometry

The use of geochemical tracers in corals is critical to provide an archive of past climates for tropical, shallow ocean regions (Table 3). Although many types of geochemical tracers and proxies have been used for palaeoclimate studies (Table 3), stable isotope temperature proxies have provided much of the research in this field (*see extensive review by Grottoli and Eakin, 2007*). Pioneering work on the use of $\delta^{18}\text{O}$ as a palaeothermometer was published by Epstein et al. (1953) following theoretical work of Urey (1947). Palaeothermometry based on $\delta^{18}\text{O}$ was applied to corals by Weber and

Woodhead (1972). The oxygen isotope ratio ($^{18}\text{O}/^{16}\text{O}$), reported as $\delta^{18}\text{O}$, depends primarily on the temperature of seawater in which the carbonate formed (Epstein et al., 1953). As the temperature increases, the ^{18}O fraction of the coral skeleton decreases (Kim and O'Neil, 1997), resulting in a change of $\sim 0.22\text{‰VPDB}$ per 1°C (Grottoli and Eakin, 2007), but the initial oxygen isotope ratio of seawater varies as a function of ice volume and, locally, by the relative significance of precipitation/evaporation. For example, increased ice volume on the continents during glacial intervals leads to higher $^{18}\text{O}/^{16}\text{O}$ ratios in seawater, as ^{16}O is impounded in glacial ice (Shackleton, 1986). However, sampling both deeper benthic and shallower pelagic foraminifer species allowed glacial and temperature signatures to be separated (e.g., see Emiliani and Shackleton, 1974). Resulting temperature-driven marine isotope curves (e.g., Emiliani, 1955; Emiliani and Shackleton, 1974; Shackleton and Opdyke, 1976) are critical for understanding Pleistocene climate. More locally, high rainfall to the surface ocean results in a decrease in the seawater $^{18}\text{O}/^{16}\text{O}$ ratio as meteoric ^{16}O -rich water is introduced, and a decrease in sea surface salinity (SSS). The reverse relationships are caused by increased evaporation (e.g., Craig, 1966; Cole et al., 1993; Urban et al., 2000), species of coral and location (Weber and Woodhead, 1972; Wellington and Dunbar, 1995; Linsley et al., 1999). Thus, variable isotopic signatures can result locally from large amounts of rain, which can decrease salinity, runoff, and water mass transport as different water bodies have slightly different isotopic signatures (Felis and Patzold, 2003). Although well established, some doubt remains as to the accuracy of the $\delta^{18}\text{O}$ proxy when using high-resolution techniques. Rollion-Bard et al. (2003a) coupled $\delta^{11}\text{B}$ analysis, believed to be a proxy for pH, with $\delta^{18}\text{O}$ and suggested rapid pH variations at the sites of calcification could control the kinetics of isotopic equilibrium and that a 'vital effect' is responsible for the observed for $\delta^{18}\text{O}$ isotopic composition.

The stable isotopic species of carbon ($^{13}\text{C}/^{12}\text{C}$), reported as $\delta^{13}\text{C}$, are primarily influenced by changes in photosynthesis, which is related to light and feeding behaviour (e.g., Fairbanks and Dodge, 1979; Shen et al., 1992a). Phototrophs preferentially take up ^{12}C from dissolved inorganic carbon (DIC) in oceans, so during periods of increased photosynthesis seawater is enriched in ^{13}C affecting the uptake of $\delta^{13}\text{C}$ into skeletal

aragonite. $\delta^{13}\text{C}$ is difficult to interpret in areas of upwelling (Felis et al., 1998) as this can influence feeding of phototrophic organisms.

Radiocarbon (^{14}C) is also archived in coral skeletons during growth. It reflects the ^{14}C of the ambient DIC content of seawater, which is ultimately controlled by the level of ^{14}C in the atmosphere and ocean mixing times. Radiocarbon is reported as $\Delta^{14}\text{C}$ (‰), which is the $^{14}\text{C}/^{12}\text{C}$ ratio relative to 19th –century wood. Besides its obvious utility in radiocarbon dating, it has been used successfully as a tracer of oceanic upwelling (e.g., Druffel and Griffin, 1993), and for horizontal advection of water masses that upwelled elsewhere (e.g., Guilderson et al., 1998). Radiocarbon is produced naturally in the stratosphere and was also introduced into the atmosphere by nuclear weapons explosions. Bomb-produced ^{14}C is represented by an increase in radiocarbon levels in the 1950's and 1960's during nuclear weapons testing (Grotolli and Eakin, 2007). Prior to this period, a declining trend in ^{14}C during the 20th century, termed the Suess Effect, has been attributed to the dilution of natural ^{14}C by the addition of CO_2 derived from burning fossil fuels, which are free of ^{14}C owing to their great age (Suess, 1953; Druffel and Griffin, 1993; Pelejero et al., 2005).

The Sr /Ca ratio has been widely cited as a proxy for SST (e.g., Beck et al., 1992; Alibert and McCulloch, 1997; Corrège, 2006). However, the validity of Sr/Ca ratios as palaeothermometer proxies has been debated due to studies that suggest that the Sr/Ca ratio is influenced more by growth rate than temperature (Weber, 1973; de Villiers et al., 1995; Allison et al., 2001; Cohen and McConnaughey, 2003; Finch et al., 2003), albeit temperature is known to influence growth rate (Clausen, 1971). In contrast Houck et al. (1977), Smith et al. (1979), and more recently, Reynaud et al. (2007) suggested that temperature controls the Sr/Ca ratio independently of growth. Additionally, the nature of the incorporation of Ca^{2+} and Sr^{2+} ions into the coral is also controversial. Some authors (Ip and Krishnaveni, 1991; Ip and Lim, 1991) suggested that Sr^{2+} and Ca^{2+} are transported by different mechanisms, while others (Goreau, 1977; Chalker, 1981; Wright and Marshall, 1991; Ferrier-Pages et al., 2002) invoke a common pathway for both ions. Hence, it is currently difficult to interpret whether the Sr/Ca ratio is influenced more by biological or environmental parameters (Corrège, 2006). A complicating factor in reference to fossil corals is that Stoll and Schrag (1998) suggested that seawater Sr/Ca

could have been significantly different (i.e., higher) during glacial intervals due to the weathering of Sr-rich aragonite minerals that were sub-aerially exposed on continental shelves when sea-levels were significantly lower.

Min et al. (1995) and Shen and Dunbar (1995) first showed that U/Ca ratios may provide another proxy for SST reconstructions. However, those authors also suggested that other environmental parameters could influence the incorporation of U in the coral aragonite, despite a potential sensitivity to SST approximately five times that of Sr/Ca (Corrége, 2006). The uncertainty is primarily due to the complicated chemical behaviour of U in seawater and the paucity of studies on the manner of U incorporation into coral skeletal aragonite (Min et al., 1995; Lazar et al., 2004). Therefore, further work needs to be done to confirm U/Ca as a proxy for SST (Eakin and Grottoli, 2007).

The potential sensitivity of Mg/Ca to SST was first described by Chave (1954). Mg/Ca ratios of coral skeleton have been successfully applied for paleothermometry by Mitsuguchi et al. (1996) who sampled at a temporal resolution of ~3 week's growth. However, studies that have sampled at higher resolution suggest that Mg content in scleractinian corals varies spatially (Allison, 1996a, b; Sinclair et al., 1998; Meibom et al., 2004), and the relationship between coral Mg/Ca ratios and SST varies between different genera and localities (e.g., Allison, 1996a, b; Fallon et al., 1999). Variable Mg content in scleractinian corals was attributed to adsorption of Mg to crystal surfaces and organic ligands that are unequally distributed through coral skeletons or in microborings (e.g., Amiel et al., 1973; Allison and Tudhope, 1992; Allison, 1996a, b; Fallon et al., 1999, 2003). Therefore, there is general consensus that the reliability of the Mg/Ca thermometer is questionable (Corrége, 2006).

Boron in coral skeletons has also been applied to paleothermometry (Hart and Cohen, 1996; Sinclair et al., 1998; Fallon et al., 2003), but more work is required to understand the B/Ca tracer (Eakin and Grottoli, 2007). Additionally, Boron stable isotopes ($\delta^{11}\text{B}$) in coral skeletons have been applied as tracer of seawater pH (Gaillardet and Allegre, 1995; Pelejero et al., 2005).

