Geochemical Ecology of Temperate Corals

Samantha Nicole Burgess

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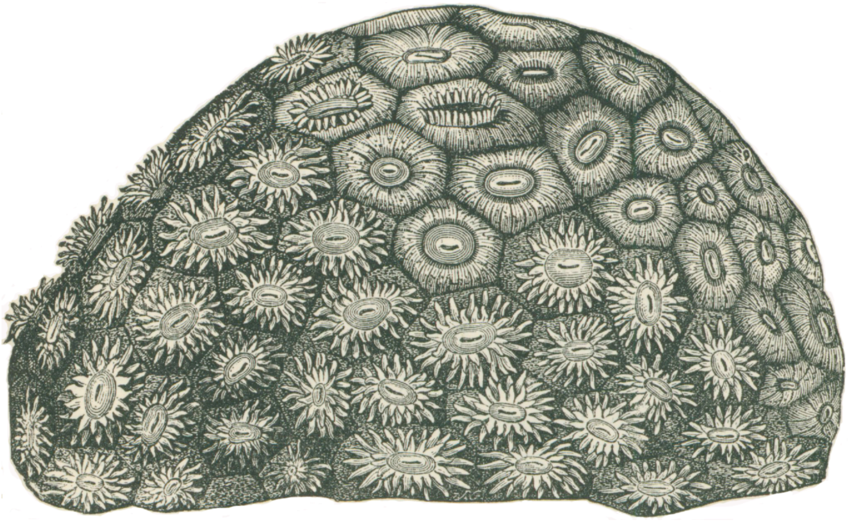
Science, while it penetrates deeply the system of things about us, sees everywhere in the dim limits of vision, the word mystery. Surely there is no reason why the simplest of organisms should bear the impress most strongly... It is not more surprising, nor a matter of more difficult comprehension, that a polyp should form structures of stone (carbonate of lime) called coral, than that the quadruped should form its bones, or the mollusc its shell.

This power of secretion is then one of the *first* and most common of those that belong to living tissue; and though differing in different organs according to their end or function, it is all one process, both in its nature and cause, whether in the Animalcule or Man. It belongs eminently to the lowest kinds of life. These are the best stone-makers; for in their simplicity of structure they may be almost all stone and still carry on the processes of nutrition and growth. Throughout geological time they were the agents appointed to produces the material of limestones, and also to make even the flint and many of the siliceous deposits of the earth's formations.

James D Dana
In: *Corals and Coral Islands.* 1875
Sampson Low, Marston, Lowe and Searle, London



Declaration

The work presented in this thesis was carried out while I was a full time student at the Research School of Earth Sciences, the Australian National University between March 2003 and March 2007. Except where referenced in the text, the research described here is my own.

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So long, and thanks for all the coffee!

Abstract

Corals are sensitive to changes in climate and, recently, high-latitude coral communities have received increased attention for their ability to act as refugia during global climate change. In this study, I report high resolution elemental ratio and stable isotope ($\delta^{18}O$, $\delta^{13}C$) time-series generated from the faviid coral *Plesiastrea versipora* to assess the fidelity of chemical variations in coral skeletons to reconstruct environmental conditions along the southern margin of Australia. This coral species has an expansive distribution throughout the Indo-Pacific and Indian marginal seas, providing a potential climate archive in a diverse range of oceanic conditions.

High resolution laser-ablation inductively-coupled plasma mass spectrometer (ICP-MS) analyses of established paleo-temperature proxies including B/Ca, Mg/Ca, Sr/Ca, Ba/Ca and U/Ca, a suite of minor trace elements (Li, P, V, Mn, Cu, Zn, Y, Zr, Mo, Cd, Sn, Ba, Ce, Pr, Nd, Pb) and milled $\delta^{18}O$ and $\delta^{13}C$ analyses were obtained from seven cores of *P. versipora* from Gulf St Vincent and Spencer Gulf (35ºS), South Australia. The annual nature of density bands were verified using U/Th ages derived from multi-collector ICP-MS analyses and colony ages ranged from 100-400 years. Large skeletal density variations were observed between the different coral colonies, including colonies sampled from the same reef. Annual extension rates for *P. versipora* varied from 1.2 to 8 mm $yr^{-1}$and these extension rates are among the slowest growth rates reported for hermatypic corals and are more comparable to growth rates of deep-sea corals.

The potential of *Plesiastrea versipora* to capture the full seasonal cycle of sea surface temperature (SST) variation (10-24°C) in the South Australian gulfs was assessed by comparing skeletal chemistry with *in situ* SST data. Proxy/SST calibrations generated from the fast growing corals (> 3 mm yr^{-1}) of Sr/Ca, U/Ca and $\delta^{18}O$ were comparable to published SST calibrations for other species. Very little temperature dependence was observed for B/Ca and Mg/Ca, and concentrations of these elements were amplified by secondary precipitates and other sources of contamination, and did not reflect temperature dependent fractionation in *P. versipora*. Ba/Ca generally displayed a strong inverse correlation with SST and was the trace element which captured the full amplitude of the seasonal cycle with highest fidelity. Ba/Ca ratios are the most reliable trace element paleotemperature proxy in *P. versipora*.

Corals with a very slow extension rate (less than 2 mm per year) did not capture the full amplitude of the seasonal cycle in either the trace elements or $\delta^{18}O$ analyses and are not useful for high resolution climate reconstructions. Sr/Ca and U/Ca from all colonies were strongly correlated with each other ($r^2 = 0.86-0.96$) in contrast to previous studies using *Porites* ($r^2 = 0.4-0.8$). Sr/Ca and U/Ca concentrations were observed to behave with a 'bimodal' distribution in the coral skeleton which was reproducible down the same laser track, but offset between adjacent tracks. The bimodal distribution in Sr and U was only observed in the corals with an extension rate of less than 2 mm yr^{-1}. This behaviour has implications for coral studies on other species with low extension rates, because it suggests that the coral polyp is mediating the fractionation of Sr and U (i.e. biological fractionation) rather than the thermodynamic fractionation exhibited by inorganic aragonite and fast growing coral species such as *Porites*.

Trace metal analyses conducted on *Plesiastrea versipora* indicate substantial contamination in several sites in Spencer Gulf and Gulf St. Vincent. Trace metal contamination was associated with changes in urban and industrial development, and land use changes. The coastal corals from Seacliff reef recorded increased concentrations of lead, most likely due to the proliferation of automobiles in the 1960s. Increased concentrations of other heavy metals including Cu, Sn, Zn and Mn may be related to the discharge of treated sewage at a coastal site less than 10 km away. High concentrations of V and Mo occurred in pulse events and correlated with luminescent bands in a fast growing metropolitan reef coral. The enriched concentrations in these elements were coincident with known oil spills in the region. The corals from Whyalla indicated higher concentrations in the heavy metals Zn, Sn and Pb and the source of the contamination is likely to be nearby smelters. Strong annual cycles of Zn were observed in two corals from different locations, this may be caused by phytoplankton blooms. Light rare earth element (Y, La, Ce, Pr, Nd) enrichment occurred in three corals. This enrichment had a positive correlation with westerly winds suggesting an aeolian dust source.

Two coral colonies separated by less than 10 m display considerably different maximum concentrations of several metals including Cu, Mn, Zn, Sn and Pb. This suggests that distribution coefficients vary within a species, and are dependent on growth rate or another colony specific mechanism. Caution should be used when applying published distribution coefficients to different species and growth rates and estimating seawater concentrations from coral trace metal concentrations. $\delta^{13}C$ analyses from a slow growing colony revealed a significant correlation with surface oceanic ^{13}C depletion from fossil fuel CO_2 (0.8‰) from the early 1930s to 2005 (the Suess effect).

The results from this study demonstrate that *Plesiastrea versipora* provides valuable paleoclimate information in high-latitude environments, recording seasonal and long-term variation in productivity regimes with high fidelity. *P. versipora* has the potential to act as a sentinel organism recording the industrial depletion in ^{13}C of DIC. This archive may be employed to reconstruct anthropogenic activity since European settlement and land-use changes not only in temperate Australia but other temperate regions in Asia and Africa.

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Chapter 1: Approach and Study Motivation

Rationale

Geological and anthropological evidence suggests that the global climate has been very different in the past than it is today. Variations in the temperature extremes and rainfall during the seasonal cycle can cause catastrophic effects for human inhabitants and other animals living in specialised environments. An example of climate related extinction is Australia's marsupial megafauna which died out during the Holocene, potentially due to vegetation changes in response to fluctuating Austral-Asian monsoon dynamics. Our knowledge of paleoenvironmental changes in the Southern Hemisphere is lacking compared with the extensive historical archives of the Northern Hemisphere. The known deficiencies in Southern Hemisphere records suggest that climate records from mid-southern latitudes would make an important contribution to understanding climate systematics and associated teleconnections. Paleotemperature reconstructions from the South Australian gulfs are influenced by complex oceanography and positioned to provide information on a broad range of climate oscillations. These gulfs are situated on the southern margin of a continental land-mass, one of the longest east-west coastlines in the world and may be influenced by three ocean basins including the Pacific, Indian and Southern Oceans. In this thesis, paleo-proxy archives from temperate corals are used to give insight into a unique ecosystem and provide greater temporal resolution on the role of the Southern Ocean in climate dynamics than has previously been achieved using speleothem or deep-sea sediment core archives.

Why the temperate coral: *Plesiastrea* versipora?

Corals growing in temperate-high latitude waters are sensitive to changes in climate, especially seasonal fluctuations in sea surface temperature. In the cool-water, high-energy environments of South Australia scleractinian corals are ideally positioned to record variability of temperature, salinity and ocean circulation along the southern margin of Australia. Scleractinia are typically stenotypic organisms with distributions limited by relatively minor fluctuations in environmental variables. In this regard *Plesiastrea versipora* (Lamarck, 1816) is an unusual species of scleractinia, because it occurs around the entire Australian coastline, which suggests it tolerates a wider range of climatic conditions. Large colonies of *Plesiastrea versipora* were first discovered in South Australia near Glenelg almost 100 years ago (Howchin 1909). Typical habitat is moderately exposed reef in water-depths of 0–30 m. *Plesiastrea versipora* is the most wide-spread of the southern Australian reef-building corals.

Background

Paleoclimate records have a unique role to play in our understanding of climate sensitivity and variability and how it changed in the past. High resolution proxy records provide detailed information on amplitude and characteristics of the seasonal cycle which have important climatic implications. In addition, high resolution climate proxies (weekly-monthly) timescales may record discrete events such as volcanic eruptions, floods and phytoplankton blooms as well as seasonal phenomena such as upwelling and winter rainfall. Paleoclimate reconstructions that have been calibrated against instrumental data offer the only source of information on long-term changes in climate variability and associated teleconnections. Paleoclimate reconstructions provide data for calibrating atmospheric and oceanic numerical models to develop predictive knowledge of these climate systems. With the modern climate concerns addressing global warming (Barnett et al. 2005) it is important to have multiple high-resolution temperature reconstructions for the last 300-400 years. A variety of proxy archives from a broad range of latitudes will allow short term changes in temperature due to anthropogenic influences to be accurately assessed and potential future impacts more accurately modelled.

Instrumental records in many locations only extend back to the mid 19th century, prohibiting the development of seasonal resolution archives at regional scales to assess climate response to increasing greenhouse gas concentrations in the atmosphere. However, the instrumental record indicates large scale changes in the average climate since the industrial revolution (Keeling et al. 1979; Thompson et al. 1993; O'Brien et al. 1995) and also provides a vital calibration for modern paleoclimate records. There is a plethora of different paleoenvironmental archives which record climate variables on differing temporal scales, including annually resolved tree-rings (Cook 1995; D'Arrigo et al. 1996), laminated lake sediments (Kotwicki & Allan 1998; Shulmeister et al. 2004), speleothems (Treble et al. 2003; Fairchild et al. 2006), Antarctic firn (Etheridge et al. 1996), coral (Fairbanks & Dodge 1979; Druffel 1982; Dodge et al. 1984), deep sea sediments (Duplessy et al. 1988; Broecker & Denton 1989; Lynch-Stieglitz et al. 1994) and historical climate data sets.

One of the most well known paleoclimate temperature reconstructions for the past millennia, known as the 'hockey stick curve' combined proxy and model reconstructions using over 400 data sets (Mann et al. 1998; Mann et al. 1999). The curve sloped gently downwards for the majority of the last 1000 years before rising sharply in the 20th century (the blade of the hockey stick) indicating global temperatures are currently warmer than the medieval warm period (~800-1000 years ago). To establish the impact of anthropogenically-induced climate change, the Intergovernmental Panel of Climate Change (IPCC) was established in 1988 to assess our understanding of the scientific basis of human-induced climate change and the 'hockey stick' curve featured prominently in the 2001 IPCC report. A great deal of criticism has been levelled at the Mann et al (1998) reconstructions due to the smaller data set from the early part of the curve (1000-1500) and the lack of data from the Southern Hemisphere but the conclusions of the study were upheld.

Once there is an understanding of natural climate variability, we can assess the anthropogenic impact on climate through increased greenhouse gases, pollution, deforestation and land-use practices. By robustly reconstructing regional, hemispheric and global climate we will be able to appreciate natural variability and disentangle the different roles which atmospheric and oceanic processes have in the climate system and the teleconnections between them. Where comparisons between the hemispheres have been made, the Southern Hemisphere temperature average indicates greater recent warming in the latter part of the 20th century and had a muted temperature response during the Little Ice Age in the 1500-1800's.

Australia is in a unique position to contribute to a regional and global understanding of how climate systems have operated in the past. Australia and its territories span a range of climatic zones including polar, temperate, arid, subtropical, tropical, oceanic and continental. The Australasian region includes several major atmospheric and oceanic boundaries that are highly sensitive to future climate change. Climate oscillations which effect Australia include the El Niño Southern Oscillation, West Pacific Warm Pool, Interdecadal Pacific Oscillation, Indian Ocean Dipole, Southern Annular Mode, Asian-Australian Monsoon and several boundary currents around the continental coastline including the East Australia Current, Leeuwin Current and the Antarctic Circumpolar Current south of the continent. By comparing records from different regions it is possible to identify unusual variation and/or synchronicity in climate cycles. This not only allows an assessment of the degree to which observed regional climate variations across Australia can be explained by natural processes, they can also improve our understanding of the relative effects of local and global climate driving forces.

Corals are well-suited to providing high fidelity climate records with which to test anthropogenic influences on the local and global environment. Corals have the potential to act as an archive of the chemical and physical environment in which they were growing (Knutson et al. 1972; Highsmith 1979), as their aragonitic skeleton incorporates trace elements and stable isotopes which reflect the local seawater chemistry (Dodge et al. 1984). Coral based geochemical proxies provide a means for temporally extending the instrumental record of climate (Fairbanks et al. 1997). The density of the coral skeleton varies seasonally; generating annual density bands that can be observed in x-ray photographs (Barnes 1970). In addition, the presence of other skeletal markers such as fluorescent bands can be used to independently verify the chronology (Lough et al. 1997). Corals are an ideal paleoenvironmental archive because they combine the chronological fidelity of tree rings with a higher resolution geochemical archive than deep-sea sediment cores. Modern scleractinian corals not only provide continuous climate data, but through the use of radiocarbon and uranium dating, fossil colonies can provide a record of climatic conditions over the last few hundred thousand years (Esat et al. 1999; Tudhope et al. 2001; Marshall & McCulloch 2002; Ayling et al. 2006).

Corals are capable of revealing subtle changes in sea surface temperature (SST) (McCulloch et al. 1996; Alibert & McCulloch 1997), rainfall and evaporation (McConnaughey 1989; Gagan et al. 1998), solar radiation (Raspopov et al. 2004) and nutrient dynamics (Lea et al. 1989; Grottoli 2002) on an intra-annual timescale and can provide clues as to how seasonal climate responds to large-scale regional forcings and background changes. New coral trace element paleothermometers combined with carbon and oxygen stable isotope ratios allow us to explore the natural variability in SST, the hydrological cycle and ocean circulation both in the recent past and by using fossil corals through the last glacial cycle.

While corals have been the subject of a considerable amount of research over the last few decades for example (Hudson et al. 1976; Nozaki et al. 1978; Smith et al. 1979; Dunbar & Wellington 1981; Shen et al. 1987; Lea et al. 1989; Beck et al. 1992; Evans et al. 1998; Cole et al. 2000; Schrag & Linsley 2002; Abram et al. 2003) there remain many areas of coral geochemistry (Sinclair 2005; Cohen et al. 2006; Gaetani & Cohen 2006) still to explore, including new chemical tracers from new locations and a greater understanding of the biochemical and biological processes influencing trace element coprecipitation. The vast majority of studies have focused on tropical corals with rapid skeletal extension rates (for reviews see (Druffel 1997; Gagan et al. 2000; Swart & Grottoli 2003; Correge 2006). A growing number of studies are examining high-latitude or deep-sea corals to further resolve natural climate variability in the recent past (Fallon et al. 1999; Roark et al. 2005; Robinson et al. 2005; Montagna et al. 2007). Studies focusing on these corals have the advantage of producing a longer paleoenvironmental archive because the corals grow more slowly.

Corals also record temporal changes in seawater carbonate chemistry and ocean acidity by varying pH during calcification and aragonite precipitation. Experimental and modelling studies suggest that rates of $CaCO_3$ deposition of marine biogenic calcifying organisms should have already declined in response to the 19th and 20th century increase in atmospheric CO_2 reducing the carbonate saturation state of the surface ocean (Gattuso et al. 1998; Kleypas et al. 1999; Leclercq et al. 2000; Langdon & Atkinson 2005; Orr et al. 2005). These studies have also suggested that the $CaCO_3$ saturation state is going to be more heavily impacted at higher latitudes.

Potentially important regions for CO_2 uptake such as the Southern Ocean are chronically undersampled.

The current global climate change debate (between scientists and sceptics) has led to renewed interest in analysing corals and other paleoclimate archives that grew during periods when the earth was warmer than modern times or during periods of rapid warming. Although past climate archives are not a direct analogue for a CO_2 warmed world (Barnett et al. 2005), these archives increase our understanding of processes driving the climate system.

Statement of Research

The aim of this research was to explore the application of a multi-proxy approach on the cold-water coral *Plesiastrea versipora* and investigate biogeochemical cycling in temperate coastal environments. Coral archives provide a continuous temporal record at higher resolution than previous studies using foraminifera in sediment cores from the southern margin of Australia.

To asses the potential of *Plesiastrea versipora* as a paleoenvironmental archive, the geochemical investigations include both trace elements and light stable isotopes. The trace elements were measured on a quadrapole Inductively-Coupled Plasma Mass Spectrometers (ICP-MS) with high spatial sampling resolution achievable by laser ablation. This study took advantage of recent improvements in increased sensitivity and interference reduction in ICP-MS to explore a broader range of transition metals to be analysed from previous ICP-MS studies. This study represents a natural progression of the method developmental work undertaken at ANU (Sinclair et al. 1998; Fallon et al. 1999; Sinclair 1999; Fallon 2000; Fallon et al. 2002; Wyndham et al. 2004; Wyndham 2005). The investigation of a new species of coral will increase our understanding of environmental variability in temperate latitudes and how sensitive this environment is to the 20th and 21st century climate change.