Other trace elements in coral skeletons have been reported as proxies for upwelling and nutrients. Cadmium concentrations are higher in the deep ocean than in surface water, and Cd/Ca ratios have been measured in corals from the Galapagos as

tracers for the frequency, relative duration and intensity of seasonal upwelling (Shen et al., 1987) making it a useful tracer for the ENSO system. Ba/Ca ratios were also applied to upwelling events by Lea et al. (1989). However, recently Ba/Ca ratios in corals from the GBR have been used to recognise changes in the influx of fine sediment particles from rivers (McCulloch et al., 2003; Sinclair and McCulloch, 2004). Other metals such as yttrium (Y) and the rare earth elements (REE) exhibit similar estuarine behaviour to Ba/Ca and could be applied in the same manner (e.g., Naqvi et al., 1996; Fallon et al., 2002; Sinclair, 2005). Lewis et al. (2007) presented a 175-year record of Ba, Y and Mn from a coral core in the same region of the GBR from which McCulloch et al. (2003) collected their data. Lewis et al. (2007) reported Y levels that rose with agricultural intensification of the region. However, Ba concentrations plateaued after 1890, indicating that Ba/Ca ratios in near-shore corals may reflect factors additional to sediment input. Previously Mn has been used as an indicator of remobilized lagoonal sediments during strong episodes of equatorial westerly winds (associated with ENSO) (Shen et al., 1992a, b). In addition, Lewis et al. (2007) suggested that Mn concentrations may be used to indicate aspects of pre-European ecosystems as well as various aspects of anthropogenic land-use in the region such as the introduction of livestock.

Other coralline geochemical tracers shown in Table 3 remain to be thoroughly tested. Such tracers include the use of $\delta^{15}\text{N}$ as a proxy for fertilizer input and symbiosis (Marian et al., 2005; Muscatine et al., 2005 respectively), and a pilot study of cosmic ray proxies (^{10}Be , ^{26}Al , ^{36}Cl) by Lal et al. (2005) may have implications for understanding interstellar-terrestrial relationships, which could affect albedo and thus climate (e.g., Shaviv and Veizer, 2003; Veizer, 2005; Scherer et al., 2006).

3. Scleractinian coral diagenesis

Carbonate Diagenesis

Most modern and ancient reefal carbonate sediments originally consisted of a mixture of minerals. The most important minerals volumetrically are aragonite, high-magnesian calcite (HMC = calcite with >4 mole% MgCO₃; e.g., Morse and Mackenzie, 1990, p. 203) and low-magnesian calcite (LMC), with the abundance of particular minerals dependant in part on secular trends in marine Mg/Ca ratios (e.g., calcite versus aragonite seas of Sandberg, 1983; Hardie, 1996). Calcite can precipitate in a variety of forms. Many biogenic and non-biogenic calcites contain variable amounts of MgCO₃ (Chave, 1954). Aragonite is orthorhombic and structurally different from rhombohedral calcite. Aragonite and HMC are the most common biogenically and abiogenically precipitated carbonates in modern shallow marine environments in the current “aragonite sea” (i.e. with high Mg/Ca ratios). However, aragonite and HMC are metastable and, in a majority of cases, are converted to LMC during meteoric diagenesis (Morse and Mackenzie, 1990). High magnesium concentrations in calcite generally are not preserved in the geological record as Mg is lost during meteoric diagenesis. LMC, the most stable carbonate phase, is characteristic of meteoric environments owing to low Mg/Ca ratios of meteoric water (James and Choquette, 1983, 1984). The metastable nature of carbonate materials results in complex histories of cementation and dissolution both in depositional and diagenetic environments. Although diagenesis has been well studied in ancient reef rocks, owing partly to the importance of diagenesis in controlling porosity and permeability in carbonate petroleum reservoirs (e.g., Sun and Estaban, 1994), the degree to which very early diagenesis affects reefal carbonate, such as scleractinian coral skeletons, on the sea floor has not been investigated previously in any systematic way. Early diagenesis may be more important than previously thought for the preservation of geochemical archives in coral skeletons.

Diagenesis of carbonate rocks includes processes involving dissolution, cementation, lithification and alteration of sediments during the interval between deposition and metamorphism (below 200°C) (Flügel, 1982). The amount of alteration is dependant on the type of diagenetic environment and the original mineralogy. Modern

reef diagenesis principally concerns three diagenetic environments: sea floor, marine burial, and meteoric (freshwater) phreatic environments. The variation in pore water chemistry between marine and meteoric environments is a major control on the type of diagenesis, and each environment has its own distinctive suites of processes and products. It is well known that aragonite and HMC alter to LMC when exposed to meteoric environments, due to their relative instability in pore fluids that are undersaturated with respect to carbonate minerals (e.g., Harris and Matthews, 1968; James, 1972; James and Choquette, 1984; Budd, 1988). Reefs, by virtue of growing in shallow water, are prone to subaerial exposure during sea-level fall. Dissolution and karstification reflect exposure to meteoric environments during lowstands of sealevel. Diagenetic studies have been carried out on diagenesis in numerous Pleistocene reefal carbonates (e.g., Land and Epstein, 1970; James, 1972, 1974; Moore, 1989; Budd et al., 1995) as a result of the major sealevel fall at the end of the Pleistocene when levels dropped to ~140 m below present sea level (e.g., Chappell, 1974; Thom and Roy, 1985; Larcombe et al., 1995; Ota and Chappell, 1999). Such karst surfaces provide possible reservoir targets in ancient reefs because of their cavernous nature and aid in the understanding of reef history in relation to sequence stratigraphy by indicating potential lowstands. Ancient and modern Scleractinian corals have been the target of many of the diagenetic studies with papers by Spiro and Hansen (1970), James (1972), Hubbard (1975) Sorauf (1980); Potthast (1992) and Gautret and Marin (1993) being among the most important, and several important review papers exist (e.g., Constantz, 1986b; Sorauf and Cuif, 2001).

Cementation

Cement Precipitation

Marine cement grows in pores and requires supersaturation of pore fluid with respect to the cement mineral. The parameters that govern non-enzymatic and abiotic carbonate precipitation and dissolution in marine waters are highly complex and, while extensively studied, are not entirely understood (*reviews by* Morse and Mackenzie, 1990; Morse and Arvidson, 2002). Primary extrinsic factors controlling non-enzymatic

and abiotic carbonate precipitation relate to: (1) the saturation state of ambient water with respect to carbonate minerals; (2) presence of appropriate nucleation sites; and (3) absence of specific inhibitors of nucleation (Webb, 2001).

Although supersaturation is generally not a limiting factor in shallow tropical marine waters, as both calcite and aragonite are supersaturated (e.g., Lyakhin, 1968; Morse and Mackenzie, 1990), a number of abiotic effects can locally increase carbonate saturation. Agitation of waters caused by wave energy results in CO₂ degassing (Hanor, 1978; Given and Wilkinson, 1985; Gischler and Lomando, 1997). Solar heating of shallow water, particularly where ponded and isolated from normal marine circulation, a common setting in the intertidal zone of shallow reef environments, causes decreased carbonate solubility as CO₂ degassing raises the pH (Revelle and Emery, 1957; Hanor, 1978; Webb, 2001). Increased pH increases carbonate alkalinity by promoting continued dissociation of carbonic acid (H₂CO₃) to yield additional carbonate (CO₃²⁻) (Morse and MacKenzie, 1990, their Fig. 1.1, p. 8). Additionally, evaporation in these ponded waters increases ionic concentrations.

Organisms and dead organic matter mediate water chemistry in a variety of different ways. Degradation of enclosed organic matter may cause dissolution of metastable carbonate minerals when anaerobic microbes create H₂S through sulfate reduction (Sass et al., 1991; Mozley and Carothers 1992). However, where the H₂S is able to escape, sulphate reduction commonly leads to precipitation as it increases the alkalinity by releasing HCO₃⁻. The activity of microboring organisms modifies the chemistry of the pore solutions, which become richer in organic compounds (Schroeder, 1972; Scherer, 1974). Gautret (2000) suggested that the diagenetic state of intraskeletal organic matrices influences the development of cements directly on the surface of skeletal substrates as well as the formation of diagenetic aragonite overlying biogenic aragonite within skeletal structures. Furthermore, biotic effects are capable of causing localised supersaturation to reach a critical level where increased carbonate alkalinity produces excess CO₃²⁻ and bicarbonate (HCO₃⁻). If this change in saturation state occurs in the presence of appropriate nucleation sites and in relative absence of inhibitors, it will result in biologically induced carbonate precipitation (*for reviews see Ehrlich, 1990; Castanier, et al., 1999; Riding, 2001; Webb, 2001*).

Non-enzymatic (biologically induced) mineralisation occurs when precipitation is a by-product of the metabolic activity or the presence or decay of an organism or organic matter (Webb, 2001). Biologically induced precipitation may be confined to organic matter or protected pore space below the inducing community in settings where water volumes are large and well mixed. However, cavity systems, common in subsurface Holocene reef-rock, may create relatively closed systems, in some cases, where water is not well mixed. Such conditions may facilitate a far greater influence of the inducing community on the localized water chemistry, generating conditions that favour precipitation in the entire localised fluid volume (Webb, 2001). This may result in precipitation away from the inducing community of apparently abiotic cement. All of those processes could greatly affect the degree and rate of lithification in modern reef settings.

In contrast to non-enzymatic mineralisation, abiotic mineralisation is spontaneous precipitation, which results from ambient physico-chemical conditions. Non-enzymatic and abiotic mineralisation processes represent a continuum that can be divided into two or three convenient categories with more or less indistinct boundaries. The semantics of the precipitate system are particularly relevant for discussions of the origin of marine cements. For example, some cement precipitated due to biological induction may be morphologically indistinguishable from abiotic cements. The biologically induced cements may be precipitated where ambient water chemistry would not have favoured carbonate precipitation were it not for the effects of the biotic community or organic matter (Webb, 2001). Several geochemical signatures have been suggested as possible methods for determining abiotic from biotic cementation (e.g., Sr-Mg trends – Carpenter and Lohmann, 1992; carbon isotope fractionation – Keupp et al., 1993; calcium isotope fractionation – Gussone et al., 2003; rare earth elements – Webb and Kamber, 2000; Nothdurft et al., 2004; trace elements - Webb and Kamber, 2004), but in many cases, the role and/or degree of biological induction/control is speculative.

Cement Facies

Pore-filling cements are precipitated in marine, meteoric and burial environments. Shallow-marine cements generally consist of aragonite and HMC. The precipitation of cement and dissolution of carbonate sediments is primarily controlled

by: the composition of the pore fluids (i.e., salinity; Mg/Ca ratio); primary porosity and permeability of the carbonates; water energy and flow rate; and carbonate ion activity and supply rates (Macintyre, 1984; Macintyre and Marshall, 1988; Morse and MacKenzie, 1990). As previously mentioned, high Mg/Ca ratios restrict most marine cementation to aragonite and HMC, but high Mg/Ca ratios also prevent calcite and aragonite from growing laterally, so that fibrous, acicular, micritic or peloidal cements are common. Additional controls on marine cements may include: the mineralogy of the substrate (e.g., syntaxial aragonite cement overgrowth on aragonite grains and Mg-calcite on HMC grains - Friedman et al., 1974); the rate of precipitation; the composition of organic matter within and on grains; and the activity of micro-organisms that may mediate carbonate precipitation (e.g., Harris et al., 1985; Lighty, 1985; McIntyre and Marshall, 1988; Castanier et al., 1999; Riding, 2001). Cement mineralogy can be diagnostic of particular diagenetic environments, but caution is required (e.g., Webb et al., 2007).

Cementation is strongly facies-related. Marine cements can be traced from beaches to deeper water with marine vadose and mixing zone cements generally characterized by gravitational and meniscus fabrics, such as those characterized in beachrock (e.g., Moore, 1989; Meyers, 1987; Gischler and Lomando, 1997; Webb et al., 1999). Marine phreatic cements are generally characterized by isopachous bladed, fibrous and microcrystalline forms as well as syntaxial overgrowths.

Most volumetrically significant cementation occurs in reef environments as a result of high levels of water agitation and a low rate of sedimentation (e.g., Lighty, 1985). Early cementation requires sufficient supply of carbonate, which is supplied by large volumes of seawater pumped through abundant primary pore space in reef environments through wave action and tidal pumping. Evaporation processes and temperature also have the effect of removing CO₂ by means of degassing and thus increasing alkalinity. Therefore, cementation is most abundant on the seaward/windward sides of shallow subtidal areas, and diminishes in leeward environments. Reef framework is commonly lithified to a depth of 50 cm below the surface (e.g., Ginsburg et al., 1971; Macintyre, 1977; Macintyre and Marshall, 1988).

Cementation in Holocene coral reefs

Studies of Holocene coral reefs indicate that early diagenesis considerably alters the original biogenic structure of the allochems (e.g., Macintyre et al., 1968; Ginsburg et al., 1971; Shinn, 1971; James et al., 1976; Macintyre, 1977; Land and Moore, 1980; Marshall, 1983; Macintyre and Marshall, 1988; Friedman, 1998; Camion et al., 1999). The alteration results from the activities of endolithic organisms, filling of cavities by sediments, and the formation of submarine cement. Limestones can be created in thousands or perhaps hundreds of years (e.g., Friedman, 1998). The process of diagenesis is ubiquitous from the first deposition of the carbonate. However, the timing of early diagenetic processes has not been adequately constrained. In particular, cementation of modern scleractinian coral skeletons has been documented in detail in Holocene reef rock containing large amount of pore-occluding cements with few attempts to constrain how long it takes for these cements to precipitate (e.g., Ribaud-Laurenti et al., 2001).

The morphology, occurrence, distribution, and facies association of Holocene marine cements have been characterised in many Holocene reef locations (e.g., Macintyre, 1977; Land and Moore, 1980; Marshall, 1983). Holocene marine cements from the GBR were characterised by Marshall (1983) for One Tree Reef, Capricorn Bunker Group (Fig. 1A, B). Both aragonite and HMC show a diversity of textures and fabrics (Table. 5). Marshall (1983) stated that there was no indication that cementation increased with depth within individual drill-holes, suggesting that most cementation occurs close to the surface of the growing reef and that there is very little cementation occurring afterwards in sections where the reef was buried by subsequent growth. Similar observations have been made on cement distribution in other Holocene reefs around the world (e.g., Ginsburg et al., 1971; Macintyre, 1977, Macintyre and Marshall, 1988). Hence, early diagenesis could be responsible for a large amount of the observed cement within a modern coral reef.

Microbialites have only recently been recognized in Holocene reef environments despite contributing large amounts of carbonate and rigidity to the reef framework. However, lithified, micritic Mg-calcite crusts have figured prominently in the literature on Quaternary coral reef diagenesis for several decades (e.g., Land and Goreau, 1970;

Friedman et al., 1974; Macintyre, 1977; Land and Moore, 1980; Marshall, 1983), but the crusts generally were considered to be abiotic marine cements, and early attempts to attribute them to biological activity were controversial (e.g., Pratt, 1982). Microbialite cements are the result of non-enzymatic biologically induced mineralisation within microbial biofilms. In Holocene reefs they generally occur in cryptic environments with significantly reduced light conditions (e.g., Reitner, 1993; Camoin and Montaggioni, 1994; Webb and Jell, 1997). Holocene reefal microbialites have now been described from reefs in the Great Barrier Reef (Reitner, 1993; Webb and Jell, 1997), Caribbean (Zankl, 1993; Reitner et al., 2000), Tahiti (Montaggioni and Camion, 1993; Camion and Montaggioni, 1994; Camion et al., 1999), Indian Ocean (Camion et al., 1997) and Vanuatu (Cabioch et al., 1999).

Early Diagenesis in Scleractinian corals

Cements

The term early diagenesis refers to diagenesis occurring immediately after deposition of the carbonate (Berner, 1980). Early diagenesis is generally interchanged with the term taphonomy, which refers to the study of the post-mortem history of organic, including skeletal, material (*see review by* Perry and Hepburn, 2008). In reference to modern reef environments early diagenesis can denote any near surface processes and products that occur up until complete lithification, which can occur very rapidly or can span several thousand years. However, for the purpose of this thesis I am focusing on the diagenetic processes that occur in the coral skeleton during the life of the coral polyp.

In Scleractinian corals natural cavities are formed within coralla as a consequence of coral growth. As living polyps secrete new skeleton, they rise within their respective corallite tubes and deposit dissepiments (more or less horizontal skeletal plates) that separate them from the abandoned portion of the tube in the underlying “dead” skeleton (Hill, 1936; Wells, 1969; Sorauf, 1970). Cement that was precipitated in the cavities of skeletons of live coral colonies has been illustrated by few authors since the early 1970’s (e.g., Hubbard, 1972, 1975; Pottast, 1992; Enmar et al., 2000;

Müller et al., 2001, 2004; Perrin and Cuif, 2001; Perrin, 2004; Nothdurft et al., 2005; Reuter et al., 2005; Buster and Holmes, 2006; Quinn and Taylor, 2006; Allison et al., 2007; Nothdurft and Webb, 2007; Nothdurft et al., 2007; Hendy et al., 2007), and most previous reports of early marine cement in living corals have been crusts of syntaxial aragonite needles (e.g., Potthast, 1992; Le Campion-Alsumard et al., 1995; Enmar et al., 2000). Additionally, acicular aragonite is the most common cement in Holocene reefs in general (e.g., Ginsburg et al., 1971; Macintyre, 1977; Macintyre and Marshall, 1988). In the GBR, acicular aragonite cement is abundant within most coral pores in Holocene framework facies and was interpreted to be the first cement formed (Marshall, 1983).