Aims:

The aim of this thesis was to sample corals from the eastern Great Australian Bight (For detailed map of field area see: Figure 3.2) to reconstruct historical upwelling proxies such as Ba/Ca and Cd/Ca (Shen et al. 1987; Lea et al. 1989), to determine temporal variability in upwelling intensity and how it may impact commercially important fisheries such as bluefin tuna in the region. However, large colonies of *Plesiastrea versipora* could not be located in this region and the focus of the study moved to comparing and contrasting Spencer Gulf and Gulf St. Vincent, where corals had been successfully located and sampled.

By focussing on corals located in the gulf environments, the thesis evolved into a more geochemically interesting study: endeavouring to not only assess the potential of *Plesiastrea versipora* as a paleoenvironmental archive and generate long seasonally-resolved records of climate, but also to ascertain what anthropogenic changes had occurred since European settlement and industrialisation in Southern Australia.

In this thesis, the following aspects will be addressed:

- Examine the growth rate of *Plesiastrea* in Spencer Gulf and Gulf St Vincent, South Australia and establish detailed chronologies for corals in this region.
- Assess trace element and stable isotope proxies incorporated into *Plesiastrea* to investigate climate variations in high latitude environments and establish this species of coral as a paleothermometer.
- Examine intra- and inter-annual variations in environmental conditions in the Gulf waters of South Australia by examining minor elements incorporated in the coral skeleton.
- Use climate and environmental records to characterise anthropogenic changes in the South Australian seawater chemistry since European settlement.
- Assess the impacts of increased CO_2 from fossil fuel burning on coral calcification, and explore the ramifications for biogenic calcification in temperate latitude surface ocean systems in the future.

Thesis Structure

The subsequent two chapters of this thesis review the literature on coral geochemistry and environmental studies; regional climate, geology and oceanography affecting the South Australian gulf environment. The next four chapters are written in a manuscript style and each chapter describes one of the aims of the thesis. The last chapter provides a synthesis of the major outcomes of this thesis and provides suggestions for future research.

Chapter 2

This chapter provides an overview of the coral paleoclimate literature, focusing on modern corals. Further to this, our current knowledge of trace metal and stable isotope paleotemperature proxies is summarised, including the large variations in transfer function equations between different coral species and locations. Published coral-proxy SST calibrations are presented in Appendix A. Previous coral pollution studies are also reviewed to provide a background for how the data generated during this thesis has extended our knowledge of trace metal incorporation in corals.

Chapter 3

This chapter presents the regional oceanography of the South Australian gulfs. Previous paleoenvironmental studies in Southern Australia were reviewed to establish potential climate forcing and associated teleconnections. The coral habitat is described and coral colony locations are provided (including maps of all colonies). The methodology of coral coring is also described. A complete field log is included in Appendix B.

Chapter 4

This chapter describes the growth histories of five colonies of *Plesiastrea versipora* through X-ray and ^{238}U/^{230}Th dating techniques. Density bands of varying widths were present in each coral, and coral growth rates varied on very small spatial scales including the same reef. Average extension rates of colonies varied between 1.2 and

7 mm yr^{-1} which are among the slowest growth rates reported for hermatypic corals. The potential mechanisms for the large variation in growth rate are discussed. Results from this chapter suggest that a combination of band counting and radiometric dating be used on future coral studies analysing corals with slow growth rates. A complete set of the coral X-radiographs and luminescence images are in Appendix C on supplementary DVD.

Chapter 5

Chapter 5 investigates the paleothermometer potential of this coral species using both trace elements and stable isotopes. The level of reproducibility is examined within *Plesiastrea versipora* and also between two different ICP-MS. Coral - SST calibrations are generated for five corals. Slow growing corals (< 2mm yr^{-1}) do not appear to accurately resolve seasonal variability in either trace element or $\delta^{18}O$ paleotemperature proxies. Long records were generated for seven coral colonies with an observed temperature increase of 1.5°C over the last 100 years. A table of the LA-ICP-MS data files is listed in Appendix D and all data can be found in digital format on the supplementary DVD provided with the thesis. The stable isotope data is in Appendix E on the supplementary DVD.

Chapter 6

This chapter examines the minor trace element records in seven coral colonies. The chapter is divided into three environmental components influencing the trace element signal in the corals, with subsections including urban impacts, industrial impacts and landscape change/agricultural impacts. The urban impacts include records of treated sewage outfall variations into Gulf St. Vincent and a historical lead record from vehicle emissions. The industrial impacts include heavy metal contamination from nearby smelters and the implications for the local environment are discussed. The landscape changes are reflected in the light rare earth element (LREE) record in the corals. Correlation tables of the trace metals for *Plesiastrea versipora* are in Appendix F.

Chapter 7

This chapter focuses on the $\delta^{13}C$ signal recorded in annual-pentannual analyses from three coral colonies and the surface ocean CO_2 increase from the Suess effect since industrialisation. The coral $\delta^{13}C$ records are compared with ice core and tropical coral records, and the potential of temperate corals to act as an archive of long term atmosphere-surface ocean mixing is discussed. The differences between temperate and tropical corals with a more complex $\delta^{13}C$ signal are also discussed.

Chapter 8

This chapter provides a summary of the key finding of this thesis and discusses the questions generated by the data analysed in the thesis. The impacts of anthropogenic change in the South Australian gulfs are discussed in terms of the regional ecology. Several future directions are suggested for addressing some of the questions raised by this research and further geochemical investigations with *Plesiastrea versipora*. The archived material remaining at the Research School of Earth Sciences, The Australian National University is listed in Appendix G on supplemental DVD.

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Chapter 2:

Literature Review: Corals as Paleoclimate archives

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Introduction

Massive corals growing in tropical and subtropical oceans contain annual density banding in their skeletons that contain physical, isotopic and geochemical evidence of past environments at sub-annual resolution. Corals are widely distributed and can be accurately dated using annual density variations (Barnes 1972; Dodge & Vaisnys 1975; Hudson et al. 1976) with some species of corals providing records for several centuries. Modern scleractinian corals not only provide continuous climate data, but through the use of radiocarbon and uranium dating, fossil corals can provide a record of climatic conditions throughout the Holocene (Gagan et al. 1998; Marshall & McCulloch 2002; Cobb et al. 2003; Correge et al. 2004; Abram et al. 2007) and through several glacial/interglacial cycles (McCulloch et al. 1999; Tudhope et al. 2001; Felis et al. 2004; Ayling et al. 2006). Overlapping records can be linked to provide records extending back thousands of years e.g. the South Western Pacific (Gagan et al. 2000; Hendy et al. 2002). Scleractinian corals record environmental features of climate at high temporal and spatial resolution in the physical, chemical and isotopic composition of their skeletons (Knutson et al. 1972; Dodge & Vaisnys 1975; Wellington & Glynn 1983; Spiro et al. 2000). Coral based geochemical proxies provide a means for temporally extending the instrumental record of climate (Fairbanks et al. 1997). Coral growth rates vary intra- and inter-annually and extreme values of geochemical proxies coincide with climate extremes (Cardinal et al. 2001). The skeletons of scleractinian coral are ideal for extracting environmental information due to their wide distribution, longevity, seasonality, stable aragonite matrix and broad array of geochemical tracers.

Annual bands are accreted in couplets and the low-density portion is produced during late summer when sea surface temperatures (SST) are highest (Highsmith 1979; Leder et al. 1996). Physical characteristics of the annual coral bands such as their density, linear extension rate, tissue thickness and calcification rate provide data about the environmental conditions controlling coral growth, and complement chemical information incorporated into coral skeletons. Luminescent banding found in corals has been used to improve dating control of coral records (Hendy et al. 2003). The aragonitic skeletal matrix of corals carries isotopic and chemical indicators that track environmental parameters such as water temperature, salinity and isotopic composition as well as site specific features including turbidity, terrestrial runoff and upwelling intensity (Weber et al. 1975; Highsmith 1979; Lea et al. 1989; Allison & Tudhope 1992; Gagan et al. 2000; McCulloch et al. 2003a). These geochemical tracers can provide otherwise unavailable data needed to assess the links between local climatic processes and global climate patterns. For example, seawater temperature has been linked to the relative ratios of the stable oxygen isotopes ($\delta^{18}O$) and concentrations of several elements including strontium, uranium, magnesium and boron (Smith et al. 1979; Mikkelsen et al. 1982; Beck et al. 1992; McCulloch et al. 1994; Hart & Cohen 1996; McCulloch et al. 1996; Alibert & McCulloch 1997; Druffel & Griffin 1999). In locations where the temperature signal is complicated by interplay between precipitation, evaporation and water temperature, the $\delta^{18}O$ composition of coral skeletons and the trace element Sr/Ca may be used to differentiate between the hydrological component and the SST component recorded in the skeleton (McCulloch et al. 1994). Coral trace element concentrations have also been correlated to other environmental variables, such as oceanic upwelling measured by inclusion of barium and cadmium into the skeletal matrix (Lea et al. 1989; Shen et al. 1992b; Delaney et al. 1993; Druffel 1997).

Investigations into the chemistry of coral skeletons began in the early 1970s (Veeh & Turekian 1968; Kinsman 1969; Thompson & Livingston 1970; Livingston & Thompson 1971; Weber & Woodhead 1972; Amiel et al. 1973a). The topic of reconstructing paleoenvironmental information from coral skeletons has expanded rapidly over the past 40 years and several excellent reviews have been published (Swart 1983; Druffel 1997; Dunbar & Cole 1999; Gagan et al. 2000; Cohen & McConnaughey 2003; Swart & Grottoli 2003; Correge 2006). However, even though long-term coral records yield robust correlations with paleoclimatic environmental variables, our level of understanding of coral biogeochemistry and the mechanisms driving elemental and isotopic incorporation into skeletons remains limited. Recent literature has concentrated on identifying new climatic tracers in coral and developing more sophisticated techniques for data extraction (Sinclair et al. 1998; Fallon et al. 1999). As a result, a multi-proxy approach to climatic reconstruction is emerging that is yielding new insights into environments inhabited by corals. The lack of long-term environmental information in temperate environments reduces our ability to interpret recent changes in regional oceanographic and climate indices due to anthropogenic mechanisms. This chapter presents an overview of literature on coral growth mechanisms and incorporation of trace elements into coral skeletons and how they relate to environmental factors to provide a context for the data presented later in the thesis. Minor elements are also reviewed in this chapter, examining how they are incorporated into coral skeletons and the associated natural and anthropogenic environmental chemistry.

Coral Calcification Mechanisms

Mechanisms that control the incorporation of isotopes and trace elements into the coral skeleton are poorly understood, and the incorporation of geochemical tracers is likely to be influenced by several factors including the ionic composition of the calcifying fluid, the calcification rate and water temperature. There are two schools of thought regarding the processes dictating biomineralisation in corals; (1) that skeletons grow from an organic matrix template (Goreau 1959; Risk & Pearce 1992; Cuif et al. 2003); or (2) the skeleton is formed inorganically inside membrane enclosed pockets of fluid (Barnes 1970; Wells 1970; Cohen & McConnaughey 2003). An understanding of the biomineralisation process is important for understanding the distribution of trace elements and the inorganic mechanistics of crystal growth within the coral skeleton. If calcification occurs from a solution, then the crystal morphology and aragonitic trace element composition are subject to thermodynamic and kinetic constraints of inorganic crystal growth once the solution is no longer saturated in particular trace elements. If calcification occurs from an organic matrix, then crystal deposition is largely controlled by biological factors including physiological transport and membrane excretion.

The organic matrix model, first proposed by Goreau (1959) suggested a mucco-polysaccharide sheath as a template for crystallisation. Coral skeletons contain small amounts (approximately 0.01-0.1%) of organic material distributed throughout the aragonite (Wainwright 1963). Organic material is believed to play a role in skeletal construction by absorbing Ca^{2+} and HCO_3^- then concentrating them spatially so that $CaCO_3$ precipitation can occur. Other possible roles include the nucleation and seating the mineral crystals controlling the size, shape and orientation of the crystals and altering the structural properties of the skeleton (Goreau 1959). A more recent study suggested that sulphated organic compounds provide the nucleation of aragonitic fibres, rather than the centres of calcification, and that calcification took place during a polycyclic model of crystal growth (Cuif et al. 2003).

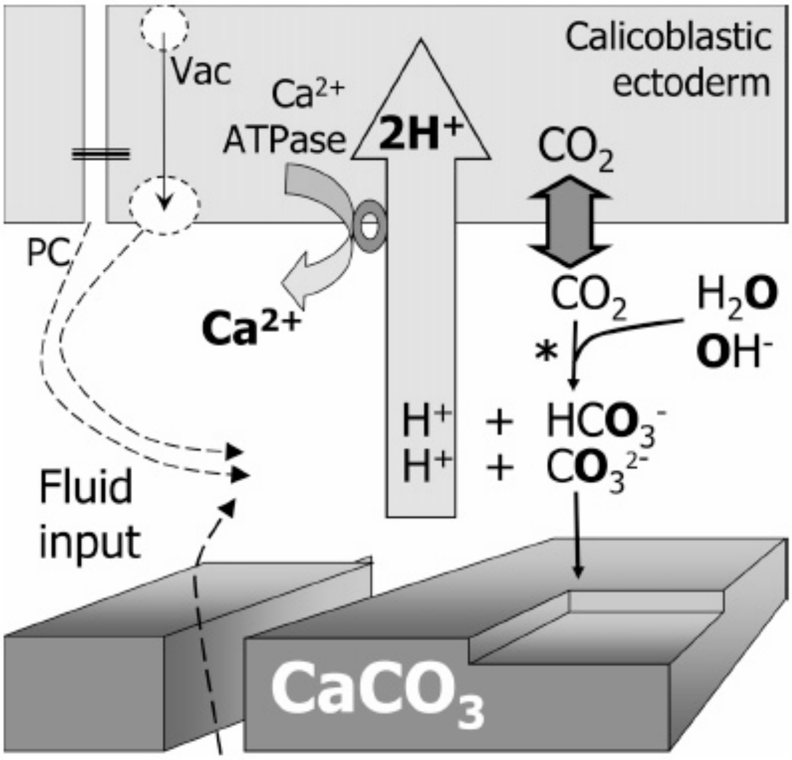

Figure 2.1: Coral skeletal calcification model, indicating ion transport occurring across the membrane by vacuoles (vac) that transfer seawater at the basal epithelium. Seawater also enters the calcifying space by diffusion through pericellular channels (PC) and the porous skeleton. The ATP pump adds Ca^{2+} through Ca^{2+}ATPase and removes protons from the calcifying fluid to raise the pH, CO_2 is diffused in and reacts with water to produce CO_3^{2-} and OH^-. Adapted from Cohen and McConnaughey (2003).

The alternative hypothesis for aragonite skeleton formation is that physiochemical growth of crystals results from unrestricted inorganic crystal growth from a physiologically modified pool of calcifying fluid. The evidence for this comes from the observation that corals are constructed from spherulitic bundles of acicular aragonite fibres (Wainwright 1963; Barnes 1970; Constantz 1986), and this mode of crystal growth is commonly observed in calcitic marine cements (Constantz 1986). These structures are hard to explain by epitaxial growth within an organic matrix, suggesting that although calcification may be biologically initiated, it progresses under physiochemical control (Hayes & Goreau 1977; Constantz & Weiner 1988).

In contrast to the idea that single crystals nucleate and grow within individual membrane sheaths, a large proportion of the literature suggests that crystal growth and nucleation occurs freely within a larger membrane bound pocket of supersaturated fluid (Figure 2.1) (Barnes 1970; McConnaughey 1989a; Clode & Marshall 2003; Cohen & McConnaughey 2003; Sinclair & Risk 2006). Crystals nucleate and grow outwards from structures called centres of calcification or early mineralisation zones. The nucleating structures appear darker than the surrounding aragonite in thin sections analysed by light microscope, and have a grainy texture in SEM analyses (Clode & Marshall 2003). The growth form of crystals in centres of calcification differs from the fibrous aragonite that makes up the bulk of the skeleton. Crystals tend to be more platy and tabular than elongated rods (Johnston 1980). Centres of calcification have been found to display significantly different trace element chemistry (Allison & Tudhope 1992; Allison 1996b). It is postulated that centres of calcification contain high amounts of organic material (Allison 1996 Allison and Tudhope 1992).

From the centres of calcification, clusters of acicular aragonite crystals grow concentrically outwards forming fan shaped bundles called sclerodermites (Barnes 1970) or fasciculi (Constantz 1986). Additional crystal nucleation occurs spontaneously in spaces between growing crystals. New crystals nucleate on the walls and ends of existing crystals and depending on the condition of the solution, this can be syntaxial (orientated the same way as seed crystals) or nonsyntaxial (Barnes 1970). The amount of spontaneous nucleation and non syntaxial growth increases with the degree of supersaturation in the calcifying fluid. Recent studies have indicated that the composition of the calcifying fluid is actively controlled by the coral polyp, with the chemistry of the seawater modified by transport of ions across the basal epithelium (Cohen et al. 2006; Gaetani & Cohen 2006). These authors concluded that the variations in concentrations of Mg^{2+}, Sr^{2+} and Ba^{2+} observed over a seasonal cycle were in fact due to the concentration of Ca^{2+} in the calcifying fluid, enriched relative to seawater in summer (lower concentrations of Sr^{2+} and Ba^{2+}) and depleted in winter (Gaetani & Cohen 2006).

Stable Isotope Proxies

$\delta^{18}O$

The first paleotemperature proxies to be extracted from coral skeletons (and other aragonitic organisms) was the stable isotope $\delta^{18}O$, which was found to be inversely variable with SST (Epstein et al. 1951; Weber & Woodhead 1972; Weber 1973a). Corals precipitate their aragonitic skeletons out of isotopic equilibrium (indicating depleted values) with the surrounding seawater. Biogenic aragonite has a depleted stable isotopic composition relative to inorganic aragonite precipitated from seawater, and this depletion is dependent on kinetic fractionation, and corals with faster growth rates display the strongest depletion in $\delta^{18}O$ (McConnaughey 1989b). Variations in coral $\delta^{18}O$ are dominated by sea surface temperature, sea surface salinity (SSS) (Cole & Fairbanks 1990) or a composite signal of both SST and SSS. Sea surface salinity is governed by evaporation, precipitation and runoff from nearby land. To extract the temperature component of the $\delta^{18}O$ signal, this data is compared with instrumental temperature data or the temperature component of the record is resolved from another proxy such as the Sr/Ca ratio.

The mechanisms for oxygen isotope fractionation into coral skeletons are not completely understood, but they are considered to be more complicated than trace elements due to the different chemical forms involved from CO_2 to CO_3^{2-}. Both these forms are present in seawater and the isotopic composition in corals can be a function of seawater chemistry, respired products from symbiotic zooxanthellae and a component from ingested food (McConnaughey 1989a). Factors known to influence $\delta^{18}O$ (apart from temperature and salinity) include; growth rates (McConnaughey 1989a); pH (Rollion-Bard et al. 2003b); light levels (Reynaud-Vaganay et al. 2001); feeding and productivity (Grottoli 1999; Juillet-Leclerc &

Schmidt 2001; Grottoli 2002). It is recognized that both $\delta^{13}C$ and $\delta^{18}O$ vary on a micrometric scale, with higher variability observed in $\delta^{18}O$ suggesting different fractionation mechanisms (Rollion-Bard et al. 2003a; Rollion-Bard et al. 2003b).