The occurrence of intra-skeletal aragonite needle cements was demonstrated in live coral skeletons in a series of aquarium-grown and natural samples from the Caribbean, East Africa and the Great Barrier Reef by Hubbard (1972; 1975). Macintyre (1977) noted, without illustration, that secondary aragonite rim cements commonly occur in the skeletal cavities a few millimeters below the tissue of living hermatypic corals. Potthast (1992) described early marine aragonite cement that precipitated syntaxially on coral aragonite surfaces in seawater within ten to twelve years of growth of *Porites* samples from water depths ranging from 1.5 to 4.5 meters in fringing reefs at Mauritius Island. Müller et al. (2001) investigated secondary aragonite at the base of a 1.9 m-long core through a colony of *Porites lobata* recovered from ~8 m of water offshore from Rabaul, Papua New Guinea. In that case the cemented basal section of the core showed a positive shift in $\delta^{18}\text{O}$ and Sr/Ca relative to non-cemented sections of coral aragonite. Palaeothermometry analysis yielded SST estimates in cemented parts of core that were ~4-5°C cooler than unaltered parts of the skeleton.

Table 5. Holocene Great Barrier Reef cements described by Marshall (1983).

Mineral	Morphology	Distribution			Occurrence	Size
		Facies	Intraskeletal	interskeletal		
Magnesian Calcite	Bladed Spar	Common in all framework facies	✓	✓	Common in pores of corals as isopachous rims - generally associated with inner micrite cement layer - also interparticle cement within grainstones	Rims - 30-120 µm thick - crystals 10-60 µm long and 4-25 µm wide - inner micrite layer 10-30 µm
	Micrite	Ubiquitous	✓	✓	Abundant around walls of coral pores or on syntaxial aragonite	uneven rims 10-60µm thick
	Peloids	Common in all framework facies	✓	✓	Widespread infill of skeletal pores, borings and cavities - commonly forms geopetal structures	Spherical bodies (10 to 80 µm in diameter) of microcrystalline HMC (1 µm) with crystalline cement fringes (crystal 5 to 40 µm)
	Lithified Crusts	Present in all major framework facies	✓	✓	Pelmicrite coatings	Crusts 0.5 to 5 cm thick
Aragonite	Acicular	Abundant within coral pores from all framework facies	✓	✗	Generally fills coral pores, in some cases coated by magnesian calcite micrite or rarely bladed spar - commonly first cement formed - syntaxial on coral fibres	Crystals 20-200 µm long and 2-20 µm wide
	Spherulitic	Exclusively within cavities between successive layers of crustose coralline algae	✓	✗	Most common as half spherulite nucleated from roof or floor of cavity - peloid inclusions common - faint concentric lamination - similar to botryoidal mammelons (Ginsburg & James, 1979)	radially oriented crystals 50-400 µm long and 10 µm wide
	Mesh	Uncommon	✓	✗	Intraskeletal cement, typically filling remaining pore space after magnesian calcite micrite - nucleated from silt-sized microcrystalline aggregates	randomly oriented 10-40 µm long and 5 µm wide
	Micrite	Ubiquitous - similar to magnesian calcite micrite but volumetrically far less important	✓	✗	Typical infill of interstices between silt-sized internal sediment - dark in transmitted light	microcrystalline cement (< 1 µm)
	Silt	Uncommon, generally fills pores	✓	✗	Pore or cavity infill - Consists entirely of sponge chips cemented by syntaxial aragonate - cement on optical continuity with fibres of sponge chips	20-60 µm sponge chips
	Blocky	Extremely rare	✓	✗	Present within coral pores that also partly filled with magnesian calcite micrite - late stage cement - could be mistaken for aragonite silt but has finer crystal size	equant 5-12 µm crystals that form interlocking mozaic

Bioerosion

Destructive processes and activities are an important part of the early diagenesis of coral skeletons. Biological erosion, termed bioerosion by Neumann (1966), denotes the organic erosion of calcareous substrates. It is associated with the grazing activities of fish and echinoids, as well as the activities of a range of endolithic borers. These are divided into two size categories; macroborers, which include specific groups of sponges, bivalves and worms, and microborers, which include cyanobacteria, chlorophytes, rhodophytes and fungi (Hutchings, 1986). Of all the macroboring groups, sponges have received the greatest attention because, on a reef-wide basis, they are typically the dominant infaunal eroders, comprising some 75–90% of the total macroboring community (in terms of the proportion of substrate infestation; e.g., Goreau and Hartman, 1963; MacGeachy and Stearn, 1976; Highsmith, 1981; Highsmith et al., 1983; Perry, 1998). The importance of sponges also stems from the morphology of their borings, because many sponge species excavate dense networks of inter-connected chambers (to depths of several centimeters) within the coral skeleton. In order for sponges to produce or extend their burrows specialized cells (archaeocytes) dislodge silt sized, lenticular fragments by etching fissures into the carbonate substrate behind them (Pomponi, 1980). The sponges use a process involving carbonic anhydrase and acid phosphatase to dissolve the carbonate (Pomponi, 1980). *Cliona*, a common genus of bioeroding sponge forms a complicated network of connecting galleries or chambers 1–15 mm in diameter that generally penetrate no more than 20 mm below the coral surface.

Early diagenesis also involves dissolution of skeleton by endoliths and the possible induction of precipitation of microbial carbonates or other minerals in the microenvironments controlled by endoliths or other endobionts. Microborings are well documented in scleractinian coral skeletons (Duerden, 1902; Risk et al., 1987). Fungi, cyanobacteria, and green algae are common borers and endobionts within cavities in coral skeletons and other carbonate substrates (e.g., Perkins and Halsey, 1971; Macintyre and Towe, 1976; Risk et al., 1987; Benth et al., 2000). Identification of filaments in interseptal spaces is difficult, but filament diameters are suggestive of fungi (diameters generally, 2 mm), cyanobacteria, and filamentous green algae. The green alga

Ostreobium has been described as ubiquitous in skeletons of live corals (Lukas, 1974). In reef environments different microboring assemblages relate to varying depths and light levels (e.g., Budd and Perkins, 1980; May et al., 1982; Vogel et al., 2000). Communities in the upper parts of the photic zone (0 to 5 m) are dominated by highly diverse cyanaobacteria and green algae. Whilst in deeper zones, the assemblage diversity of phototrophic organisms is reduced and progressively lost as heterotrophs increase (i.e., fungi) (Perry and Hepburn, 2008, their Fig. 4).

Some microbes have been shown to induce and/or localize the precipitation of secondary aragonite, HMC (Schroeder, 1972), LMC (Nothdurft et al., 2007) and even different Mg-bearing phases, such as brucite [Mg(OH)₂] (Smith and De Long, 1978; Nothdurft et al., 2005; Buster and Holmes, 2006). Exotic cements (e.g., brucite; Nothdurft et al., 2005) associated with organic biofilms in live-collected corals highlight the presence and importance of intra-skeletal micro-environments that reflect chemistry that is significantly different from ambient seawater. Microenvironmental precipitates are common in the abandoned cavities of the dead parts of coralla, but they also may occur within borings within the skeleton, where they may affect skeletal trace element inventories (e.g., Allison and Tudhope, 1992).

Additionally, bioeroding sponges may occur in very young parts of coralla (Schönberg, 2002) where they may alter internal fluid flow or diffusion characteristics (Schroeder, 1972; Scherer, 1974). Such changes to the hydrodynamics within individual coralla could have significant local effects on the chemistry of pore-waters and their throughput.

Cement Geochemistry

Coral skeletons that are to be used for geochemical analysis are routinely vetted to check for diagenetic alteration. It is generally assumed that fossil coral skeletons that have not been exposed to freshwater (meteoric) diagenesis should retain reliable marine trace element inventories (Bar-Matthews et al, 1993; McGregor and Gagan, 2003). In the case of meteoric diagenesis altered corals will contain calcite. Live-collected corals are also checked for early marine aragonite cement that precipitates syntaxially on coral aragonite surfaces in seawater (e.g., Enmar et al., 2000; Quinn and Taylor, 2006). These

aragonite cements have the potential to disturb important geochemical proxies in the coral skeletons (Figs. 4 and Allison et al., 2007, their Fig. 4), because the cements generally have higher Sr and lower Mg concentrations than the aragonite of the coral skeleton (e.g., Enmar et al., 2000). Aragonite cement contains a distinct isotopic and geochemical composition that differs from that of the coral skeletons (e.g., Enmar et al., 2000; Quinn and Taylor, 2006). Enmar et al. (2000) estimated the rate of cavity filling by aragonite cement to be 1.5 ± 0.3 kg aragonite per year which equates to 0.15% of the coral's weight. Analysis of pore-water extracted from the coral indicated that secondary aragonite precipitation may have been responsible for filling up to 2% of the initial porosity within 100 years. The mixture of pristine and secondary aragonite can lower (by about 2°C) the estimated SST according to the conventional Sr/Ca thermometry. Similarly, Lazar et al. (2004) measured uranium concentrations in secondary aragonite to be significantly higher than that in skeletal aragonite (17.3 ± 0.6 and $U/Ca = 1.79$ $\mu\text{mol/mol}$ compared to 11.9 ± 0.3 nmol.g^{-1} and $U/Ca = 1.23$ nmol/mol respectively). The result would be a small but measurable effect on the U/Ca thermometry and the U/Th ages (7% apparent age rejuvenation effect) (Lazar et al., 2004). Secondary marine aragonite and Mg-calcite are enriched in ^{13}C relative to aragonite (Müller et al., 2006). Quinn and Taylor (2006) also calculated a shift in stable isotopic values resulting in calculated mean SST's that are $\sim 2.5^\circ\text{C}$ ($\delta^{18}\text{O}$) and $\sim 6^\circ\text{C}$ (Sr/Ca) colder than unaltered coral. Therefore, the products of very early diagenesis (i.e., diagenesis within a few years of skeletal biomineralisation), including cementation and bioerosion, in modern coral skeletons could potentially influence data collected for palaeoclimate analysis.

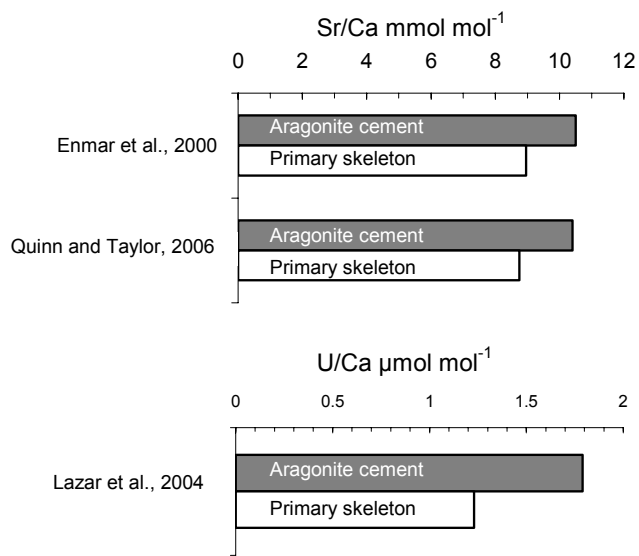


Fig. 4. Trace element ratios of aragonite needle cements and primary skeletal aragonite in live collected *Porites* corals.

PUBLISHED PAPERS / SUBMITTED MANUSCRIPTS

Paper 1. Nothdurft, L. D. and Webb, G. E. (2007) Microstructure of common reef-building coral genera *Acropora*, *Pocillopora*, *Goniastrea*, and *Porites*: constraints on spatial resolution in geochemical sampling. *Facies* **53**, 1-26.

This paper presents a comprehensive review of scleractinian coral microstructure and serves as the basis from which diagenetic alteration of coral skeletons can be compared. Unlike many previous studies of gross coral microstructure, which have focused on specific genera (e.g., Cuif and Perrin, 1999) or on scleractinia as a whole (e.g., Sorauf, 1972) this study specifically compares four important common genera that have very different arrangements of microstructural elements. Hence, the paper highlights the complexity and spatial variability of skeletal growth in different coral genera focussing on the reef-building genera: *Acropora*, *Pocillopora*, *Goniastrea* and *Porites*. A new growth model is proposed for *Acropora* to add to existing, generalised growth models so as to highlight differences between different genera. The implications of microstructural analysis are then applied to geochemical sampling methods that are commonly used for palaeoclimate investigations of coral skeletons. This study highlights the pitfalls of using coral skeletons for high spatial resolution geochemical analysis with the aim of fine temporal resolution data. This paper was peer-reviewed revised following the editor's and reviewer's comments, and published in the international journal *Facies*.

Contribution of authors

Field work and collecting of samples was done by me and G. E. Webb. I prepared and identified the coral samples, prepared thin sections and polished etched and broken sections for Scanning Electron Microscope (SEM) analysis at the QUT Analytical Electron Microscopy Facility. I prepared the original and final manuscript for publication. G. E. Webb provided supervision throughout the project and provided editing comments on the original and final manuscripts.

Paper 2. Nothdurft, L. D. and Webb, G. E. (submitted) Earliest diagenesis in scleractinian coral skeletons: implications for palaeoclimate-sensitive geochemical archives. *Facies*

This paper presents a comprehensive study of early diagenetic products that occur in live-collected scleractinian coral from the Great Barrier Reef (i.e., the same coral genera for which microstructural data were documented in Paper 1). The paper basically represents a test of the hypothesis that live-collected corals preserve pristine coral skeleton, which should contain unaltered geochemical proxies that reflect ambient seawater conditions. Diagenetic products investigated include early marine cements and bioerosion. Corals collected live on the reef flat can show extensive alteration where parts of coralla less than 2-3 years old contain abundant microborings and high-Mg calcite, aragonite and even brucite [Mg(OH)₂] cements. These cements can vary significantly in terms of chemistry from the aragonite coral skeleton, and if inadvertently sampled would cause geochemical interpretation to be erroneous. Studies such as this one are necessary in order for coral diagenesis to be understood adequately to allow coral skeletons to serve as repositories of temporally constrained geochemical data at fine spatial and temporal scales.

Contribution of authors

Field work and collecting of samples was done by me and G. E. Webb. I prepared and identified the coral samples, prepared thin sections and polished etched and broken sections for SEM microanalysis at the QUT Analytical Electron Microscopy Facility. I prepared the original and final manuscript for publication. J. T. Kloprogge assisted me with gathering the Raman spectroscopy data and interpretation of this data. G. E. Webb supervised the project, and provided editorial comments on the original and final manuscripts.

Paper 3. Nothdurft, L. D., Webb, G. E., Bostrom, T. and Rintoul, L. (2007) Calcite-filled borings in the most recently deposited skeleton in live-collected *Porites* (Scleractinia): Implications for trace element archives. *Geochimica et Cosmochimica Acta* **71**, 5423-5438.

This paper documents live-collected *Porites lobata* specimens wherein as much as 60% of the skeletal aragonite has been bored by microbes (cyanobacteria) and replaced by calcite cement. Most previous geochemical analysis of coral skeletons have been carried out under the assumption that corals that have not been affected by meteoric diagenesis should retain geochemical signatures reflecting ambient seawater. Here, we demonstrate the effects of the very early cements within microborings on trace element ratios (Sr/Ca and Mg/Ca) and discuss their effects on palaeoclimate proxies. We additionally suggest a model to explain their occurrence. These very early cements may be widespread, and failure to recognise them in corals used for palaeoclimate studies would compromise high resolution palaeotemperature reconstructions. Hence, the paper highlights the great care that must be taken in vetting samples for microanalysis, and the results will be useful for any researchers using coral skeletons as repositories of geochemical data. This paper was peer-reviewed revised following the editor's and reviewer's comments, and has been published in the international journal *Geochimica et Cosmochimica Acta*.

Contribution of authors

Field work and collecting of samples was done by me and G. E. Webb. I prepared and identified the coral samples, prepared thin sections and polished etched and broken sections for microanalysis on the SEM at the QUT Analytical Electron Microscopy Facility. I prepared the original and final manuscript for publication. T. Bostrom assisted me with the use of JOEL 840 microprobe for geochemical data acquisition, statistical interpretation of this data, and provided editorial comments on the manuscript. L. Rintoul aided with vibrational spectroscopy analysis. G. E. Webb supervised the project, assisted in the development of ideas and interpretations, and provided editorial comments of the original and final manuscripts.

Paper 4. Nothdurft, L. D., Webb, G. E., Buster, N. A., Holmes, C. W., Sorauf, J.E., and Kloprogge, J. T. (2005) Brucite microbialites in living coral skeletons: Indicators of extreme microenvironments in shallow-marine settings. *Geology* **33**, 169-172.