The complex interactions between the different environmental variables impacting the $\delta^{18}O$ record in coral skeletons suggests that there is not a universal calibration of coral $\delta^{18}O$ to SST due to site specific and colony specific fractionation ('vital effects'). A range of published calibrations for inorganic aragonite and different coral species has been listed in appendix A. The value of the slope of the temperature-transfer function usually varies between $0.18‰°C^{-1}$ and $0.22‰°C^{-1}$ (Correge 2006). Yet despite the many environmental and biological factors that influence $\delta^{18}O$ in coral skeletons and introduce error into SST calibrations, this stable isotope system is still considered to be one of the most reliable coral-derived temperature proxies available to investigate relative temperature changes over time.

Long records of $\delta^{18}O$ spanning several centuries have been constructed for corals in the Pacific, Indian and Atlantic Basins, providing evidence of variation in climate processes including: changes in monsoon dynamics (Charles et al. 1997; Klein et al. 1997; Greer & Swart 2006; Pfeiffer & Dullo 2006), variations in the frequency of El Niño (Cole & Fairbanks 1990; Carriquiry et al. 1994; Evans et al. 1999; Cole et al. 2000; Gagan et al. 2000; Urban et al. 2000; Cobb et al. 2003; Damassa et al. 2006); the Indian Ocean Dipole (Abram et al. 2003; Zinke et al. 2004); Pacific Decadal Oscillation (Correge 2006); and movement of the Subtropical Convergence (Linsley et al. 1994; Juillet-Leclerc et al. 2006; Linsley et al. 2006).

$\delta^{13}C$

The $\delta^{13}C$ in coral skeletons is impacted by kinetic isotope fractionation and metabolic isotopic fractionation (Weber & Woodhead 1972) and also reflects a number of environmental variables. Thus coral $\delta^{13}C$ records are difficult to interpret. Kinetic fractionation is the dominant process, whereby the heavier ^{13}C isotope is discriminated against during the hydration of CO_2. The $\delta^{13}C$ composition of coral aragonite is also influenced by metabolic effects of the zooxanthellae undergoing photosynthesis and respiration (Swart et al. 2005), while photosynthesis varies with external factors such as depth, cloudiness or water turbidity. Other factors known to influence coral $\delta^{13}C$ include the proportion of dissolved inorganic carbon (Swart 1983), coral spawning (Gagan et al. 1996), and changes in the dietary component of carbon with heterotrophic feeding exceeding autotrophic support from zooxanthellae (Grottoli et al. 2004).

Determining past changes in the carbon cycle is the key to understanding paleoclimate forcing, and also provides an insight into how the oceans may respond to present and future changes to the climate system. The depletion of ^{13}C in the atmosphere due to industrialisation increasing the amount of ^{12}C emitted to the atmosphere through fossil fuel burning is known as the ‘Suess effect’. Several studies have detected the changing ratio of $^{13}C/^{12}C$ in biogenic organisms such as corals and sclerosponges as a record of the oceanic Suess effect (Nozaki et al. 1978; Druffel & Benavides 1986; Böhm et al. 1996). Since the Subantarctic Zone is considered one of the strongest sinks for atmospheric CO_2 (Quay et al. 1992; Lo Monaco et al. 2005), identification of biogenic proxies from the Southern Ocean is central to our understanding of the global carbon cycle,

Trace element proxies

During precipitation of the aragonite lattice, substitution occurs between calcium and a range of divalent metals including Mg, Sr and Ba. The trace element/calcium ratios (M/Ca: metal/calcium) correlate with sea surface temperature, but other environmental variables are believed to influence M/Ca, including salinity, vital effects, pH and kinetic factors (Min et al. 1995; Shen & Dunbar 1995; Hart & Cohen 1996; Mitsuguchi et al. 1996; Cardinal et al. 2001). The utility of an individual trace element ratio as an independent paleotemperature proxy is hampered by the limited understanding of the factors controlling trace element incorporation into coral aragonite. However, by using multiple trace elemental ratios, a more complete picture of environmental conditions can be generated. Growth effects can be minimised by consistently sampling down a corals major growth axis (Shen & Dunbar 1995; Alibert & McCulloch 1997; Cohen & Hart 1997). Many calibrations have been calculated and published for different species of corals worldwide using the equation (x = a + b.SST°C where x is the M/Ca ratio). These calibrations are similar, except differences exist between the degree of temperature dependence and the intercept value. A range of published calibrations are presented for Sr/Ca, B/Ca, Mg/Ca U/Ca and Ba/Ca in Appendix A.

Boron

Boron has a long oceanic residence time of 16-20 million years implying studies of boron concentration in paleoenvironmental reconstructions are robust over long timescales. Boron has a concentration range of 3.5-5 ppm and has two dominant species boric acid $B(OH)_3$, or borate iron $B(OH)^-_4$ in seawater (Schwarcz et al. 1969). The relative proportion between the 2 species is a function of pH (Hemming & Hanson 1992), with boric acid the main species at low pH (< 7) and borate ion exists predominantly at high pH (> 10) (Hershey et al. 1986). There is also a temperature control on the $B(OH)_3/B(OH)^-_4$ speciation in seawater, with a 1.8% increase in the ratio per temperature increase of 1°C (Hemming & Hanson 1992).

Boron isotopic studies on biogenic organisms have established that B is incorporated into coralline aragonite by substituting for the CO_3^{2-}, and most likely derived from $B(OH)^-_4$ as a solid phase HBO_3^{2-} (Vengosh et al. 1991; Gaillardet & Allegre 1995; Hemming et al. 1998). The distribution coefficient for B in corals is low (D =~0.011), probably because the species incorporates as a negative ion complex and replaces CO_3^{2-} rather than direct substitution for Ca^{2+} as other divalent cation paleotemperature proxies (Gaillardet & Allegre 1995). The boron concentration and isotopic composition in corals can be controlled by several environmental factors including: temperature, salinity, pH, $B(OH)^-_4/H(CO_3)^-$ ratio in seawater, biological controls on calcification, calcite/aragonite mineralogy and kinetic fractionation (Hemming & Hanson 1992; Hemming et al. 1998).

A seasonal cycle was first established for B/Ca when correlated with Sr/Ca using ion microprobe analyses (Hart & Cohen 1996). However Hart and Cohen (1996) did not correlate B/Ca with temperature. Laser ablation ICP-MS analyses further explored B/Ca as a paleotemperature proxy and have shown B/Ca to change by approximately

3-5% per 1°C in tropical corals (Sinclair et al. 1998; Fallon et al. 1999). A study on the high-latitude coral *Cladocora caespitosa* from the Mediterranean indicated that B/Ca was the most reliable temperature proxy (Montagna et al. 2007). However, Fallon et al. (1999) observed large variations in B concentration over small spatial scales, indicating temperature was not the only environmental variable influencing B/Ca concentrations.

Magnesium

The dominant species of magnesium in seawater is Mg^{2+}, and average concentrations are approximately 1300 ppm. Magnesium has a very long oceanic residence time, 13 million years, suggesting suitability for paleoclimate reconstructions (Broecker & Peng 1982). The mechanisms of Mg incorporation into carbonate have been widely studied due to the contribution Mg makes to the different carbonate species (aragonite, calcite and High-Mg calcite). At seawater Mg concentrations the majority of carbonate precipitated is in the form of aragonite (Chave 1954; Kinsman 1970; Amiel et al. 1973a).

The mechanisms controlling incorporation of Mg into coral skeletons have not been well established, and the possible locations for Mg incorporation include loosely bound in the aragonite crystal lattice, bound to organic compounds or adsorbed to crystal surfaces (Amiel et al. 1973a; Oomori et al. 1987). There is a large difference in the ionic radius between Ca^{2+} (1.06 Å) and Mg^{2+} (0.78 Å) which is thought to preclude direct substitution when there is a difference greater than 15% between ionic radii (Amiel et al. 1973a). Aragonite has an orthorhombic structure and when Mg^{2+} is present in solid solution ($MgCO_3$) the structure is rhombohedral, which does not fit into the aragonite crystal lattice (Mitsuguchi et al. 1996). This suggests that Mg^{2+} concentrations in aragonite may be easily affected by diagenesis (Cross & Cross 1983).

Mg/Ca has proven to be one of the most reliable and reproducible paleotemperature proxies in molluscs (Chave 1954; Katz 1973; Kolesar 1978), but did not appear to be reliably recording temperature in corals until the study by Mitsuguchi and co-authors

(1996). In early studies on coral the Mg/SST relationship was not very clear, although small positive correlations with sea surface temperature were observed (Chave 1954; Weber et al. 1975). The lack of correlation between Mg/Ca and temperature in the early work may have been due to a combination of large sample size, different coral genera and varying locations (Mitsuguchi et al. 1996). The positive Mg/Ca-SST relationship may have several potential mechanisms including increased tolerance of the crystalline lattice to distortion or increased activity coefficient of Mg^{2+} compared to Ca^{2+} with temperature (Kinsman & Holland 1969; Swart 1981). There is large variation in the Mg/Ca content of corals, with concentrations ranging between 700-2400 ppm and this variation cannot be accounted for by changes in water chemistry or temperature (Chave 1954; Swart 1981; Oomori et al. 1987; Allison & Tudhope 1992). Ion microprobe and laser ablation analyses have provided evidence of micron-scale heterogeneity in Mg^{2+} concentration unrelated to temperature fluctuations, with centres of calcification (or early mineralisation zones) enriched in Mg/Ca (Allison 1996a; Fallon et al. 1999; Sinclair 1999; Meibom et al. 2004; Cohen et al. 2006). The heterogeneity in Mg/Ca may be related to Mg^{2+} not bound in the crystalline lattice or presence of other forms of carbonate and up to 40% can be removed by extensive cleaning (Mitsuguchi et al. 2001; Watanabe et al. 2001).

Strontium

The calibration of Sr/Ca versus SST has been the most studied elemental proxy aside from the $\delta^{18}O$, for example (Smith et al. 1979; Beck et al. 1992; McCulloch et al. 1994; Alibert & McCulloch 1997; Schrag 1999). The concentration of Sr in seawater is approximately 8000 µg/L with a long residence time of 4-5 million years (Brass & Turekian 1974). The main Sr species in seawater is Sr^{2+} and it displays a predominantly conservative behaviour in nutrient rich waters and ‘nutrient type’ behaviour in the shallow zone of oligotrophic waters due to the formation of celestite ($SrSO_4$) skeletons by radiolarians (Brass & Turekian 1974; de Villiers et al. 1994). The primary method of incorporation into the crystal lattice is direct substitution of Sr^{2+} for Ca^{2+}, although Sr^{2+} has a larger ionic radius (1.31 Å compared with 1.06 Å), strontium forms an orthorhombic isomorph of aragonite called strontianite ($SrCO_3$)

(Kinsman 1969; Cross & Cross 1983; Speer 1983; Greegor et al. 1997). Therefore, Sr/Ca has the potential to be a more reliable paleotemperature proxy than $\delta^{18}O$ because it is not influenced by precipitation/evaporation to the same extent and is more stable through time. However, small variations in Sr concentration in seawater occur in different locations due to continental weathering (de Villiers et al. 1995).

The distribution coefficient for Sr in coralline aragonite is negatively correlated to temperature, and displays an offset from inorganic aragonite values, suggesting that corals do not incorporate Sr in equilibrium with seawater concentrations during calcification (Weber 1973b; Gaetani & Cohen 2006). There have been various discussions concerning the variability of the Sr/Ca SST calibration differences such as different species, sampling, reliability of SST measurements, inter-laboratory spikes and calibrations on instrumentation (Shen et al. 1996; Alibert & McCulloch 1997; Allison et al. 2001; Cohen et al. 2001; Cohen & Sohn 2004; Allison et al. 2005). Studies on inorganic aragonite found no correlation with precipitation and Sr incorporation (Kinsman & Holland 1969; Dietzel et al. 2004). However, because corals precipitate aragonite approximately six times faster than inorganic rates, the distribution coefficient of Sr for biogenic aragonite may be lower than inorganic experimentally derived values (de Villiers et al. 1994). An accepted value of the distribution coefficient in corals was determined to be $D_{Sr} = 1.1$ at 20°C (McCulloch et al. 1994). Several studies have reinforced the need for consistent sampling of the main growth axis for the most reproducible results in Sr/Ca concentrations with higher Sr/Ca values attributed to suboptimal growth conditions resulting in smaller corallites, lower calcification and skeletal density (Alibert & McCulloch 1997; Cohen & Hart 1997).

A wide range exists between published Sr/Ca SST calibrations since the early work by Beck et al. (1992) (for details see Appendix A). Micron-scale studies have indicated heterogeneous distributions of Sr/Ca in coral skeletons, over spatial scales which are too short for temperature or seawater chemistry fluctuations and may reflect the biological control in Sr incorporation (Allison 1996b; Allison et al. 2001; Cohen et al. 2001; Sinclair 2005).

Although it is well established that Sr/Ca is a reliable paleotemperture proxy and many long climate records have been generated for this proxy e.g. (Cole et al. 2000; Correge et al. 2000; Linsley et al. 2000; Hendy et al. 2002; Kuhnert et al. 2005) there is not a universal calibration either for a location or for a particular coral genus (Appendix A). However, the percent change per 1°C between published calibrations is very similar with the values of 0.7/°C at 25°C.

Uranium

Uranium also has a long residence time in the ocean at approximately 300,000 years and the average oceanic concentration is 3.3 µg/L (Ku et al. 1977). Uranium has several species in seawater including UO_2^{2+}, UO_2CO_3, $UO_2(CO_3)_2^{2-}$ and $UO_2(CO_3)_3^{4-}$ (Langmuir 1978). The majority of U in corals appears to be lattice bound with UO_2^{2+} substituting for Ca^{2+} (Min et al. 1995) or as a carbonate ion complex $UO_2(CO_3)_2^{2-}$ or $UO_2(CO_3)_3^{4-}$ substituting for CO_3^{2-} (Swart & Hubbard 1982; Meece & Benninger 1993; Shen & Dunbar 1995). Although U has a larger ionic structure than Ca, there is a naturally occurring orthorhombic carbonate, rutherfordine (UO_2CO_3) with a similar crystal lattice to aragonite (Christ et al. 1955).

The CO_3^{2-} activity in seawater varies as a function of temperature, pH and total CO_2 suggesting that U/Ca concentrations in corals are variable due to changes in pH and total CO_2 in microenvironments (Min et al. 1995). Early studies observed no seasonal dependence on U/Ca concentrations, probably due to large sample sizes and analytical limitations (Veeh & Turekian 1968; Schroeder et al. 1970; Livingston & Thompson 1971; Amiel et al. 1973b). Shen & Dunbar (1995) reported seasonal variations in U/Ca correlating with $\delta^{18}O$ in Galapagos corals; and Min et al. (1995) observed an inverse correlation between U/Ca and SST from New Caledonian and Tahitian corals. The inverse relationship between U/Ca and SST has been documented by several studies with a temperature dependence of 3-5% per 1°C temperature change (Sinclair et al. 1998; Fallon 2000; Wei et al. 2000; Cardinal et al. 2001; Quinn & Sampson 2002). The sensitivity of U/Ca to SST is approximately five times that of Sr/Ca, however, temperature is not the only control on U/Ca in corals and salinity, alkalinity and U speciation and incorporation into aragonite also effect the U concentration (Swart & Hubbard 1982; Shen & Dunbar 1995; Pingitore et al.

2002). The concentration and speciation of U in seawater can vary temporally with high rainfall causing lower salinities and stratification, as well as terrestrial input of U from carbonate weathering (Shen & Dunbar 1995).

Barium

Barium has an average residence time in seawater of approximately 84,000 years and principally behaves as a ‘nutrient-type’ elemental distribution in seawater compared to the ‘conservative’ distribution behaviour of B, Mg, Sr and U. Concentrations of Ba in surface waters are approximately 4.5 ppb and increase to 15-30 ppb in deeper waters (near the seawater-benthic boundary) due to the production of barite ($BaSO_4$) by marine organisms (Riley & Chester 1971; Bacon & Edmond 1972). Barium also rapidly desorbs from suspended sediments when river water encounters highly ionic seawater in estuarine or coastal environments (McCulloch et al. 2003a). Barium substitutes directly for Ca^{2+} in coral skeletons (Speer 1983), forming a stable isomorph of aragonite called witherite ($BaCO_3$). The processes driving incorporation of Ba^{2+} may be similar to Sr^{2+} as they are both alkaline earth elements with larger ionic radii (Ba = 1.47 Å; Sr = 1.31 Å) than Ca^{2+} (Lea et al. 1989). The Ba^{2+} incorporation into corals is considered to be proportional to seawater concentrations, with a partition coefficient close to 1 (Lea et al. 1989).

High Ba/Ca concentrations have also been observed in contaminant phases including organic matter trapped in pore spaces of the coral skeleton (Allison & Tudhope 1992; Tudhope et al. 1996). Coral tissue has also been shown to have higher Ba/Ca concentrations than the majority of the coral skeleton (Buddemeier et al. 1981) or contaminant phases such as barite crystals (Tudhope et al. 1996). Ion microprobe studies have determined no association with high Ba concentrations and organic carbon and concluded that Ba/Ca was not controlled by organic material (Hart et al. 1997) although it may be present as a contaminant phase (Pingitore et al. 1989; Hart et al. 1997).

Trace elements such as B, Mg, Sr and U have displayed potential application as paleotemperature proxies and have stable seawater concentrations over short-medium timescales. Barium concentrations can be influenced by oceanic sources including upwelling of deep-water (Lea et al. 1989; Shen et al. 1992a; Reuer et al. 2003) and by terrestrial sources such as river runoff (Fallon 2000; McCulloch et al. 2003b; Sinclair & McCulloch 2004; Fleitmann et al. 2007). Correlations have been found between Ba/Ca and water temperature in Galapagos corals recording changes in the thermocline depth and associated upwelling (Lea et al. 1989). Variations in Ba/Ca concentrations have been related to upwelling influenced by different environmental variables including El Niño events effecting the strength of upwelling and thermocline depth (Shen et al. 1992a) and wind-induced upwelling (Fallon et al. 1999). Another significant source of Ba to the coastal zone is from river runoff, as seawater Ba concentrations are increased by the desorption of Ba from particulate material (Riley & Chester 1971). This desorption process can increase coastal seawater Ba concentrations by more than 50% (Hanor & Chan 1977). Corals collected from near shore waters adjacent to river systems have peak skeletal Ba/Ca concentrations that are correlated to the magnitude of flood events (Shen & Sanford 1990; Sinclair 1999; Fallon 2000; McCulloch et al. 2003b).

Lea et al. (1989) suggested Ba/Ca concentrations may have a temperature dependence in Galapagos corals and concluded that one-third of the Ba/Ca signal was related to seasonal variations in SST. If Ba is incorporated with a similar mechanism to Sr, then the temperature dependence of partitioning may be similar, based on Sr/Ca-SST calibrations this would suggest an ~ 0.7% change in Ba/Ca per °C (Lea et al. 1989). A recent study on high-latitude corals from the Mediterranean observed a seasonal cycle in the Ba/Ca concentration and suggested a temperature dependence of 3% per °C at 25°C (Montagna et al. 2007). These authors concluded that there was a close relationship between Ba/Ca and SST in *Cladocera* with a temperature dependence of -0.18 μmol/mol. Gaetani and Cohen (2006) also observed a temperature dependence of Ba/Ca in *Diploria* of -0.16 μmol/mol. Few other studies on coral geochemistry have observed any temperature dependence in the Ba/Ca concentrations, even once removed from upwelling or runoff influences.

However, experimental precipitation studies have found a strong temperature dependence on Ba/Ca incorporation into inorganic aragonite (Dietzel et al. 2004; Gaetani & Cohen 2006). Dietzel et al. (2004) observed the effect of temperature on Ba was an order of magnitude higher than on Sr and suggested that Ba may be a potential paleothermometer if the composition of the solution is known. Gaetani and Cohen (2006) observed a disparity between experimental Ba/Ca concentrations and concentrations in annual cycles of a coral skeleton, and interpreted the difference between inorganic and biogenic aragonite to be the magnitude of the coral 'vital effects' caused by modification of the fluid composition during calcification.

Minor trace elements

Divalent cations of trace abundances can be incorporated into coral skeletons at concentrations that are proportional to ambient seawater concentrations (Figure 2.2). The trace metal/calcium ratio (M/Ca) in coral skeletons can be used to reconstruct past concentrations of trace metals in seawater. Many trace metals have a nutrient-like behaviour and are enriched in upwelled waters and low in oligotrophic waters.

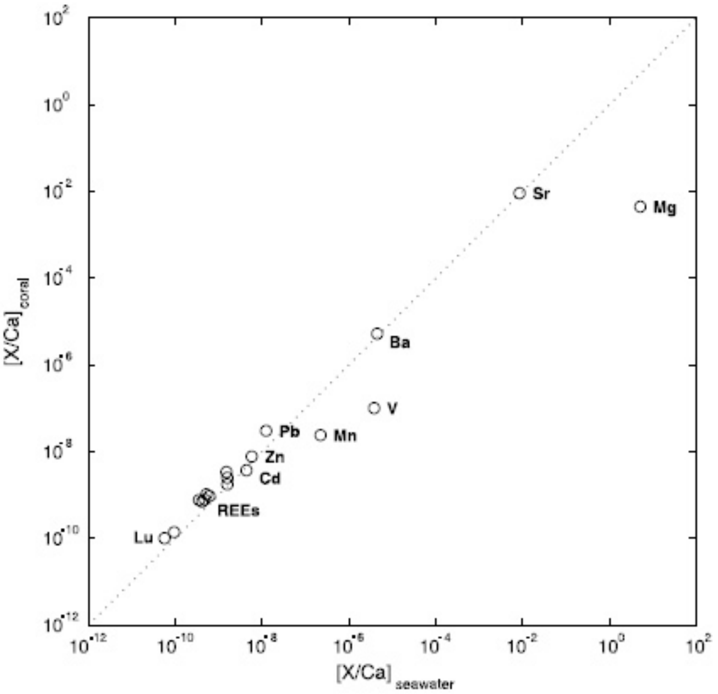

Figure 2.2: Trace element/Calcium ratios for tropical scleractinian corals and seawater. The dashed line represents the partition coefficient (D_p) between the Y axis (X/Ca $_{coral}$) and the X axis (X/Ca $_{seawater}$). The points above the line correspond to preferential uptake by corals and the elements below the line correspond to preferential exclusion of these elements by corals. Figure adapted from Reuer et al. (2003).

There is a growing body of literature examining trace and minor elemental concentrations in corals and associated environmental changes. The majority of these studies have focused on anthropogenic impacts to coastal and coral reef environments (St John 1974; Brown & Holley 1982; Howard & Brown 1984; Brown 1987; Shen & Boyle 1987; Scott 1990; Fallon et al. 2002). However, some studies have found evidence of trace metals varying in relation to climate related phenomena including regional scale upwelling and the El Niño Southern Oscillation (Shen et al. 1987; Shen et al. 1991; Shen et al. 1992c; Reuer et al. 2003).

Corals may be used as biomonitors of anthropogenic environment modification or pollution, since they incorporate trace metals into the annual growth bands of their skeletons (Shen & Boyle 1988; Fallon 2000). Corals can be exposed to high metal concentrations as a result of industrial activities (Howard & Brown 1987; Fallon et al. 2002; David 2003); or environmental modification near urban areas including harbour dredging or sewage discharges (Dodge et al. 1984; Bastidas et al. 1999; Esslemont 1999).

However, few studies have investigated the rate of trace metal uptake, or the transfer between tissue and skeleton (Esslemont et al. 2000; Reichelt-Brushett & McOrist 2003). There is also no clear correlation between metal exposure and metal accumulation (Hanna & Muir 1990). Incorporation of trace metals into corals can be the result of coral feeding (Hanna & Muir 1990; Ferrier-Pages et al. 2005), zooxanthellae uptake (Reichelt-Brushett & McOrist 2003), organic matter from coral tissue (St John 1974; Glynn et al. 1989), particulate matter trapped within skeletal cavities (Howard & Brown 1984; Hanna & Muir 1990) or incorporation (via substitution with Ca) into the aragonite crystal lattice (Dodge & Gilbert 1984; Shen et al. 1987; Shen & Boyle 1988; Delaney et al. 1993; Esslemont 1999; Fallon et al. 2002; David 2003; Wyndham et al. 2004). The variability in the different mechanisms of incorporation into coral skeleton may account for the large variations in metal concentrations in published studies (Appendix A).

The majority of minor trace elements have a ‘nutrient-like’ behaviour in seawater and many elements produce a stable carbonate mineral phase in solution with calcite or aragonite (Speer 1983). One example is cadmium, with a similar ionic radius to Ca and forms the mineral otavite, $CdCO_3$. Cadmium has been suggested to be lattice bound in corals, with a distribution coefficient close to 1 (Shen & Boyle 1988). Shen et al (1987) related Cd concentrations in corals from Bermuda with historical upwelling and industrial fallout.

Phosphorus acts as a limiting nutrient that plays a key role in sustaining the biological productivity of the oceans. Phosphorous has also been used as an anthropogenic tracer, with increases in P concentrations of North Atlantic corals recording historical variations in treated sewage (Dodge et al. 1984). Phosphorus inclusion into the skeletons of deep-sea corals has been shown to be directly proportional to the ambient seawater phosphorus concentration serving as a paleo-productivity proxy (Montagna et al. 2006).

The manganese seawater concentration is influenced by a variety of sources including dissolved and particulate Mn from rivers, reduction of Mn and shelf sediments and aeolian inputs dominates the coast seawater manganese concentrations (Bender et al. 1977; Klinkhammer & Bender 1980; Shen et al. 1991). Manganese is predominantly lattice bound, however it is discriminated against in the coral lattice, with a distribution coefficient of D_{mn} =~ 0.2-0.6 (Linn et al. 1990; Shen et al. 1991; Delaney et al. 1993). Manganese has been measured in corals from the coastal locations Gulf of Panama, the Galapagos islands (Shen et al. 1991; Delaney et al. 1993), and open ocean Tarawa Atoll, (Shen et al. 1992b). In these studies manganese displays a clear strong annual signal (Delaney et al. 1993), or a series of pulse events (Shen et al. 1992b). Mn/Ca concentrations have been related to a range of environmental factors including movement of surface ocean currents (Linn et al. 1990; Shen et al. 1991; Delaney et al. 1993); variations in wind strength and direction (Fallon 2000; Alibert et al. 2003; Wyndham 2005) and deep-sea hydrothermal vent activity (Shen et al. 1991).

Concentrations of dissolved zinc in surface waters of the open ocean are often very low, therefore, it has been suggested that low levels may limit phytoplankton growth, and their ability to acquire inorganic carbon (Morel et al. 1994). Zinc may be an important trace metal for corals, assisting in photosynthesis of their dinoflagellate symbionts and calcification. Metals such as zinc, can be substituted for calcium in the skeleton or can be associated with the organic matrix (Howard & Brown 1984). The incorporation of zinc into coral skeleton is dependent on zinc concentration in seawater and on the duration of the exposure (Ferrier-Pages et al. 2005). A recent study observed that zinc accumulation in the coral skeleton was dependent upon light stimulation suggesting that zooxanthellae are involved in the process of zinc uptake through photosynthesis (Ferrier-Pages et al. 2005). However, no previous studies have established the role of zinc in coral skeletons as an environmental biomarker of natural fluctuations in zinc. Studies on calcification in phytoplankton (coccolithophores) indicated the importance of zinc in calcification, and noted slower cellular growth and nitrogen utilisation rates with zinc deficiency (Schultz et al. 2004).

Lead also forms a stable orthorhombic carbonate, cerussite ($PbCO_3$), therefore it is suggested that Pb substitutes directly into the coral lattice (Speer 1983). Lead is enriched in coral skeletons relative to seawater with a distribution coefficient $D_{Pb} = \sim 2.3$ (Shen & Boyle 1987). Increases in Pb/Ca concentrations in corals have been attributed to anthropogenic sources including industrial sources, fossil fuel burning and sewage (Dodge & Gilbert 1984; Shen & Boyle 1987; Shen & Boyle 1988).

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Chapter 3:

Regional Oceanography and Climate in South Australia

Chapter 3: The South Australian Gulf Environment

Regional Climate, Geology & Oceanography

The southern coastline of Australia (Figure 3.1) is the longest east-west coastline in the world. The regional climate is similar to the Mediterranean with hot, dry summers and cool, moist winters. Winds are generally NW to SW during winter caused by low pressure systems in the Southern Ocean between 40-50°S. The geological provinces in this region include the Gawler Craton and the Adelaide Geosyncline with orogenic processes occurring between 2300-600 for Gawler Craton and 1400-560 million years ago (Adelaide Geosyncline). The Gawler Craton is predominantly weathered granite overlain by Quaternary aeolian and marine sediments (Belerio et al. 1984). The Adelaide Geosyncline consists of heavily folded metasediments, mainly comprised of steeply dipping sandstones and quartzites. The peninsulas are influenced by moderate wave energy, resulting in extensive beaches and large, open embayments backed by stable Tertiary-Quaternary dunes.

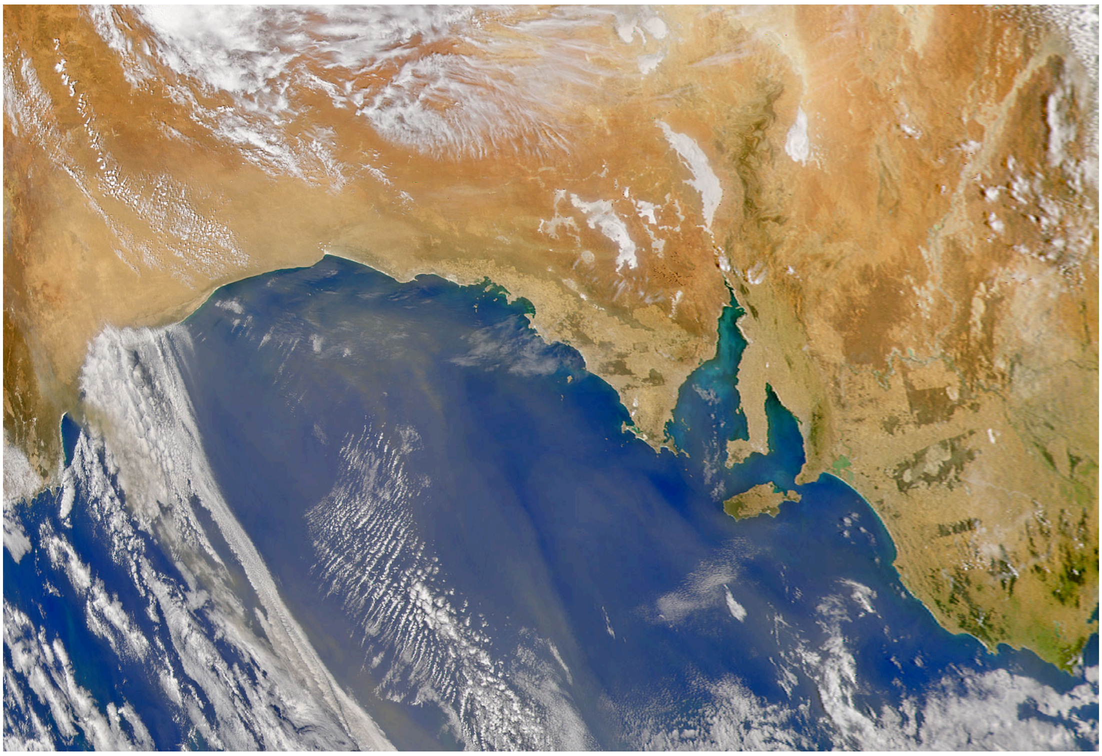

Figure 3.1: LANDSAT image of part of the southern coastline of Australia including the Great Australian Bight, Spencer Gulf and Gulf St Vincent. Image captured on 22nd December 2004. Image from http://modis.gsfc.nasa.gov/index.php.

The regional climate displays strong annual cycles in all environmental variables including temperature (SST), salinity, rainfall, sea level and cloud cover. There is a large annual temperature range of over 50°C between summer and winter for some regions in South Australia. The annual temperature range in Gulf St. Vincent is approximately 10-11°C from 12°C in winter to 23°C in summer (Figure 3.2). During El Niño years (such as 1998 – Figure 3.2) the amplitude of the seasonal variation increases up to 15°C with summer maximums around 26-27°C.

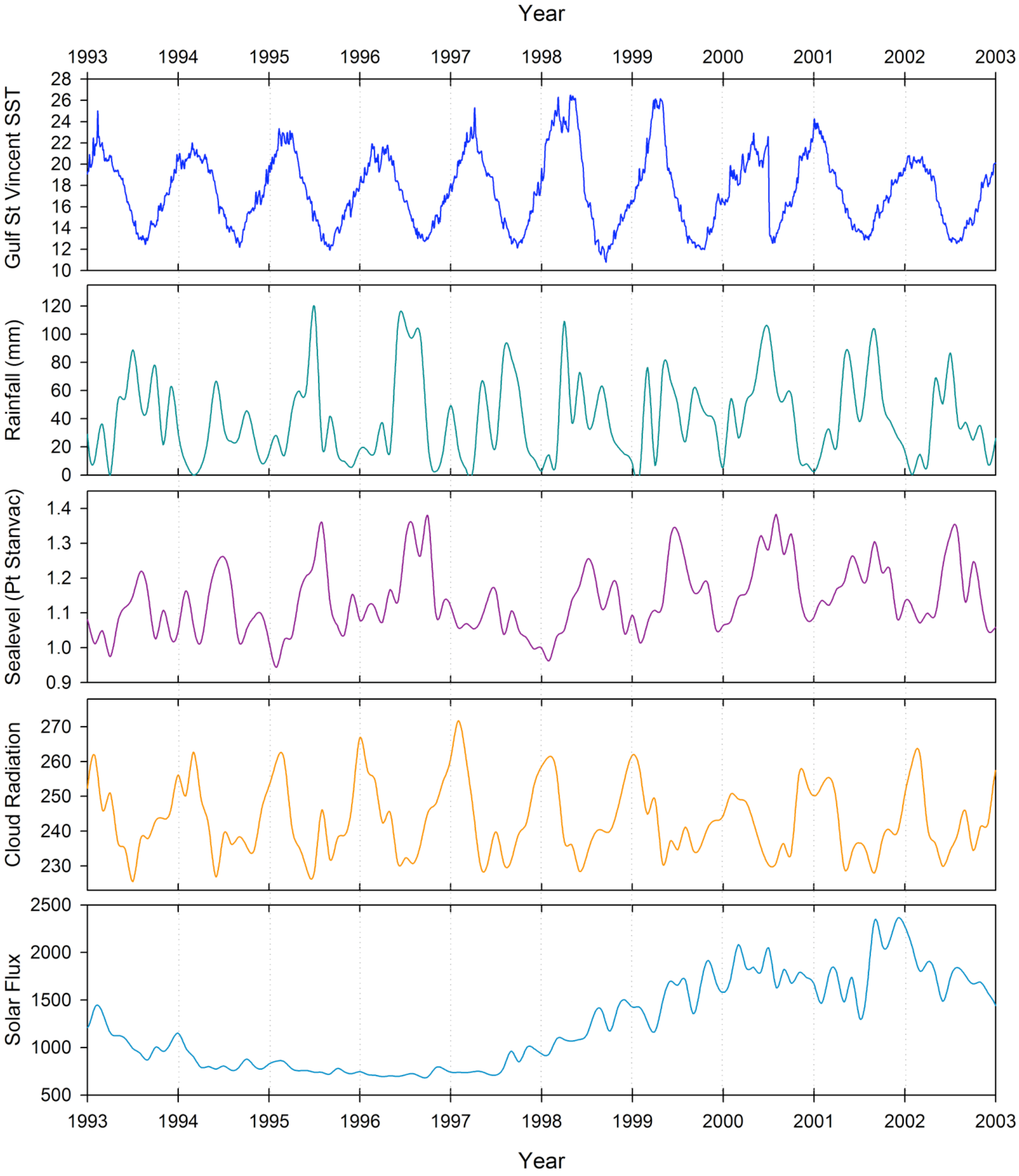

Figure 3.2: Environmental variables influencing the South Australian Gulfs. Sea surface temperature, rainfall and sea level data were provided by the National Tidal Facility, part of the Bureau of Meteorology. Cloud radiation and solar flux were sourced from the data library International Research Institute for Climate and Society at Columbia University (http://iridl.ldeo.columbia.edu/SOURCES/).