This paper provides new insight into the important role of microenvironments in early diagenesis in shallow marine carbonate environments. The presence of brucite and in live-collected coral skeletons specifically highlights the importance of such microenvironments in these settings and the role that microbes play in altering local water chemistry and subsequent mineral composition, relative to ambient seawater. Use of skeletal carbonates that are contaminated by such precipitates as proxies for ambient seawater are problematic for palaeoclimate reconstruction. Hence, their recognition is critical. This paper was peer-reviewed revised following the editor's and reviewer's comments, and has been published in the international journal *Geology*.

Contribution of authors

Samples were collected by me and G.E. Webb. I prepared and analysed samples from the Great Barrier Reef for microanalysis, and Buster, Holmes and Sorauf independently analysed samples that were discovered in Florida at the same time. The global coverage afforded by including data from both teams is significant. Kloprogge and I performed infrared spectroscopy on samples from both locations to confirm the identity of the brucite. I prepared the original and final manuscripts. G. E. Webb supervised the project, brought in the international collaborators and made editorial comments on the manuscripts.

GENERAL DISCUSSION

As stated in the introduction of this thesis, geochemical data obtained from coral skeletons must meet certain criteria in order to be useful for palaeoclimate reconstruction. Firstly, data must reflect a true time series with a known degree of time averaging. This is especially critical for high resolution sub-monthly data. Even in relatively low-resolution bulk sampling the degree of time averaging must be established to account for, for example, seasonal overlap. Secondly, microstructural data must be adequately constrained to account for the normal degree of geochemical heterogeneity (scatter) in coral skeletons. Finally, sampled skeletal aragonite must reflect the seawater in which it was precipitated (e.g., lack of subsequent diagenetic alteration), or at least the diagenetic products must be recognised and their effects taken into account. The aim of the thesis research was to focus on 1) coral microstructure and 2) earliest diagenesis to provide constraints on those criteria.

Coral Microstructure

Constraints on temporal series geochemical data

This study highlights the difficulties of geochemically analysing coral skeletons at high spatial resolution with the aim of achieving fine temporal resolution data (Paper 1). For corals to serve as ideal geochemical proxies, their skeletons would accrete along smooth, continuous fronts at a uniform rate in the direction of extension, thus forming layers analogous to tree rings. However, the complex three-dimensional microstructure of coral skeletons and differential timing of emplacement of different fibre associations (e.g., trabeculae before bundles) are far from ideal. Various types of skeletal infilling and thickening deposits postdate initial wall and septal formation to various degrees, as constrained by the timing of dissepiment emplacement when surfaces are isolated from living tissue and further growth. Hence, immediately adjacent parts of the skeleton may have formed at different times of the year, and depending on overall extension rates, calice depth, and rates of dissepiment emplacement, adjacent skeletal accretion may even span different seasons or years. However, the temporal discontinuities between, for

example, older trabeculae and significantly younger shingle thickening deposits in *Acropora*, may be no more prominent than individual growth lines in fibrous skeleton. Thus, the fine-scale temporal relationships of coral skeleton are very important if high resolution geochemical techniques (e.g., LA-ICP-MS, ion microprobe) are to be capable of obtaining reliable temporal sequences of data useful for palaeoclimate analysis; understanding the microstructure of the corals being analysed is critical. It is not adequate to have small sample sizes (beam diameters and laser spots); the exact spatial relationship of those samples to growth lines and specific microstructural elements within coral microstructure is critical to ensure time-series data.

As analytical spot sizes have decreased, the amount of time averaging has decreased. As a trade-off discrepancies between measured and expected values for environmental proxies have increased (Allison et al., 2001; Finch et al., 2003, Paper 3). Recent micro-analytical studies of coral skeletons show clearly that the skeletal chemical and isotopic composition are not uniform over the skeleton, suggesting strong biological control on skeletal formation. In part, this variation reflects vital effects wherein trace-element distributions correlate directly to microstructural patterns (i.e., early mineralising zones vs thickening deposits) (e.g., Cohen et al., 2001; Marshall, 2002; Rollion-Bard et al., 2003; Allison and Finch, 2004; Meibom et al., 2004; 2006). New analytical instruments permitting 50 nm spatial resolution (e.g., Nano-SIMS) are capable of mapping the variability of diurnal biogeochemical signatures (Meibom et al., 2004). At fine scale the need to know exactly what part of the skeleton is sampled is amplified because vital effects apparently differ in different microstructural settings (e.g., EMZs versus thickening deposits). Additionally, understanding the heterogeneity as it relates to microstructure may help understand skeletogenesis itself. If the heterogeneity represents vital effects, then element distributions should tell us something about the biomineralisation process.

This study shows that the variety of different microstructures in different coral genera place real constraints on sample placement and that microstructure cannot be ignored. All current laser and microprobe spot sizes for geochemical sampling involve a degree of time averaging that may also include seasonal overlap where temporal discontinuities in skeletal microstructure occur. Even high resolution analysis must be

combined with observations of microstructure with an emphasis on differential timing of emplacement of different fibre associations to ensure temporal sequences of environmental proxies with known degrees of time averaging of geochemical data. Time averaging varies from place to place due to local complexities of microstructure. In some cases, the degree of time averaging can be calculated using growth lines as daily increments (Cuif and Dauphin, 2005a). Light acid etching enhances these growth lines and when viewed using SEM, thus allowing the exact degree of time averaging to be understood. Fine scale geochemical sampling of coral skeletons for high temporal resolution will be distorted where sampling does not take microstructure into account directly. Thus, attention must focus on the relationship between different microstructural fibre associations (trabeculae, fibronormal layers and bundles) in order to establish the fine-scale temporal relationships within coral skeletons.

Existing models for the growth of scleractinian coral skeletons already have highlighted differences in the timing of growth of different skeletal elements (e.g., Cuif et al., 1997; Stolarski, 2003), and advances from the traditional trabecular model to incorporate stepped growth and organic layering have greatly improved our understanding of coral microstructure. However, the present study highlights the complexity and spatial variability of skeletal growth in different coral genera at levels of organisation far above the nano-scale of individual fibres. One basic model of organo-matrix-controlled skeletogenesis may account for the formation of individual fibres in and out of EMZ, but a variety of different microstructural growth models are required to characterise the temporal relationships of particular associations of fibres within a given skeleton. As an example, a new growth model was proposed for *Acropora* to add to existing, generalised growth models for scleractinian coral skeleton so as to highlight differences between the different genera (see Paper 1). In this model, the initial stage of layered trabecular growth is followed by fibre growth organized into shingles that are almost parallel to the surface of the ectoderm in pockets. Importantly for palaeoclimate studies, the layers of shingles may contain various temporal discontinuities without obvious growth breaks. The time difference between trabeculae and shingles was calculated to potentially span several months (Paper 1). Such new models are required if

coral skeletons are to be interpreted adequately to serve as repositories of temporally constrained geochemical data.

Taxonomy of Scleractinian coral

Better understanding of coral microstructure also has implications for other areas of investigation, such as for scleractinian coral taxonomy and phylogeny. Approaches to microstructural analysis similar to those applied in this study (Paper 1) could be applied to other species, genera or families of corals. Skeletal microstructure-based characters may more accurately reflect skeletal growth than traditional macro-morphological characters, and therefore serve as better phylogenetic markers (e.g., Stolarski, 2003). The detailed microstructural data reported here add weight to a recent push toward microstructural-based phylogenetic approaches. Detailed microstructural research seems to be getting more and more attention from biologists and palaeontologists because skeletal microstructure correlates better with phylogenetic analyses based on mitochondrial and nuclear DNA than do traditional macro-scale skeletal characters (e.g., Fukami et al., 2004; Benzoni et al., 2007; Budd and Stolarski, 2007; Cuif, 2007; Stolarski, 2007a). In a recent survey of the family Mussidae, Budd and Stolarski (2007) reported that micro-morphological and microstructural characters reveal far less homoplasy, have higher consistency indices and are diagnostic to higher level clades than macro-morphological characters. Furthermore, Stolarski (2007b) suggested that minute-scale patterns of skeletal fibre organisation (e.g., surface expression of shingles of *Acropora* described here) may be shared by related taxa (species/genera) and thus represent valuable skeleton-based criteria in morpho-molecular phylogenetic analyses. The organisation of skeletal fibres may be much more diverse than previously assumed and suggests intimate guidance by the organism (Stolarski, 2007b), and thus presumably reflects genetic control. Hence, microstructural studies will be useful for biologists and palaeontologists for resolving genetic relationships and questions relating to coral evolution.