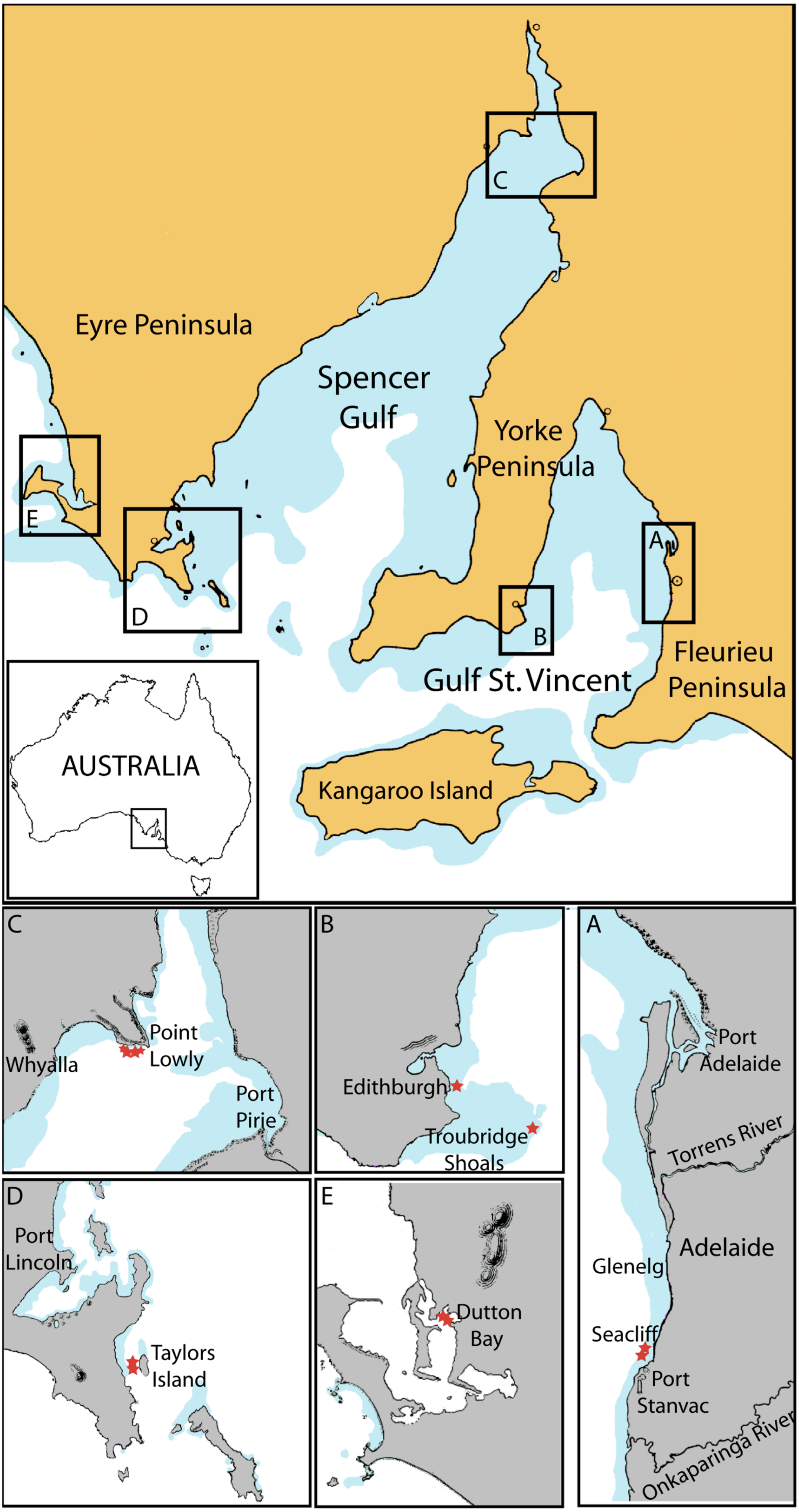
Eyre Peninsula
Spencer Gulf
Yorke Peninsula
Gulf St. Vincent
Fleurieu Peninsula
Kangaroo Island
AUSTRALIA
A
B
C
D
E
C
Whyalla
Point Lowly
Port Pirie
B
Edithburgh
Troubridge Shoals
A
Port Adelaide
Torrens River
Adelaide
Glenelg
Seacliff
Port Stanvac
Onkaparinga River
D
Port Lincoln
Taylors Island
E
Dutton Bay

Figure 3.3: Map of Spencer Gulf and Gulf St. Vincent with insets of coral collection sites. A: Seacliff; B: Edithburgh and Troubridge; C: Whyalla and Point Lowly; D: Taylors Island, E: Dutton Bay. Locations of local rivers including the Torrens River and Onkaparinga River are labelled in 3.3.A. Sources of point source pollution including the waste water treatment plants at Port Adelaide and Glenelg, oil refinery at Port Stanvac in 3.3.A and the smelters present at Whyalla and Port Pirie in 3.3.C.

Rainfall predominantly occurs during winter and maximum monthly rainfall can be up to 120 mm. Since there is a considerable temperature variation in regional SST and depressed winter rainfall during El Niño years, corals collected from the South Australian gulfs, Spencer Gulf and Gulf St. Vincent (Figure 3.3) may record these temperature anomalies in their skeletal geochemistry. Sea level varies by approximately 400 mm throughout the year with sea level highs recorded during winter months (July-September). Satellite derived information (Figure 3.2) for the region including cloud radiation is highest in summer and solar flux varies on a decadal timescale.

Great Australian Bight

The Great Australian Bight (GAB) is a latitude-parallel shelf with complex oceanography facing the Southern Ocean approximately 500 km north of the Subtropical Convergence (Rochford 1986). The eastern Great Australian Bight supports one of the most diverse soft-sediment communities (Ward et al. 2006). The present sea level was reached approximately 1700 years BP (Belerio et al. 1984) and future predictions by the IPCC suggest an increasing rate of sea level rise by up to 0.9 m by 2100.

The Great Australian Bight waters change markedly between seasons; in winter the region is crossed by a series of cold fronts extending from low pressure systems originating in the Southern Ocean moving eastwards, in summer high pressure cells develop with anti-cyclonic wind circulation (Herzfeld 1997). This results in predominantly south-easterly summer winds, and westerly winter winds. In general, the GAB is a region of sustained coastal downwelling, with local, diffuse upwelling in summer partly maintained by bottom Ekman transport in the eastern GAB along the western coast of Eyre Peninsula (Figure 3.4). Strong currents occur on the shelf slope boundary, with the South Australian current (Figure 3.4) a continuation of the Leeuwin current which predominantly lies on the continental shelf/slope boundary with eddies intruding onto the continental shelf in summer. The strength of the Leeuwin current can vary with Indian Ocean Dipole events causing temperature anomalies on the northwest Australian continental shelf and stronger trade winds increase the influence of the current along the southern coastline of Australia (Meyers et al. in press). The Flinders current is a westerly flowing current and may be dependent on the strength of the East Australia current reaching past Tasmania.

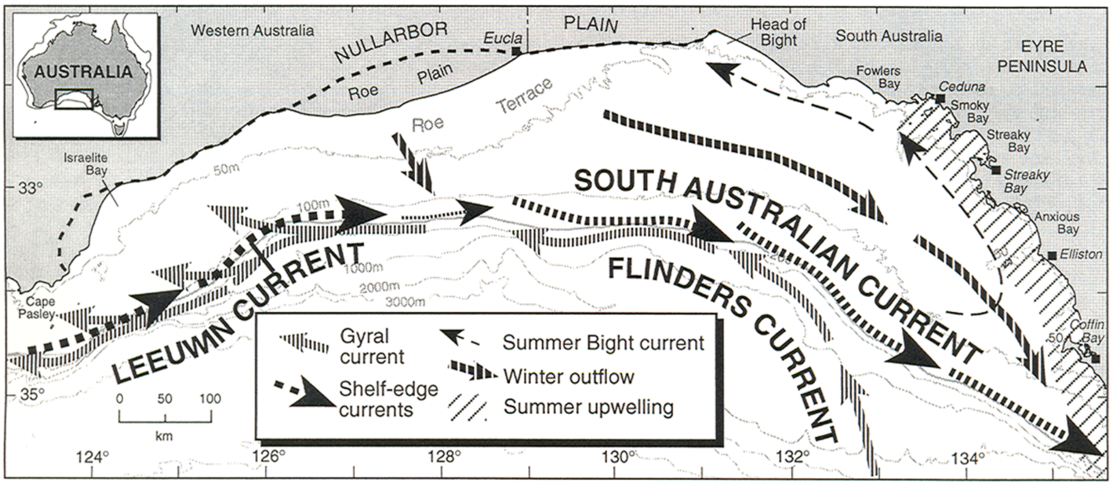

Figure 3.4: The major currents in the GAB region. The Leeuwin Current and South Australian Current are strongest in winter. Winter outflow is a south-eastward movement of saline, oligotrophic water off the shelf generated by evaporation and solar heating during summer. Adapted from (James et al. 2001) and http://www.es.flinders.edu.au/~pbarker/bye.html

The environment is generally oligotrophic, with surface inorganic phosphate levels the lowest measured in the Indian and Southern Oceans (Rochford 1986). The eastern Great Australian Bight is one of the few regions in Australia where predictable, large-scale upwelling occurs providing nutrient-enrichment on to the shelf (Lewis 1981). Cold water intrudes onto the shelf in the eastern GAB during summer-autumn, (Figure 3.5) reaching the surface in coastal waters of the south-western Eyre Peninsula (Herzfeld, 1997), but is not present on the shelf during winter.

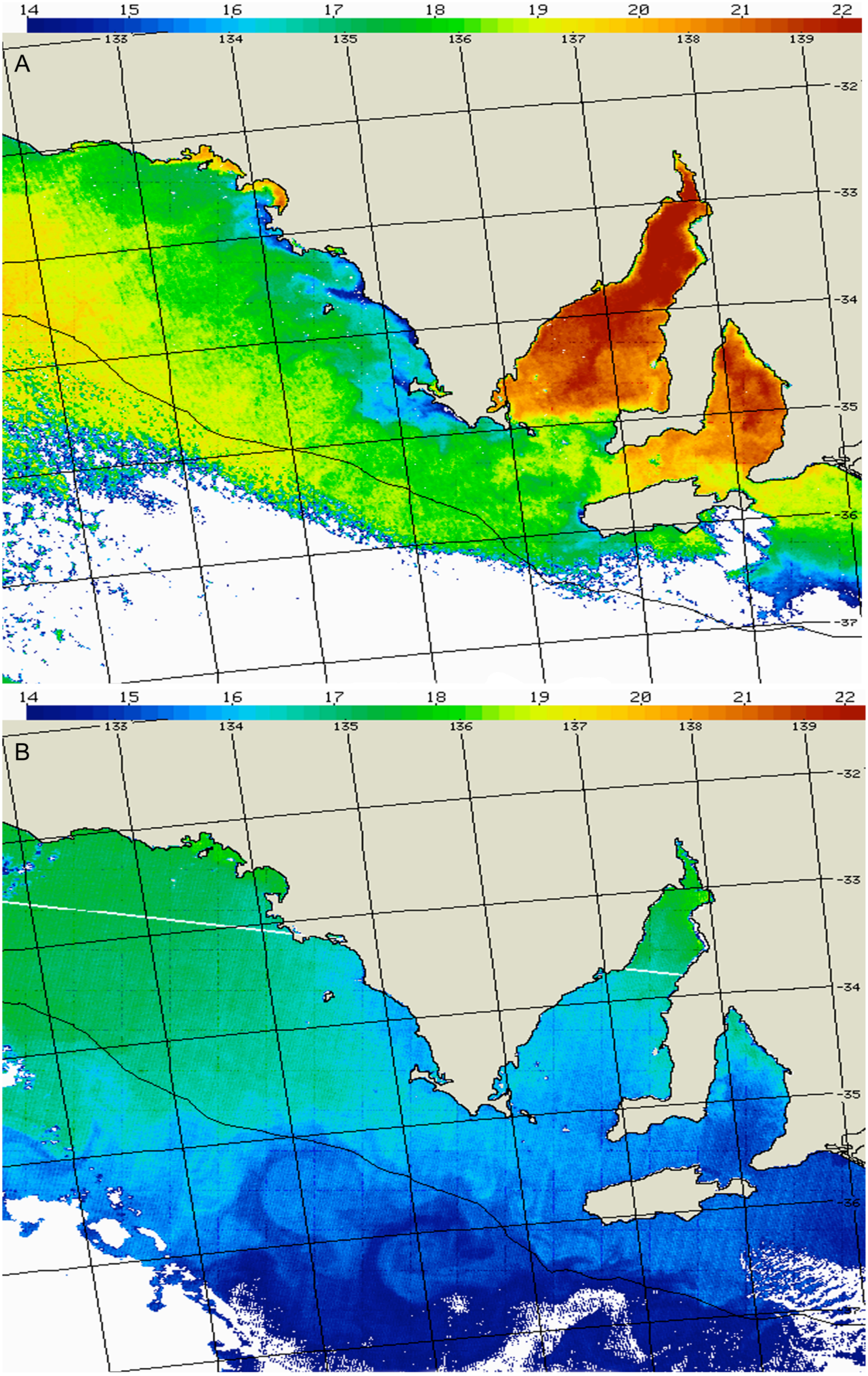

Figure 3.5: Sea Surface Temperature maps of the South Australian Gulfs and GAB. Summer map collected on 13 March 1995. Winter map collected on 13 October 1998. Maps courtesy of CSIRO Division of Marine Research.

The extensive gulf systems of Spencer Gulf to the west and Gulf St. Vincent represent one of the largest sheltered coastal ecosystems in Australia (Edyvane 1999). The waters of the two South Australian gulfs influence the regional peninsula weather, producing a temperate climate with smaller monthly temperature deviations than inland areas at similar latitudes. Both Spencer Gulf and Gulf St Vincent behave like inverse estuaries, due to minimal fresh water input from rivers or groundwater, and high evaporation rates at the head of the gulfs. This results in a double layered circulation, with oceanic water entering the gulf in the upper layer and hyper-saline water leaving in the lower layer.

Gulf St. Vincent

The dominance of evaporation over rainfall and virtual absence of river runoff increases the salinity at the head of Gulf St Vincent (GSV) from 39 ‰ in winter to over 42 ‰ in summer. The average salinity across the mouth of Gulf St. Vincent (Cape Jervis to Troubridge shoals) is ~ 36.5 ‰ (de Silva Samarasinghe et al. 2003). The general circulation is clockwise, with less saline shelf water entering through Investigator Strait, flowing up the western side of the gulf, and more saline outflow along the eastern side. Outflow of Gulf water in summer is restricted by the formation of temperature fronts over the western end of the Strait. The rate of salt flushing is influenced by variability in general circulation, and the directional variability in currents is a hindering factor for the transport of tracers (de Silva Samarasinghe et al. 2003).

Ecologically, the waters of Gulf St. Vincent are relatively diverse with sand, seagrass and rocky reef ecosystems providing important nursery and feeding grounds for molluscs, crustaceans, fish and marine mammals. Significant pollution comes from many sources, including stormwater runoff, river catchment discharges. Urban runoff contains solid wastes, chemical pollutants, vehicle pollutants and pesticides, whereas rural runoff includes a combination of fertilisers, agricultural chemicals, animal waste, pesticides, herbicides and soil. Wastewater treatment plants discharge secondary treated effluent from four locations into Gulf St. Vincent including Port Adelaide and Glenelg. These discharges are high in nutrients and suspended solids and contain heavy metals. Historically, sewage sludge has been discharged at Glenelg causing over 1000 Ha loss of seagrass (Gaylard 2004). Port Adelaide and Port Stanvac have been the site of several oil spills with 10 spills at Port Stanvac between 1988 and 1992 and the largest spill of 234,325 litres in 1982 (Edyvane 1999). The use of tributyl tin (TBT) as boat antifoulant has been proven to cause growth abnormalities and is banned in all states of Australia except South Australia.

The metropolitan water supply of Adelaide (> 1,300,000 people) has a major impact on the natural flows of a number of catchments draining into Gulf St. Vincent. The largest river in the region, the Torrens River has a catchment of approximately 500 km^2 and has two distinct catchment regions, a watershed in the upper catchment and an urbanised lower catchment. Annual average rainfall varies from 1200 $mmyr^{-1}$ in the upper catchment to 400 $mmyr^{-1}$ on the coastal plains (Gaylard 2004). The current outlet of the Torrens River, was constructed in the 1930s and bypassed the coastal wetlands, resulting in direct discharge of turbid stormwater into the coastal zone (Lewis 1975). A three year study on river health suggested that most nutrient loading into the coastal zone is episodic with over 80% of suspended solids, 50% of nitrogen and 67% of phosphorus discharged in a two week period (Schultz et al. 2000). Results of this study imply infrequent loading on the marine environment during large floods every few years.

Spencer Gulf

Spencer Gulf is a large (length ~ 325 km, mean width ~ 60 km) relatively shallow (mean depth ~ 22 m) semi-enclosed sea, with evaporation exceeding precipitation for most of the year (Nunes Vaz et al. 1990). There are no significant rivers providing runoff into the gulf and groundwater contributions are believed to be minimal. Salinity increases with distance from adjacent shelf waters to a maximum of ~ 48 ‰ at the head of the gulf in late summer. Gulf temperatures vary considerably between seasons with minimums of ~ 10˚C in late winter and rising to 25˚C in late summer. Large temperature gradients occur across the mouth of the gulf at summer and winter extremes. The low thermal inertia of the gulf means that its annual temperature variability (18 ± 7˚C) is much greater than the adjacent shelf seas (17.6 ± 1.8˚C), and the gulf/shelf temperature gradients reverse in spring and autumn (Nunes Vaz et al. 1990). During summer, temperature gradients reverse at the mouth of the gulf, preventing the release of the highly saline fluid and creating a frontal boundary of salinity and temperature. Previous research has found the frontal zone to be a region of subsurface convergence and surface divergence, and this separation of gulf and shelf vertical circulation acts to inhibit exchange of oceanic water across the mouth (Nunes & Lennon 1986). Therefore on a seasonal timescale, the density gradients reverse across the mouth of the gulf, assisting water exchange in winter but blocking water exchange in summer.

Benthic habitats vary between sandy seabeds, extensive areas of seagrass and algal dominated rocky reefs. Large colonies of *Plesiastrea versipora* have been observed on isolated reefs, however large colonies are thought to be rare in Spencer Gulf due to long term benthic trawling for prawn fisheries (Edyvane 1995). Primary production in Spencer Gulf is sustained by internal recycling of essential plant nutrients (C, N, P) by about 90% (Smith & Veeh 1989). The most important primary production in this system is by seagrass and the fisheries yield of Spencer Gulf is a relatively low proportion of the primary production (Smith & Veeh 1989).

Major industries operate in the region of Spencer Gulf including: iron ore mining, steel production, petrochemical processing and food additive production such as beta carotene (DEH 2003). The smelter at Port Pirie is one of the largest zinc and lead smelters in the world and has been operational since 1889, causing heavy metal pollution in the form of particulate emissions from smoke stacks, dust blown from sites, spillage from ship loading and discharging of liquid effluent. Heavy metal contamination (including zinc, cadmium and lead) within proximity of mines and smelters in Spencer Gulf has been the subject of several studies (Ward & Young 1981; Ferguson 1983; Ward & Young 1983; Harbison 1984; Noye 1984; Harbison 1986; Maher 1986; Ward 1989; Edwards et al. 2001) with most biota sampled in the contaminated areas indicating elevated levels of Zn, Pb and Cd. Seagrass habitats near Port Pirie have been monitored in the past for metal accumulation (Ward 1989; Edwards et al. 2001) and closures have occurred in shellfish harvesting areas in parts of Spencer Gulf. Oil spills have also occurred in Spencer Gulf, the largest recorded occurred in August 1992 at Port Bonython. During this spill over 300,000 litres of bunker oil was released with environmental damage occurring on nearby mangrove and seagrass habitat.

Australian climate forcing

Long-term historical studies allow an assessment of the natural variability within ecological systems and the response and resilience of systems to environmental change. Historical studies also provide a way to interpret the significance of recent human driven transformations (Bickford & Gell 2005). Detailed correlations of marine and continental paleoclimate records over glacial and interglacial periods at a global scale are essential if we are to ascertain climate complexities in the Quaternary. There are very few paleoclimate records from the Southern Hemisphere in comparison to the Northern Hemisphere. There is also a bias present in the spatial distribution of records from Australia with most speleothem, lake core and tree ring records clustering in eastern Australia with very few records extending further west than the southeast of South Australia. Recent paleoclimate studies have sought to address this issue and establish changes in the Australian monsoon in the southern and western part of Australia and the strength of different tropical climate teleconnections such as ENSO (Treble et al. 2003; Magee et al. 2004; Bickford & Gell 2005). Coral records from southern Australia would complement the speleothem and lake core records, providing a clearer picture of the environmental variability at high-resolution over the last few hundred years.

The southern coastline of Australia is influenced by large-scale climate systems from three ocean basins. Therefore El Niño Southern Oscillation, Indian Ocean Dipole, Pacific Decadal Oscillation and the Southern Annular Mode can play an influential role in local and regional climate in the South Australian gulfs. The northern regions of South Australia are part of a large drainage basin, including the Lake Eyre Basin which are influenced by latitudinal variations in the extent of the Austral-Asian monsoon system.

Lake Eyre is the largest ephemeral lake in Australia and lies in the southwest margin of a large drainage network dominated by summer monsoon rainfall, in an area with Australia's lowest rainfall, which is far exceeded by evaporation (Magee et al. 2004). Cores from Lake Eyre provide one of the few paleoclimate archives from South Australia and enable comparison to be made with marine isotopic records of insolation changes, sea level variation, and monsoon dynamics the over the last 150,000 years. The Australian monsoon recorded in Lake Eyre (at the periphery of the Southern Hemisphere monsoon) is spatially and temporally erratic, varying significantly with tropically driven climate systems such as the Walker circulation and the El Niño Southern Oscillation (Magee et al. 2004). On shorter time-scales high-resolution lake cores from the Fleurieu Peninsula observed differences in vegetation type and cover following European settlement (Bickford & Gell 2005), whereas the natural environmental variation throughout the Holocene suggest that recent human changes cannot be considered as part of the natural ongoing trajectory of environmental change and ecosystem adaptation. Very few studies in Australia have examined the anthropogenic impact in the coastal marine environment, however, tropical corals have successfully recorded local pollution (Shen & Boyle 1988; Esslemont 1999; Esslemont et al. 2004; Inoue et al. 2004).

The El Niño Southern Oscillation (ENSO) is a coupled cycle with atmospheric-oceanic exchange. ENSO is considered to be the strongest, natural source of global interannual climate variability. However, the intensity, frequency and longevity of ENSO events have varied through time and are still not well understood (Evans et al. 1998; Kotwicki & Allan 1998; Correge et al. 2000; Turney et al. 2006). This phenomenon alternates between two phases, termed El Niño and La Niña on a 2-7 year cycle. During an El Niño event, warming of the Central and Eastern tropical Pacific Ocean and decreased trade winds suppress rainfall in the western Pacific basin. The opposite occurs during a La Niña event with enhanced rainfall in the western Pacific and reduced rainfall in the eastern Pacific. The maximum amplitude of the Southern Oscillation Index (SOI) generally co-occurs with the Austral summer, however the associated anomalies in sea surface temperature, rainfall and wind direction differ considerably between different ENSO events (Rasmusson & Wallace 1983). Teleconnections associated with ENSO events occur at higher latitudes due to Hadley Cell circulation, these are known to have varied through time (Charles et al.

1997; Marshall & McCulloch 2001; Gagan et al. 2004; D'Arrigo et al. 2005). ENSO teleconnections have varied with changing intensity of atmospheric and oceanic anomalies during the last 150 years of instrumental monitoring (Mann et al. 1998). Since the 1970s, ENSO has altered its dominant signal to El Niño conditions (Allan & D'Arrigo 1999) and, any mid-latitude teleconnections may lag equatorial anomalies by several months (Power et al. 1999). The dynamic fluctuations of ENSO make accurate reconstructions of historical events from paleoarchives problematic (Mann 2002).

El Niño and the Southern Oscillation Index have been recorded in several mid-latitude (D'Arrigo et al. 2005) and high-latitude archives and it is likely that they have some influence over regional climate in South Australia. The Southern Oscillation Index has been associated with changes in wave dynamics and beach rotation on the eastern Australian (New South Wales) coastline (Ranasinghe et al. 2004). This study found that offshore wave height was positively correlated with the SOI, while offshore wave direction was negatively correlated with the SOI. In addition, the northern end of this type of beach accretes during the El Niño phases while the southern end erodes, resulting in a clockwise rotation of the beach and anticlockwise rotations during La Niña phases (Ranasinghe et al. 2004).

While there are strong teleconnections associated with ENSO between the tropics, the mid-latitudes and the extra-tropics the mean wave direction is also influenced by varying atmospheric circulation associated with the Southern Annular Mode (SAM) (Goodwin 2005). The Southern Annular Mode describes the seesaw of atmospherics with opposing geopotential height perturbations between the mid-latitudes (~45°S) and Antarctica (Gillett et al. 2006). When the Southern Annular Mode index is positive, and the mid latitude westerlies (roaring 40's) are latitudinally displaced poleward (towards 60°S). When the index is negative, the westerlies are displaced towards the equator (Rogers & van Loon 1982).

An Indian Ocean Dipole (IOD) event begins with anomalous SST cooling along the coastline of Java and Sumatra during the Austral winter (May-June). The equatorial westerlies weaken and reverse direction, following the wind reversal, the Indian Ocean Dipole event peaks in September-October with anomalously warm SSTs over large parts of the western Indian Ocean Basin (Saji et al. 1999). Some Indian Ocean Dipole events are coincident with strong ENSO events (Saji et al. 1999) and when these events co-occur in an Indian Ocean Dipole positive phase (Figure 3.6), the Leeuwin current flows more strongly around Cape Leeuwin and brings anomalously warm water east past the south Australian Gulfs (Meyers et al. in press).

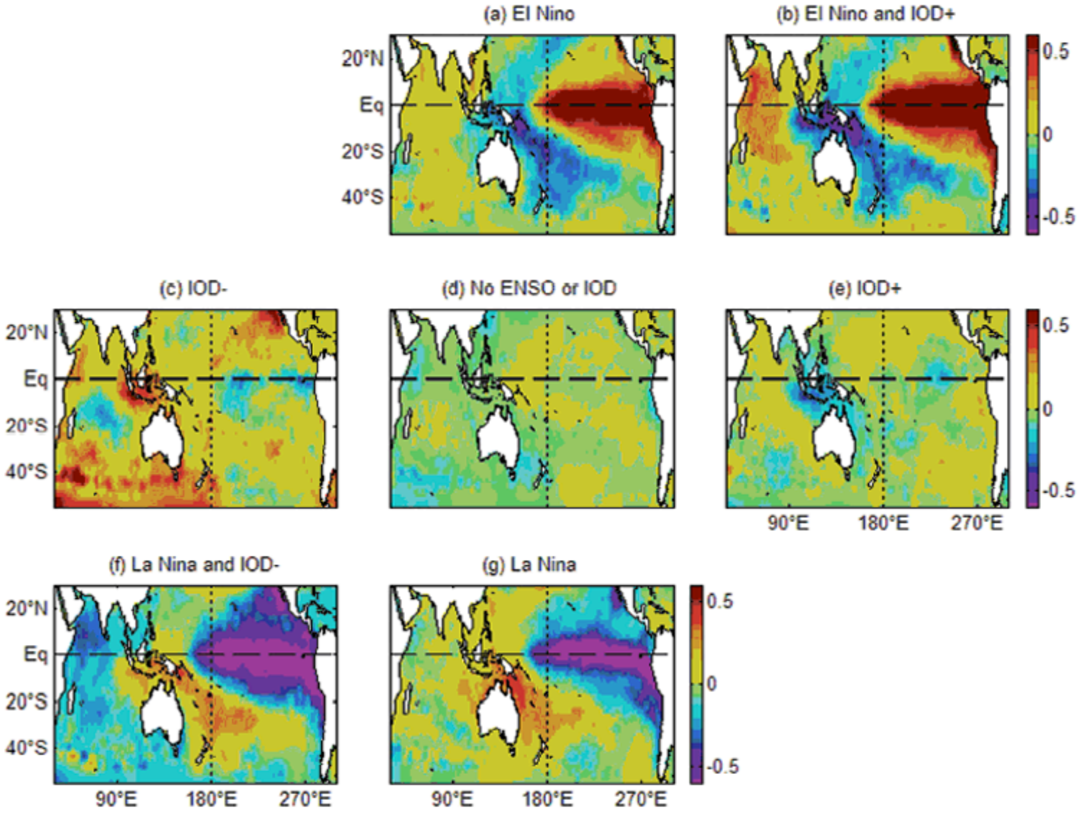

Figure 3.6: Composite averages of SST anomaly for the period of Austral winter-spring (June-November). (a) and (b) indicate typical SST anomalies for El Niño events including a warm anomaly in the eastern Pacific and a cooler SST anomaly in the western Pacific. Southern Australia indicates a slight positive SST anomaly. (c) Indicates a positive SST anomaly during negative IOD mode off Indonesia and also southern Australia. (d) Displays the normal SST conditions in the southern Pacific Basin with no El Niño or IOD. (e) Indicates a positive IOD mode and a cooler SST anomaly in the Indonesian Archipelago (f) Indicates a strong negative anomaly in the Indian Ocean, Eastern Pacific and southern Australia during a La Niña and IOD$^-$ mode. The cool temperature anomaly in southern Australia is not replicated during a La Niña event without the IOD (g). Adapted from Meyers et al. (in press).

Evidence of interdecadal fluctuations in the Pacific known as the Pacific Decadal Oscillation (PDO) is documented in oceanic, atmospheric, and sedimentary records in the region of the Pacific basin. The Pacific Decadal Oscillation has been defined as the low-frequency SST variability across the Pacific basin (Power et al. 1999). Previous authors have found a large positive anomaly with the Pacific decadal oscillation-SST pattern south of Australia (Figure 3.7), however, details of the driving mechanisms of the Pacific interdecadal variability are not well understood (Mestas-Nunez & Miller 2006).

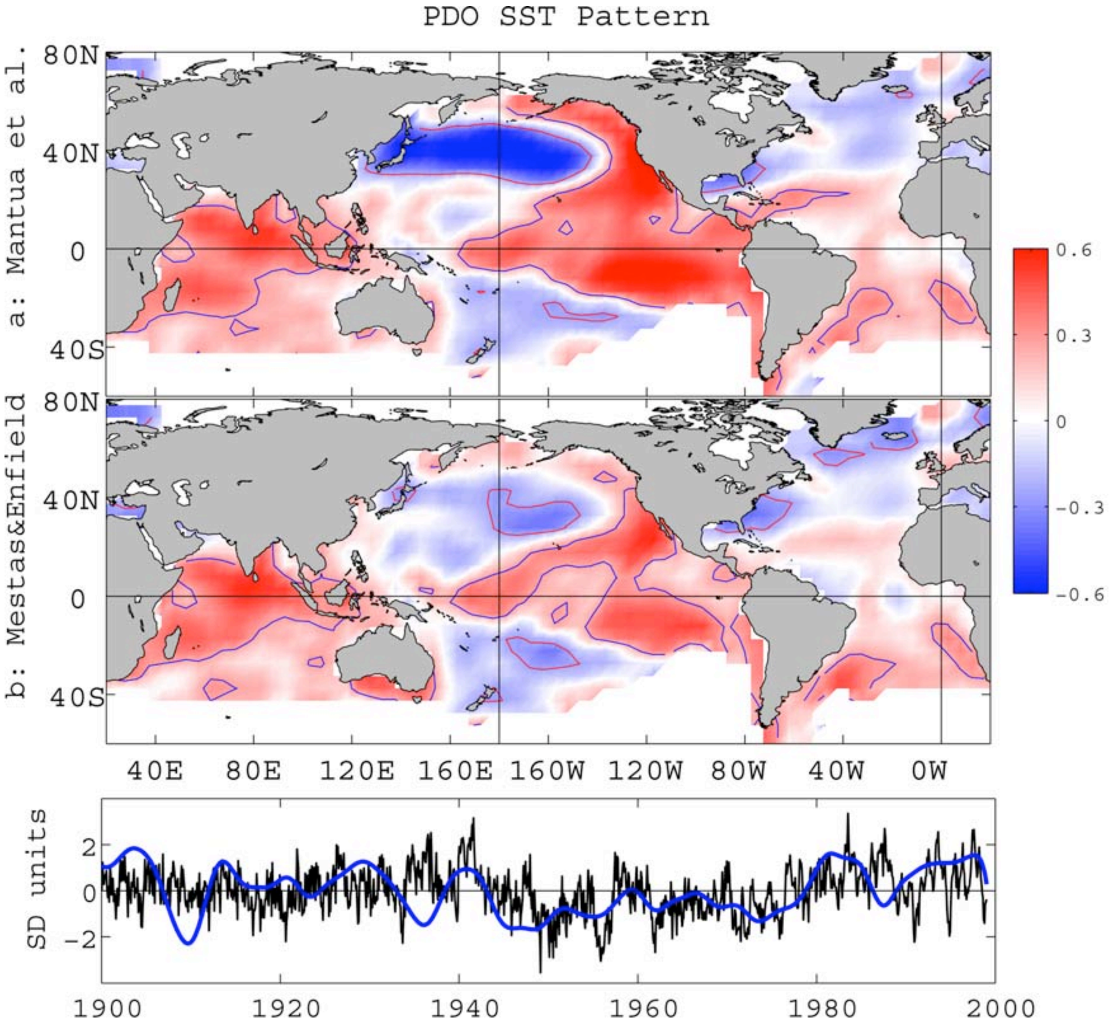

Figure 3.7: Correlation patterns constructed for the Pacific Decadal Oscillation (PDO)-SST anomaly using data sets from (Mantua et al. 1997; Kaplan et al. 1998; Mestas-Nunez & Enfield 2001). A positive temperature anomaly can be observed in southern Australia coincident with the warm anomaly in the eastern Pacific Basin, especially with the Mestas-Nunez & Enfield (2001) PDO data set in (b). The 5 year running average of the PDO SST anomaly indicates increased warming in the later part of the 20th Century. Figure adapted from (Mestas-Nunez & Miller 2006).

The large-scale structure of the Pacific Decadal Oscillation is similar to ENSO with large amplitudes in the tropical Pacific and out of phase variations in the central mid latitude Pacific. Recent work on Australian and South Pacific climate has identified interdecadal climate variability described by the Pacific Decadal Oscillation modulate into interannual fluctuations described by ENSO with an approximately 15 to 30 year period (Power et al. 1999). Studies examining the mean wave direction on the New South Wales coastline found that it varies with a strong annual cycle with significant multidecadal fluctuations correlating with the periodicity of the Pacific Decadal Oscillation (Goodwin 2005). The significant correlation between annual mean wave direction and SOI indicates that mid-shelf wave direction behaviour can be interpreted in association with ENSO and the multidecadal variability in wave direction data suggested a combined influence of both the Pacific Decadal Oscillation (15 to 30 year periods) and the Southern Annular Mode (10.5 to 23 periods) (Goodwin et al. 2004; Goodwin 2005).

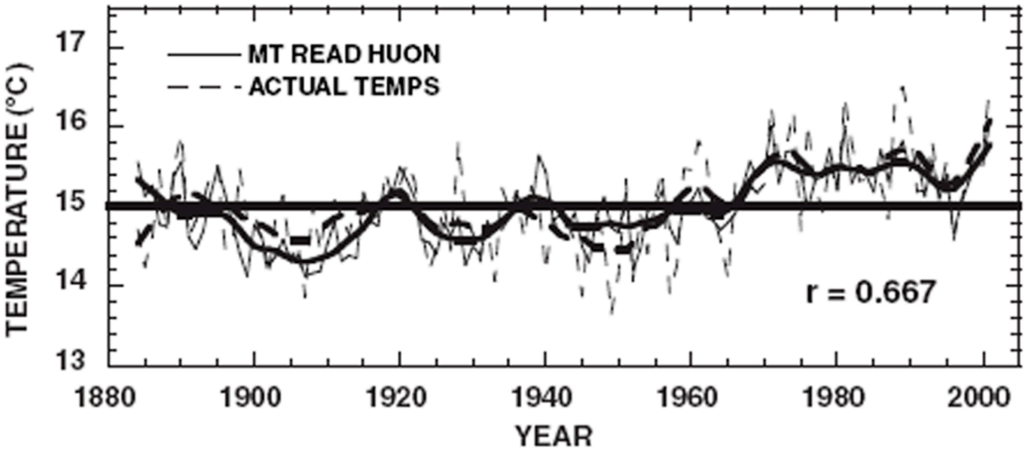

Figure 3.8: Austral warm season (November-April) temperature reconstruction for Tasmania based on ring widths from subalpine Huon Pine indicating a warming trend from the 1960s onwards. Dashed line displays a 5 year running average. Figure adapted from Cook et al. (2006).

To date, tree ring temperature proxy reconstructions from Tasmania offer some of the only high-resolution temperature reconstructions for southern Australia. A Tasmanian summer temperature reconstruction from Huon Pine tree rings (Figure 3.8) indicates warming beginning in 1965 with the trend sustained until the end of the record in 2001 (Cook et al. 2006). The authors of this study noted that the recent warming period included the warmest temperatures in the last 2000 years of the record and only exceeded by 0.2°C three times in the entire 3600 year record. However, Tasmania experiences higher frequency variability in the regional climate (more oceanic, island-like) compared with continental Australia. A Tasmanian speleothem study did not find any significant correlation with published tree-ring records, suggesting the regional climate is more variable than the proxy recorded in summer growth tree rings (Desmarchelier et al. 2006). Evidence for the observed increase in temperature in the last 50 years in the tree ring record has also been shown by coral records from the mid-latitudes of Western Australia, with a 1.4°C increase over the length of the 200 year record (Kuhnert et al. 1999).

Coral Occurrence

The original premise of the project included collecting coral samples from the Great Australian Bight to assess temporal variations in the summer wind-driven upwelling as this is an important nutrient source for several commercial fisheries in the region (including Southern Blue Fin Tuna). While massive colonies were found in the GAB during towed video transects, none were located during dive surveys and the focus of the project shifted to an intra- and inter- gulf comparison as sampling success had been achieved in both gulfs. By directly comparing coral proxy records between the two gulfs, which have vastly different anthropogenic influences, the scope of the project was broadened significantly.

Fieldwork was initially conducted during April-December 2003 in Gulf St. Vincent and Spencer Gulf (Figure 3.3). The fieldwork was carried out over an extended season as coastal rocky reefs required extensive surveying to find coral colonies suitable for coring. Before this study, there were minimal records of colony locations and due to lower visibility in temperate waters and the lower depth of *Plesiastrea* colonies; they could rarely be seen from the surface. Four coral colonies were revisited in May 2005 and longer cores were taken. The temperature loggers which had been placed on Seacliff and Troubridge corals in 2003 were also collected.

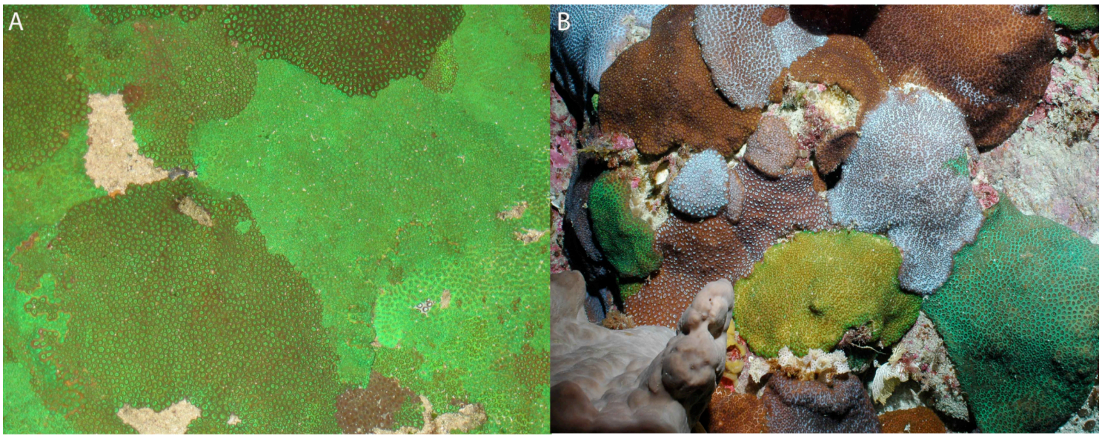

Figure 3.9: Encrusting form of *Plesiastrea versipora* colonies from other high-latitude sites. A: Batemans Bay, New South Wales, photo by Adrienne Grant. B: Kent Group Islands, Bass Strait, photo by Neville Barrett.