Early Diagenesis

Implications for palaeoclimate records

Although live-collected corals would be predicted to preserve pristine coral skeleton, corals collected live on the reef flat of Heron Reef have been shown in the present study to have suffered extensive diagenetic alteration where parts of coralla less than 2-3 years old contain abundant microborings and several different types of cement (see Papers 2, 3 and 4). A range of early marine cements were identified in coralla of common reef building corals, including several mineral species, that precipitated in intra-skeletal cavities located immediately beneath living coral polyps. Aragonite cements were precipitated in a range of morphologies including needles, rods, and botryoids. HMC cements were observed as splays, needle-fibres and scalanohedra. LMC was observed as coarse textures filling in microborings in even the youngest parts of some coralla. Brucite cements occur in the interseptal spaces of some coral colonies in a range of morphologies. Early diagenetic cements are an acknowledged source of error in geochemical analyses of coral skeletons, and aragonite cements contain distinct isotopic and trace element compositions that differ from those of coral aragonite (e.g., Enmar et al., 2000; Quinn and Taylor, 2006; Allison et al., 2007). This study showed that even LMC cements that formed in a confined environment with relatively low levels of water-rock interaction still contained radically different trace element concentrations than their host coral aragonite, which would have severely disturbed SST calculations if even small amounts of the cements were inadvertently sampled (Paper 3). Contamination by brucite would especially affect Mg/Ca ratios (e.g., Paper 4; Buster and Holmes, 2006). Hence, cements documented in this study vary significantly in terms of chemistry from the aragonite coral skeleton, and if inadvertently sampled would cause erroneous geochemical interpretations.

Most previous studies have attributed geochemical differences between coral skeleton and cements to differences in trace element incorporation or isotopic equilibria during coral skeletogenesis (i.e., vital effects) as compared to physico-chemical (i.e., abiotic) precipitation. Thus, both coral skeleton aragonite and cements are inferred to basically reflect ambient seawater. Thus, provided the nature of vital effects were

understood, coral skeleton and physico-chemical cements could serve as direct proxies for seawater. However, the present study suggests that many of the early cements in coral skeletons grew in microenvironments wherein the water chemistry did not reflect that of ambient shallow seawater. That observation has important implications for palaeoclimate archives.

Microenvironments

Distribution of cement within live coralla is controlled by both abiotic and biological processes, but the latter processes are more important in the present samples (Papers 2, 3 and 4). Some aragonite needle cement is consistent with abiotic precipitation reflecting increased carbonate saturation typical of the warm and well agitated tropical seawater. The distributions of all other cement types appear to be entirely controlled by microbially-mediated microenvironments, although broader physico-chemical forcing may have enhanced precipitation. Nucleation of aragonite, HMC and brucite cement on organic matter, microendolithic filaments, and the increased cementation associated with boring sponges suggests that some cementation was biologically induced or at least biologically localized. The lack of isopachous cements in some cavities may also reflect biological control wherein nucleation was inhibited by organic matter within those cavities. Different minerals precipitated within the same intracorallum spaces and non-uniform distribution of the various minerals at fine scales, commonly occupying only small parts of available surfaces within a given cavity, is consistent with their formation in microenvironments constrained by biofilms.

As stated earlier, the sampled skeletal aragonite must reflect the seawater in which it was precipitated in order to be useful as a seawater proxy. Ambient seawater within a cavity could not have produced aragonite, brucite and HMC over the same time frames, without some of the cements being isolated within biofilm-controlled microenvironments. The brucite (Paper 4) and LMC (Paper 3) cements particularly highlight the importance of microenvironments in these settings and the role played by microbes in altering confined water chemistry. Neither mineral should precipitate naturally in shallow seawater. Hence, microenvironments are important in early coral diagenesis and may not reflect ambient seawater chemistry.

Despite the clear positive correlation of cements and microbial endoliths documented in this study and the ubiquitous occurrence of endobionts in coral skeletons in general (Risk et al., 1987; Le Campion-Alsumard et al., 1995a,b; Allison, 1996b; Benthis et al., 2000; Golubic et al., 2005), there has been little previous discussion of causal links between bioerosion and cementation in corals (e.g., Scherer, 1974; Rehman et al., 1994). Research has focused more on coral dissolution (e.g., Barnes and Lough, 1993; Le Campion-Alsumard et al., 1995a). However, skeletal dissolution may increase alkalinity and lead to enhanced precipitation as discussed previously for sponges. Additionally, density loss due to bioerosion almost certainly affects the hydrodynamics within the coral skeleton, and resulting alkalinity may be related to localized cement precipitation (e.g., Scherer, 1974). As microboring assemblages in reef environments relate to bathymetry and light penetration (e.g., Budd and Perkins, 1980; May et al., 1982; Vogel et al., 2000) and seasons (Risk et al., 1987), cementation might be expected to vary in a similar way. Furthermore, microborings may be more abundant in corals when growth rates are slowed due to stress, such as that associated with bleaching events (e.g., Golubic et al., 2005). If the correlation observed in this study holds in those cases as well, it may be possible to use cement types to recognize intervals of stress or changes in growth rates in Pleistocene or older corals where organic matter is no longer preserved.

Implications for future research

Obviously the most important implication of the outcomes of this study is that the techniques used here should be applied to the vetting of corals to be used for geochemical analysis to ensure reliable and accurate results. Firstly, microstructural analysis should be applied to high resolution geochemical analysis to ensure accurate temporal sequences with known degrees of time averaging, and to account for vital effects in different microstructural units. Secondly, SEM analysis should be done to avoid marine cements that reflect different chemistry to the coral skeleton. Finally, visual vetting for diagenetic alteration is required for analysis at all sampling scales, if only to determine what types and abundances of cements are present that might affect geochemical proxies. X-ray diffraction is clearly inadequate as a sole vetting tool.

It is also clear that a greater understanding of vital effects is required to fully understand the spatial constraints of various palaeoclimate tracers used in coral skeletons. Thus, high resolution chemical investigations (e.g., NanoSIMS) of the relevant elements in mineral and organic phases of the coral skeleton and comparisons of chemical variations between different microstructural units within a given coral and between corals with different microstructures are warranted.

Perhaps the most fundamental question that arises from the present research relates to how representative the studied samples are. Despite the wide array of diagenetic alteration observed in coralla in this study, published SEM images of studied coral cores suggest that some scleractinian coral skeletons are in very good condition from a diagenetic point of view (e.g., Meibom et al., 2003). Additionally, I have surveyed large sections of cores of live *Porites* coral heads where cements and boring were minimal or absent. Such coral samples clearly were not affected by endolithic activity to the degree observed in the studied Heron Reef corals. This could reflect the large size of coralla that are sampled for geochemical cores (up to several meters in diameter representing centuries of continuous coral growth), if they reached a critical point where they were able to 'outgrow' microbial infestations (Paper 2). Alternately, the larger coral heads typically grow in deeper water (2 to 10 m) than the corals sampled in this study, so better preservation could reflect lower light penetration, less active borers, and a lower degree of physico-chemical forcing (e.g., degassing of CO₂ due to water agitation). However, an alternative hypothesis also exists where the current samples reflect unusually warm years and may not serve as a good guide for older corals. Coral bleaching events are undocumented prior to the 1970's but have expanding since then in frequency, severity, and geographic scale (Hoegh-Guldberg, 1999). Therefore, the levels of early diagenesis documented in the present corals may not be widespread in modern or particularly older corals (although they all still must be vetted!). If so, the present levels of diagenesis may be a good indicator of stress, even in older corals. In order to test those hypotheses, studies similar to the present one need to be carried out on larger coral heads and on corals from a wider suite of environments including deeper environments.

Another direction for future research is to examine scleractinian corals in Holocene reefrock using the same techniques to elucidate the types of diagenetic changes that occur during early burial. Combined with dating techniques, such studies would allow determination of the rates of early diagenetic change during the Holocene. The live collected samples documented here could provide a reference of original microstructure and geochemistry of the different reefal carbonate types, allowing for comparison with Holocene reef rock of different ages to evaluate the degree of change in the reef through time.

Many of the cements observed in these live collected corals have been described in the pores of older Holocene reef rock (e.g., Lighty, 1985; Macintyre and Marshall, 1988). So the question arises: 'what are the implications of these very early marine cements for subsequent diagenesis?' As coral reef rock is commonly a good hydrocarbon reservoir (e.g., Sun and Esteban, 1998), a better understanding of the effects of early diagenesis on later diagenesis would be important for hydrocarbon exploration and for reservoir engineering. The relationship between particular reef facies and reservoir is dependant on a variety of synsedimentary and subsequent diagenetic behaviours, and resulting distributions of porosity and permeability may be very irregular and complicated. Hence, appropriate means of better understanding reefal plays in general are critical for hydrocarbon exploration and development.