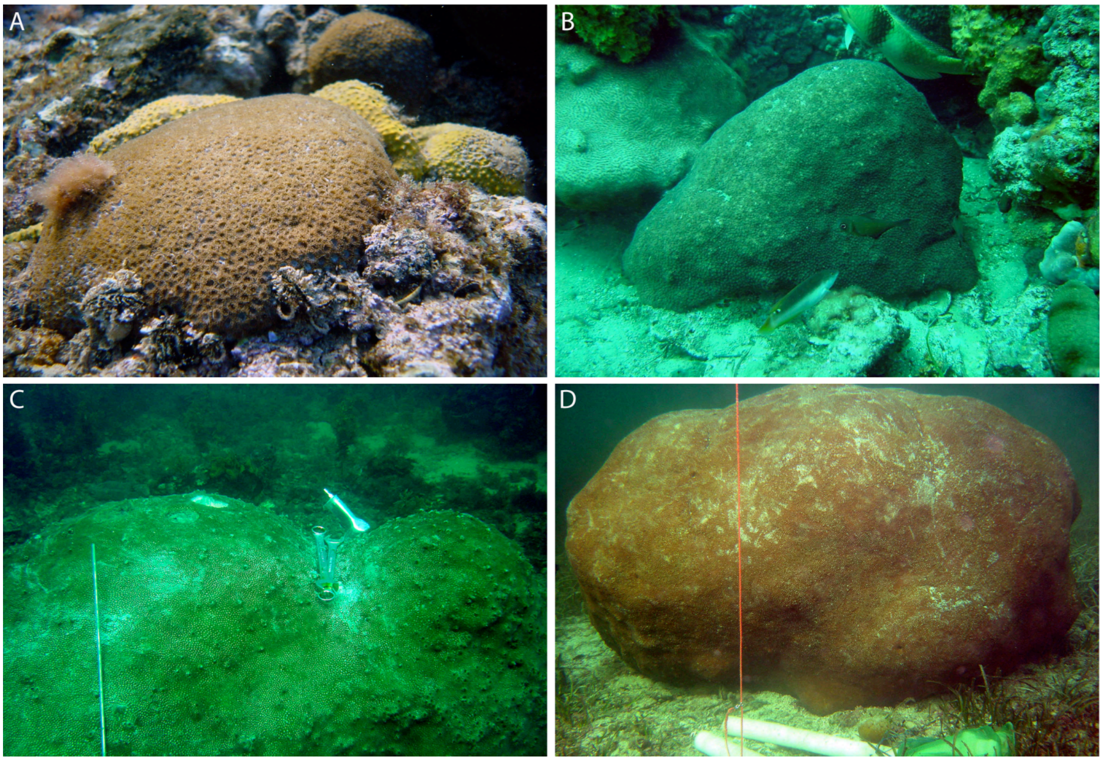

Figure 3.10: Massive forms of Plesiastrea versipora colonies from South Australian gulfs. A: Whyalla, Spencer Gulf, colony approximately 15 cm photo by James Brook. B: Edithburgh colony, Gulf St. Vincent, approximately 28 cm. C: Seacliff A colony, Gulf St. Vincent, approximately 150 cm high. D: Troubridge colony, Gulf St. Vincent, approximately 180 cm.

All fieldwork was conducted with the assistance of South Australian Research and Development Institute: Aquatic Science staff and resources from the West Beach and Port Lincoln offices. Core samples of up to 750 mm were obtained using an initial 500 mm core barrel and extension rods to collect longer cores of up to 1500 mm. The drill bit is a modified commercial design (developed by the workshop at the Research School of Earth Sciences) with tungsten carbide teeth attached to a pneumatic air drill. The coring techniques required some modification from *Porites* coring due to the increased density of *Plesiastrea* and the depth of colonies (2-20 m). Depending on the depth of the colony the pneumatic drill was attached to a standard steel dive tank, with a second tank set up (including first stage valve) to exchange during the one dive. For shallow corals, the drill was connected to a surface supply (hooker system) on the dive vessel.

Although *Plesiastrea versipora* is ubiquitous around the entire coastline of Australia (Veron 1986) the most common colony habit is the encrusting form (Figure 3.9). In the waters of South Australia, both the encrusting form and the massive form (Figure 3.10) are present. It remains unknown what environmental or genetic triggers exist in juvenile corals to determine which growth habit they will form, impacting coral biomineralisation processes. For geochemical studies, only massive colonies with sufficient vertical extension to record several decades of climate information are useful, and therefore were targeted for sampling.

The *Plesiastrea versipora* samples collected in 2003 and 2005 are listed in Table 3.1, the associated field notes can be found in Appendix B. The deepest location for coral collection was on the western side of Taylors Island (Figure 3.3D) in Spencer Gulf. Oceanic water enters Spencer Gulf through this channel and currents are exceptionally strong with visibility commonly less than 1 m (known as the ‘milk run’). Several bioeroded and encrusted corals were observed before two live corals were located and core samples collected near Taylors Island. Both of these colonies have been heavily bored by barnacles and one colony (Taylors Island B) had rolled losing the primary growth axis but continued growing. Severe storms may cause corals in the South Australian gulfs to dislodge from the substrate they attached to and roll along the seafloor. Most of the *Plesiastrea versipora* colonies observed during the surveying were located on sandy bottom (Dutton Bay, Taylors Island) or seagrass habitat (Edithburgh, Troubridge). The few that were located on rocky reefs (Seacliff and Whyalla) had a higher profile than the surrounding unconsolidated reef complex.

Table 3.1: Location of coral colonies collected in 2003. Depth and size of colony also listed. All colonies had polyps extended during the day except for the Dutton Bay colonies. Corals from Edithburgh, Troubridge and both colonies at Seacliff were recored in May 2005.

Location	*Gulf*	*Depth*	*Size of colony*	*Remarks*
Seacliff: Coral A	Gulf St. Vincent	12 m	~ 150 cm	Very dense coral – short core obtained in 2003 Colony recorded in 2005 till growth axis was lost during coring
Seacliff: Coral B	Gulf St. Vincent	12 m	~ 120 cm	Coral partially dead on one side. Covered with encrusting invertebrates. Easy to core. Colony recorded in 2005 till growth axis was lost during coring
Broken Bottom	Gulf St. Vincent	14 m	~ 20 cm	Loose colony on bottom, mostly dead. Very large calices
Edithburgh	Gulf St. Vincent	4 m	~ 28 cm	Coral to the north of jetty Recored in 2005
Troubridge	Gulf St. Vincent	5 m	~ 170 cm	Coral partially dead on one side. Covered with encrusting invertebrates. Easy to core. Colony recorded in 2005 till growth axis was lost during coring
Dutton Bay	Coffin Bay	2 m	~ 20 cm ~ 25 cm	Corals located under jetty, calice shape different to other corals. Three corals collected
Taylors Island A	Spencer Gulf	22 m	~ 25 cm	Some boring by barnacles
Taylors Island B	Spencer Gulf	21 m	~ 31 cm	Heavily bored throughout core, coral rolled and axis changed mid way through core
Whyalla	Spencer Gulf		< 15 cm	Dominant invertebrate on rocky reef. Four collected.

Two coral cores were collected from Seacliff Reef (Figure 3.3A), a coastal reef near a large urban centre (Adelaide) and these corals were the most different in terms of their density. Seacliff A was the most dense coral cored, whereas Seacliff B was quite easy to core and the northern side of the colony was bioeroded and covered with encrusting organisms. The density difference between these two corals is surprising as they are located approximately 5 m apart and there are no discernable environmental differences on such a short spatial scale.

The coral colony sampled at Troubridge Shoals (Figure 3.3B) was the largest colony sampled and also the least dense skeleton. The coral is situated on a seagrass sand bar in an open part of Gulf St. Vincent. The northern face of this coral was also bioeroded and covered with encrusting invertebrates and algae. The coral cored at Edithburgh was located on seagrass and patchy reef less than 50 m away from the coastline.

The shallow reefs at Whyalla are well known as the spawning site for the giant cuttlefish during winter and *Plesiastrea versipora* was the dominant encrusting organism present on this reef. There is a fishery associated with the cuttlefish. Several colonies were collected in this location (Figure 3.3C), and they have the potential to contain a record of environmental modification from the lead and zinc smelters at Whyalla and Port Pirie.

The shallowest site that cores were collected from was at Dutton Bay (Figure 3.3E), a shallow embayment with a long seawater residence time on the Eyre Peninsula. Two cores were collected from colonies in this location. The entire bay is very shallow (< 10 m) and reaches high salinities in summer. The corals from this location were visually the most different to other corals collected and did not have extended polyps during the day.

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Chapter 4:

Validating Annual Deposition of Density Bands Using U/Th aging

Chapter 4: Validating annual deposition of density bands in the high-latitude coral: *Plesiastrea versipora* using U/Th aging techniques

Introduction

Corals record useful information about the environment prevailing at the time of growth in their skeletons (Barnes 1970; Dodge & Vaisnys 1975; Weber et al. 1975). Massive corals have linear extension rates of 1–30 mm per year, distinctive annual skeletal banding, and have life-spans of several centuries. Density bands in the skeleton are used to establish annual cycles of growth (Barnes 1972; Hudson et al. 1976; Highsmith 1979). The annual bands are accreted in couplets and the high-density portion is usually produced during winter when sea surface temperatures (SST) are lowest, however, banding patterns vary not only between species but also between colonies. The low-density portion of annual bands accounts for a greater portion of the linear growth (Highsmith 1979; Leder et al. 1996).

Hermatypic coral growth rates have been extensively documented for tropical and subtropical regions since the early 1970's (Bak 1974; Hart & Cohen 1996; Alibert & McCulloch 1997) and research on growth rates from deep-sea corals is also increasing (Squires 1964; Druffel et al. 1990; Adkins et al. 2004). These studies show that coral growth rates vary in response to a multitude of factors including; temperature, nutrient availability, turbidity, depth and cloud cover. Coral-based geochemical proxies provide a mechanism for temporally extending the instrumental record for environmental parameters such as water temperature (McCulloch et al. 1994; Gagan et al. 2000), salinity and turbidity (Alibert et al. 2003), terrestrial runoff (McCulloch et al. 2003) and upwelling intensity (Lea et al. 1989).

In some corals luminescent features are sometimes associated with annual bands. These features were initially attributed to the incorporation of humic acids from terrestrial runoff (Boto & Isdale 1985). However, recent research has suggested that bands result from variations in microporosity and changes in the skeletal architecture (Barnes & Taylor 2001; 2005).

There have been few studies of environmental records in corals from temperate latitudes. The South Australian continental margin is one of the world's largest cool-water carbonate factories (James et al. 1997) and scleractinian corals are well positioned to record variability of temperature, salinity, nutrient dynamics and oceanic influence from the Southern Ocean.

Large colonies of *Plesiastrea versipora* (Lamark 1816) were first discovered in South Australia near Glenelg, Adelaide almost 100 years ago (Howchin 1909). The typical habitat is moderately exposed reef in water-depths of 2–30 m. The two South Australian gulfs, Spencer Gulf and Gulf St. Vincent are semi-enclosed 'inverse estuaries' (Nunes & Lennon 1986), which occur when there is little or no input of fresh water from rivers, and high evaporation rates at the head of the estuary/gulf. Both gulfs display seasonal reversals in water temperature gradients, the northern waters have an annual range of 12-25˚C (Petrusevics 1993), with warm summers and cold winter temperatures due to the influence of insolation and heat loss. The southern gulfs experience more moderate seasonal variation of ~ 14-19˚C due to a strong oceanic influence (de Silva Samarasinghe 1998).

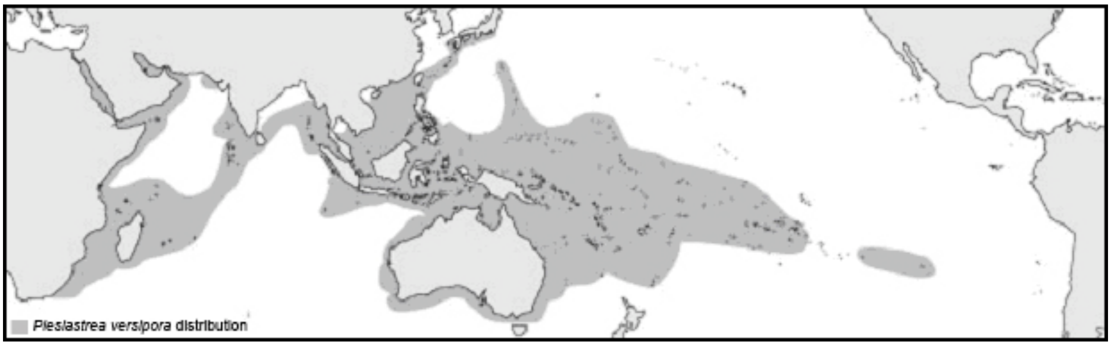

Figure 4.1: Distribution map of *Plesiastrea versipora* throughout the Indo-Pacific adapted from Veron (1986).

Plesiastrea versipora is one of two species in the genus *Plesiastrea* (Edwards and Haime 1848), within the family Faviidae. Colonies range from encrusting to massive forms (Veron 1974). High-latitude colonies form a distinct geographical subspecies, which was formerly considered a separate species, *Plesiastrea urvillei* (Veron 1986).

The level of variability in colour and morphology of the high-latitude colonies of *P. versipora* was described as a distinct ecomorph (Wijsman-Best 1977). *P. versipora* has arguably the broadest latitudinal range of any hermatypic coral (Figure 4.1). The distribution of this species contrasts with other hermatypic corals that are restricted to warm, high light intensity tropical regions (25˚N – 25˚S). At the highest southern latitudes in the habitat range of *P. versipora*, water temperature minimums in winter are ~ 10˚C and light intensity may be 30% of levels observed at low latitude sites (Kleypas et al. 1999). The polyps of *P. versipora* are fully extended during the day, almost doubling the surface area of the corallite available for photosynthesis, with higher zooxanthellate densities than tropical colonies, a advantageous feature in low irradiance environments (Kevin & Hudson 1979). The capacity of this coral to adjust to different environments may be due to acclimatisation processes associated with a wide phenotypic plasticity or to independent populations adapting to different environments (Grant et al. 1998; Rodriguez-Lanetty et al. 2001; Howe & Marshall 2002; Rodriguez-Lanetty & Hoegh-Guldberg 2002).

In this study, we describe and compare the growth rates of some high-latitude colonies of *Plesiastrea versipora* using the standard density band counting technique. The periodicity of growth band formation was validated using U/Th dating techniques. Establishing the chronology of *P. versipora* provides a basis for assessing the suitability of this coral as a paleoenvironmental archive for temperate environments in the Indo-Pacific region. This paper also demonstrates the usefulness of U/Th dating for young carbonate material.

Materials and Methods

Sampling

Fieldwork was conducted during April-December 2003 and May 2005 in Gulf St. Vincent and Spencer Gulf, South Australia. Fieldwork involved surveying coastal reefs through SCUBA diving to find coral colonies suitable for coring. *Plesiastrea versipora* colonies (up to 1.7 m in vertical height) were collected from seven sites, four in Gulf St. Vincent, two in Spencer Gulf and one colony in Dutton Bay, Southwestern Eyre Peninsula (Figure 3.3). Six cores from four sites were included in this study: two from corals on a rocky reef close to the city of Adelaide (Seacliff Reef 12 m); one from a coral located near a jetty at Edithburgh (4 m); one from a coral on sand bar in the middle of GSV known as Troubridge Shoals (5 m); and two from corals located on seagrass/patch reefs near Taylors Island (22 m), Spencer Gulf.

X-ray density Analysis

Coral cores collected along the axis of maximum vertical extension were cut into 7-8 mm slabs for X-ray and luminescence analysis. Coral sections were X-rayed at a commercial X-ray medical facility, using an exposure of 55 kV and 5 mA for 15 sec with a Kodak CR500. Luminescence photographs were taken under black ultra-violet fluorescent lights, with a yellow filter to enhance the differentiation of luminescent bands. Linear extension was measured for the (assumed annual) high and low-density band couplets using an arbitrary measurement feature in the software SigmaScan Pro 5. Annual growth increments were calculated for three transects across the coral core where the banding was well defined, years were assigned to each couplet by counting backwards from the year of collection.

U-Th Dating

Coral samples of 1 g were used for the Th-U isotope ratio analysis to ensure enough ^{230}Th was present for accurate measurements. A *Porites* sample (AC-1) from Huon Peninsula, Papua New Guinea was used as an internal laboratory standard to check for instrument reproducibility. This sample has been analysed an average of six times over the past two years and the age from this analysis was consistent with previous results. The coral samples were carefully cleaned and immersed in an ultrasonic bath for one hour to remove detrital material. Samples were wetted with HNO_3 until samples were completely dissolved and spiked with a ^{229}Th/^{233}U mix, to produce the desired ratio of ^{233}U/^{235}U of ~ 0.2. Samples were evaporated to a minimum volume of <0.5 ml and H_2O_2 was added to remove organic material, each sample was redissolved in 2N HNO_3 for TRU ion exchange columns (Luo et al. 1997).

For the chemical separation of U and Th from carbonate matrices, the chemical procedures of Luo et al. (1997) were applied and further developed as described by McCulloch & Mortimer (in press). Uranium and Th were collected separately from TRU.spec ion exchange medium, Th in 0.1M HCl + 0.1M HF, and U in 0.1M HCl + 0.3M HF. Both fractions were evaporated and separately re-dissolved in 1 ml 2% HNO_3. An aliquot from the U fraction was added to the Th fraction, and diluted to 2 ml to yield a ~30 ppb Uδ solution for Th analysis. An aliquot from the U fraction was diluted to 2 ml to yield a ~30 ppb U solution for U analysis.

Mass spectrometry

U/Th dating has been established for decades using thermal ionisation mass spectrometry (TIMS), however, recent advances have improved the precision of dates using MC-ICP-MS. Multi-collector ICP-MS offers greater precision in measurements with a reduced sample size when compared with TIMS (Seth et al. 2003). This feature of MC-ICP-MS allows lower concentrations of U to be measured, extending U-Th dating to modern corals such as those in this study.

The U and Th solutions were aspirated separately into the plasma of a Finnigan Neptune multi-collector ICP-MS system using an APEX desolvator fitted with a Teflon PFA flow path and a low-flow Teflon PFA nebuliser operating at ~100 microlitre per minute uptake. The Neptune MC-ICP-MS is equipped with nine moveable Faraday cups and one central secondary electron multiplier (SEM), deployed by navigating the ion beam from the central Faraday cup (Eggins et al. 2005). Amplifier gains and electronic baselines were only measured at start of the day, because they were shown to be stable over a 24 hour period. U and Th measurements were performed separately. Blank subtractions were determined by preceding blank HNO_3 analysis. Washout was facilitated by HNO_3+HF and Triton surfactant.