The obvious result of cementation is a reduction in porosity and permeability affecting subsequent fluid flow. However, sequestering of Mg in minerals like brucite might promote subsequent mineralisation, including dolomitisation. There is some evidence of natural brucite dissolution occurring in live collected corals (Paper 2), and dissolution was induced in corals treated with hydrogen peroxide, illustrating the low stability of brucite in slightly more acidic solutions. The release of large amounts of Mg via brucite dissolution could result in localised conditions suitable for precipitation of other shallow marine Mg phases, such as dolomite or HMC. For example, HMC peloids are one of the most common cements in Holocene reef rock, but are notably absent in the samples documented above. Additionally, cements that nucleated on organic matter substrates, such as microbial filaments, may become mechanically unstable on

degradation of the organic matter, thus releasing particles into the pore spaces of the coral to act as nucleation points for subsequent cement growth.

Summary

The technique employed, and resulting level of spatial resolution, for geochemical sampling of coral skeletons requires specific degrees of vetting for early diagenetic features and skeletal microstructure as documented in live-collected corals from Heron Reef. XRD will detect large scale meteoric diagenesis. However, XRD is not able to detect diagenetic contaminants at small concentrations that could still affect high resolution geochemical data. Large scale, low temporal resolution sampling techniques, such as solution ICP-MS on powders generated by scraping or drilling (e.g., Yu et al. 2005; Calvo et al. 2007; Morimoto et al. 2007) and even LA-ICP-MS where spot sizes are greater than $\sim 50 \mu\text{m}$ (e.g., Fallon et al., 2002; 2003) could potentially sample all of the diagenetic cement types documented in this research. Techniques with smaller spot sizes (e.g., LA-ICP-MS, NanoSIMS, ion microprobe) can target individual skeletal structures and so avoid cements that occur on the surfaces of cavities. However, they must still avoid cements and organic matter that occurs within microborings, and that may be difficult in cases such as the LMC-filled borings because such cements are difficult to see on polished coral sections (Paper 3). Additionally, caution is required when microsampling targets specific skeletal structures. Direct observation of microstructural elements with SEM on polished and etched section are required to account for differences in microstructural patterns in different genera, both to ensure known time series and to account for differences that may occur due to the differential distribution and abundance of trace element due to vital effects. Observation of daily growth increments allows microsamples to be placed into series that represent temporal sequences with known degrees of time averaging. Hence, petrographic examination by optical and/or scanning electron microscopy on polished etched sections is necessary to ensure the quality of geochemical archives in coral skeletons to be used for palaeoclimatic reconstruction

CONCLUSIONS

1. Scleractinian coral genera have varying complex microstructures, and no single growth model is adequate to describe coral skeletogenesis in all genera at a scale relevant to palaeoclimate studies. Immediately adjacent portions of skeleton may have formed at different times of the year, and depending on overall extension rates, calice depth, and rates of dissepiment emplacement; adjacent skeletal accretion may even span seasons or different years. Current laser and microprobe spot sizes for geochemical sampling involve a degree of time averaging that may also include seasonal overlap. Thus, fine scale geochemical sampling of coral skeletons for high temporal resolution may be distorted where sampling does not take microstructure into account directly. The age of coral skeleton decreases both along trabeculae in the direction of corallum extension and laterally, from the center of trabeculae towards the septal flank within the corallite. Hence, both microstructure and coral extension rate data are required to interpret the temporal relationships of microsamples.

The variation of microstructures between different genera (particularly the interplay between trabeculae and thickening deposits) is especially important where temporal discontinuities in skeletogenesis are recorded and represent potentially significant time differences. Therefore, a greater understanding of the microstructure of specific coral genera is required if coral skeletogenesis is to be understood adequately for coral skeletons to serve as repositories of temporally constrained geochemical data. Direct observation of microstructure may be required in order to place geochemical samples in positions that will yield a known time series.

2. Corals collected live on the reef flat can show extensive diagenetic alteration where parts of coralla less than 2-3 years old contain abundant macro- and microborings and a variety of cements, including aragonite, high-Mg calcite, low-Mg calcite and brucite [Mg(OH)₂]. Most cement varieties documented here have not previously been reported in live coral colonies. However, many of the

cements have been documented in older Holocene/Pleistocene corals and in reef rock, or in other non-reefal carbonate environments. The distributions of most cements appear to be strongly influenced by organic matter associated with microbial organisms and sponges that inhabit the coral skeleton. This highlights the importance of microenvironments in these settings and the role that microbes play in altering local water chemistry and subsequent mineral composition, relative to ambient seawater. The examples of brucite and LMC cements specifically highlight the importance of microenvironments in these settings and the role that microbes play in altering local water chemistry and subsequent mineral composition, relative to ambient seawater. Identification of such contaminants is critical where corals are being analysed for geochemical proxies that are meant to inform palaeoclimate studies.

3. Compared to subtidal environments, coral growing on the reef flat in the intertidal environment may undergo more rapid diagenetic alterations due to extrinsic factors that increase carbonate saturation, such as evaporation and increased temperature at low tide.
4. Of the tested samples, massive corals were more heavily affected by cementation and bioerosion than branching coral forms. This may be due in part to the lower growth rate of massive growth forms compared to those with branching habits. Lower growth rates allowed endolithic microbes to keep pace with the rate of coral skeletal extension in the slower growing massive corals, but less so in the fast growing coral branches.
5. Most attempts to vet coral samples for geochemical studies have utilised basic petrography and X-ray diffraction analysis to look for calcite formed during meteoric exposure. This study illustrates that many diagenetic changes that can radically alter important geochemical characteristics of coral skeleton occur very early on the sea floor. Significant diagenetic changes that jeopardise palaeoclimate data do not require long-term diagenesis or exposure. Some of the

diagenetic changes (e.g., calcite filled borings) occur at scales that are very difficult to detect short of visual inspection using SEM. Hence, such vetting may be required before any sample is subjected to geochemical analysis.

6. The dominant remaining question is: How typical are the presently studied samples of corals in general? As better preserved corals have been documented and studied, it is important to determine if the present samples reflect the more diagenetically active environment of the shallow reef-flat, or if they have enhanced diagenesis owing to stress from having grown during a particularly warm interval. The present study clearly demonstrates the need for increased vetting of corals to be used for geochemical analysis, but determining the answers to the questions above will allow the present results to be applied more broadly to older corals. For example, if these corals are representative of the shallow reef flat, then similar high levels of diagenesis could be used to recognize such facies in older successions with implications for ancient sea levels. However, if the diagenetic levels reflect more stress owing to high temperatures, then similar high levels of diagenesis could be used to recognize stress, possibly including intervals with coral bleaching, in older successions.

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APPENDICES

Appendix 1. Nothdurft, L. D. and Webb, G. E. (2007) 'Shingle' microstructure in scleractinian corals: a possible analogue for lamellar and microlamellar microstructure in Palaeozoic tabulate corals – In: Hubmann, B. & Piller, W. E. (Eds.): Fossil Corals and Sponges. Proceedings of the 9th International Symposium on Fossil Cnidaria and Porifera. – Osterr. Akad. Wiss., Schriftenr. Edwiss. Komm. 17: 85-99, 2 Figs., 2 Pls., Wien.

Although the purpose of the PhD research was to investigate the effect of different coral microstructures and early diagenesis on the spatial characteristics and preservation of geochemical proxies in scleractinian coral skeletons, documentation of a new microstructural growth model for *Acropora* allowed for comparison with ancient coral microstructure (in the case, Tabulata). A long standing debate has existed as to whether or not the 'microlamellar' microstructure observed in tabulate corals is original or purely diagenetic (e.g., Rodriguez, 1989; Sorauf, 1996). The purpose of this paper is to: 1) describe microstructural elements in acroporid scleractinian corals that are similar in some regards to lamellar-microlamellar microstructure in Palaeozoic tabulates; and 2) directly compare the microstructures of extant *Acropora* and the extinct Mississippian tabulate coral, *Michelinia meekana* Girty from Arkansas, using the same analytical techniques (i.e., ultra-thin section and scanning electron microscopy – SEM). The 'shingle' microstructure of *Acropora* may provide an analogue for lamellae/microlamellae, and thereby provide the basis for interpreting some ancient microstructures in light of scleractinian biomineralization models. This paper was peer-reviewed and revised on the basis of editor's and reviewer's comments, and has been published in the conference proceedings of the 9th International Symposium on Fossil Cnidaria and Porifera held in Graz, Austria in August 2003.

Contribution of authors

Carboniferous and Holocene age coral samples for this manuscript were provided by G. E Webb. Live-collected coral samples were collected by me and G.

Webb from the Great Barrier Reef. I prepared thin-sections and polished-etched section for microanalysis on the SEM. G. E. Webb assisted in the development of ideas and interpretations, and provided editorial comments on the original and final manuscripts.