The retarding potential quadrupole lens (RPQ) was not utilised for U measurements because the SEM/Faraday gain was not stable with RPQ filter engaged. However, the

^{238}U tailing is significant without the RPQ lens. (I) 234.5 in SEM, (II) ^{238}U, ^{235}U and ^{233}U and ^{232}Th were measured in Faraday cups at the same time as ^{234}U in SEM, (III) 233.5 in SEM. Tail from ^{238}U was subtracted from ^{234}U by linear interpolation between 234.5 and 233.5. SEM/FAR gain was calculated by linear interpolation between repeat SRM 960 U measurements to bracket the unknown samples. Mass fractionation for both U and Th isotopes was corrected using the Step (II) ^{238}U/^{235}U ratio. U concentrations were calculated based on isotope dilution measurements of ^{233}U/^{235}U and delta ^{234}U that were calculated after adjustment for SEM gain.

The RPQ lens was utilised to minimise the ^{238}U (and occasionally ^{232}Th) tailing, and the ^{230}Th analytical protocol employed being independent of SEM/Faraday gain. (I) ^{238}U, ^{235}U and ^{233}U and ^{232}Th were measured in Faraday cups at the same time as ^{234}U in SEM, (II) ^{230}Th in SEM and ^{238}U in Faraday cup; (III) ^{229}Th in SEM and ^{238}U in Faraday cup, (IV) 229.4 in SEM. Mass fractionation for both U and Th isotopes was corrected using the Step (I) ^{238}U/^{235}U ratio. The ^{230}Th/^{229}Th ratio was calculated by dividing the Step II ^{230}Th/^{238}U ratio by the Step III ^{229}Th/^{238}U ratio. ^{232}Th/^{229}Th was calculated by dividing Step (I) ^{232}Th/^{238}U by Step (III) ^{229}Th/^{238}U. SEM backgrounds at ^{230}Th and ^{229}Th, due to tailing from ^{238}U (and/or ^{232}Th) were determined from the 229.4 measurement. A scan on the SEM of the mass region 228 to 235 was performed to assess the contribution of potential near-isobars at ~229.8, often accompanied by ~230.8.

Results

Skeletal structural variability and density bands

Broad morphological variation was observed between colonies collected from rocky reefs in water depths of 3-21 m in Spencer Gulf (SG) and Gulf St. Vincent (GSV), South Australia. There was high diversity in corallite shape between corals in SG (Figure 4.2), GSV and Dutton Bay. Architectural components were better defined in the colonies with higher density (Figure 4.2: d-f). The depth of the tissue zone was similar (~4 mm) for all corals examined.

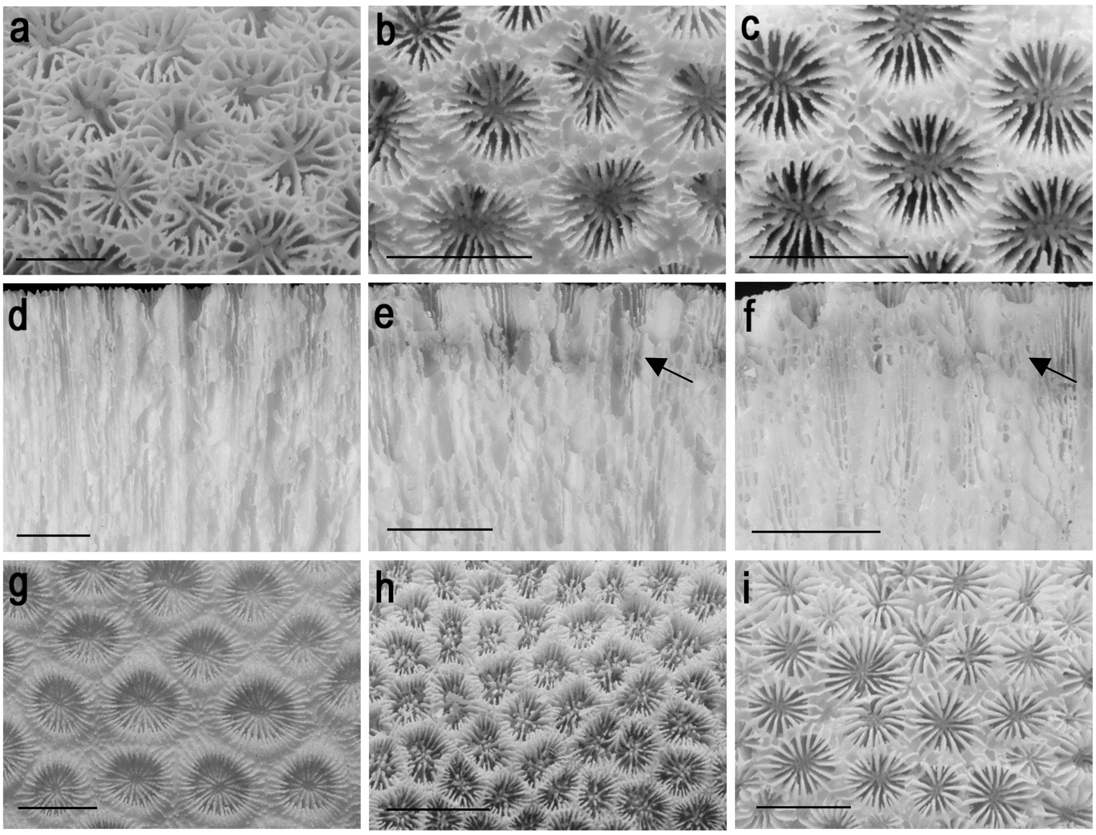

Figure 4.2: Photographs of morphological variation in corallite structure from different reefs in South Australian gulfs. Collection sites are (a), (d) Troubridge colony GSV; (b), (e) Seacliff colony B GVS; (c), (f) Seacliff colony A; (g) Broken Bottom Reef, GSV (h) Whyalla colony SG (i) Dutton Bay colony. Scale bar = 5 mm for all photographs. Differences in corallite structure can be observed in (a-c) and (g-i) with the thickness of the corallite wall (theca) and also the septa. (e) and (f) indicate the depth of the tissue zone (arrow) and (d–f) indicate the increasing clarity of skeletal elements with increasing density of the coral skeleton. (f) Dissepiments and theca are pronounced compared with (d-e)

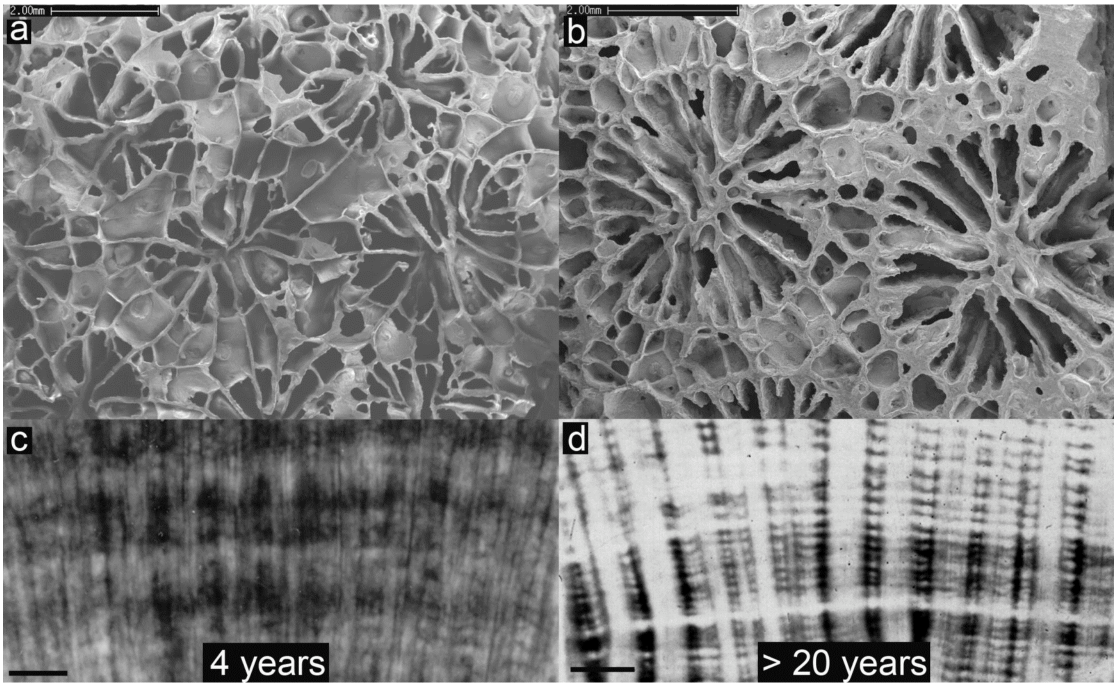

Figure 4.3: Scanning electron micrographs of Troubridge colony (a) and Seacliff A (b) scale bars = 2 mm. X-radiographs of low-density/high growth rate coral (c); and high density/low growth rate coral (d). Scale bars for c and d = 5 mm.

The different colonies were examined under scanning electron microscope (Figure 4.3 a-b) to determine the differences in density and calcification. The low-density corals have a more fibrous skeleton with no columella and thin theca walls, whereas the high density corals have well-established theca walls. The high density skeleton was observed to be primary aragonite due to the crystal structure observed under scanning electron microscopy (SEM), not thickening from accretion of secondary aragonite. Due to the varying morphology and density of each colony, the X-rays were highly variable (Figure 4.3 c-d).

The core lengths varied between 280–740mm and band chronology derived from the X-rays is summarised in Table 4.1. Age of the coral cores was determined by three counts (following corallite walls down different parts of the X-ray), these counts were then averaged, and age of the core was divided by the length of the core to establish a mean annual extension rate. Mean extension for the six colonies (Figure 4.4) varied between 1-8 mm yr^{-1}. Replicates from the same coral colony (cores extracted in 2003 and 2005) are not shown here. The last band accreted before core collection at the end of summer/autumn was a low-density band.

Table 4.1: Ages derived from density band counting (average of 3 counts) and the mean annual extension rate per core.

Coral specimen	*Height of colony (mm)*	*Length of core (mm)*	*Ave of 3 x-ray counts*	*Mean ext from x-ray (mm)*
Seacliff A03	1500	166	112 ± 4	1.5
Seacliff A05	1500	650	324 ± 6	2
Seacliff B03	1600	480	94 ± 2	5
Seacliff B05	1600	630	108 ± 3	5.8
Edithburgh 03	280	280	130 ± 4	2.1
Troubridge 03	1700	490	74 ± 3	6.9
Troubridge 05	1700	700	89 ± 3	7.8
Taylors Island 03	245	245	143 ± 4	2

There was interannual variation in extension rate within each core and a high level of variability between colonies from the same reef (Figure 4.4 b and d) and different parts of the gulfs. There was no depth-dependent growth rate observed between different colonies, as coral Seacliff B had a mean growth rate of 6 mm yr^{-1} (Figure 4.4b) (ranging 4–9 mm yr^{-1}) and coral Seacliff A (Figure 4.4d), averaged 2 mm yr^{-1}, (ranging 1–5 mm yr^{-1}). The deepest corals collected near Taylors Island (at 22-24 m) were living in a marginal environment, with both corals scarred from boring barnacles. Coral Taylors Island B03 (Figure 4.4f) had rolled, most likely in a large storm, evident by the loss of vertical growth axis in the X-ray. (~ 85 years ago from x-ray chronology).

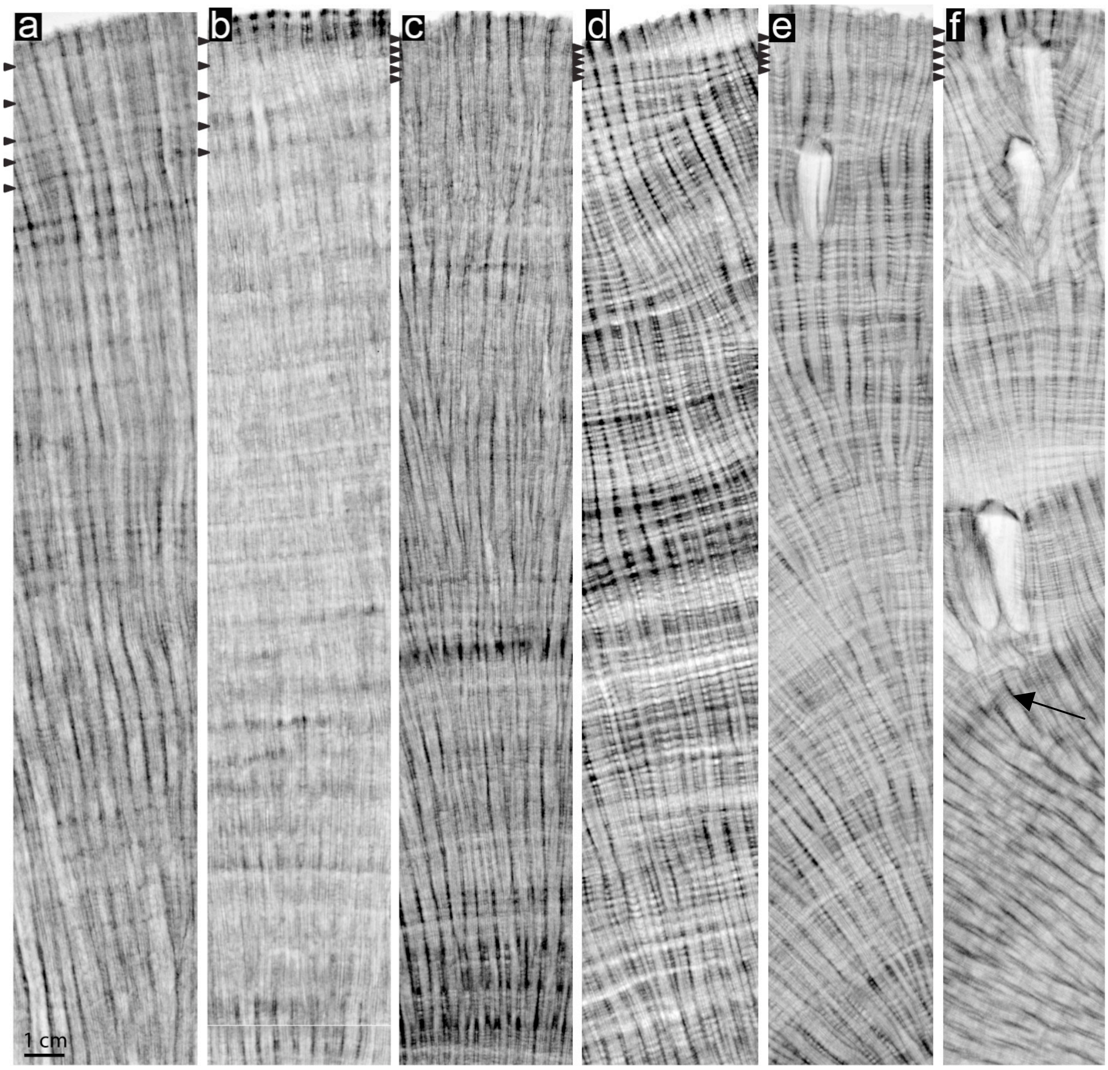

Figure 4.4: X-radiographs of (a) Troubridge; (b) Seacliff B; (c) Edithburgh; (d) Seacliff A; (e) Taylors Island A; and (f) Taylor's Island B. Annual extension rate indicated by black arrows decrease from (a)-(f) as corals grow in less optimal environments., including loss of primary growth axis in (f) (arrow) Horizontal scale is 40 mm per core. Only the top 220 mm of cores is shown for comparison purposes.

Luminescent banding and skeletal architecture

Luminescent bands were present in only one colony Seacliff B, and were associated with the high density winter bands. These luminescent bands were a light blue colour, with a wavelength emission in the UV range. Other cores displayed irregular, faint luminescent lines and were not considered to provide chronological information. The strength of the luminescence varied between years in Seacliff B with the strongest band recorded in 1982 (a severe El Niño year) and luminescent band frequency increased since the 1970s. The luminescent bands in Seacliff B indicate the mechanism of coral growth, reflecting the shape of the coral polyp in individual calices, with the theca calcified at a different time to the basal plate (Figure 4.5). The nearby slow growing coral Seacliff A, only displayed faint luminescent bands and had a growth hiatus possible due to boring organisms (Figure 4.5). The slow growing, denser coral, indicates the variation in the 'z direction' exposing different coral calices even though the core was collected on the primary growth axis. Whereas, in the fast growing coral (Seacliff B), there is little definition between the septal region and corallite wall (theca) region in the skeletal architecture.

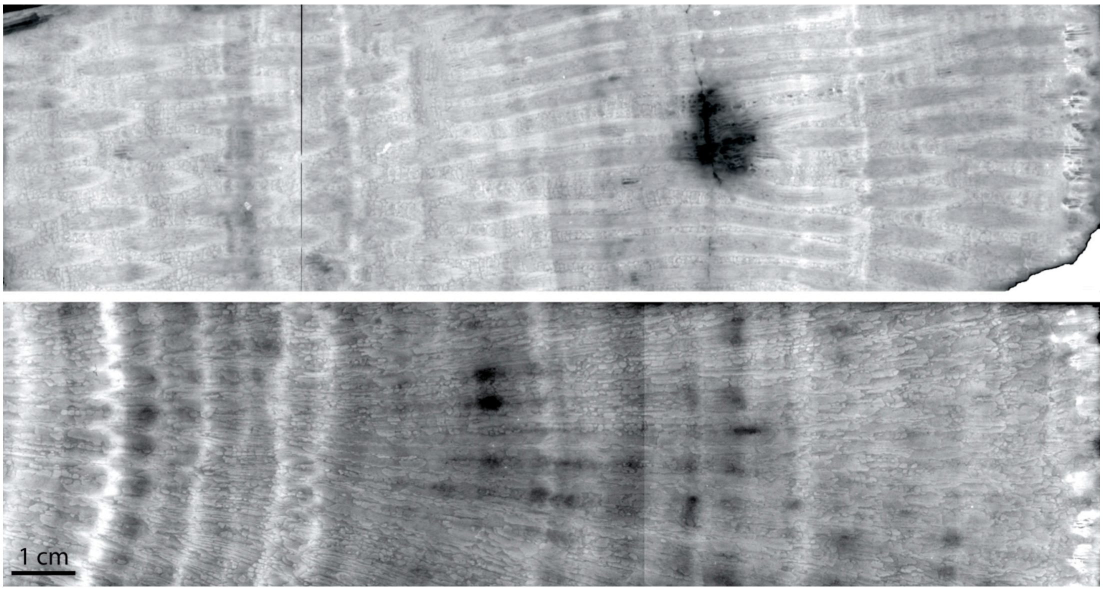

Figure 4.5: Photographs of Seacliff A (top) and Seacliff B (bottom) taken under black fluorescent lamps to indicate luminescent banding. The tissue zone indicates strong luminescence in both corals. Seacliff A has a growth hiatus in the middle of the core, possibly due to boring organisms. The Seacliff A image was overexposed to display skeletal architecture and does not represent true luminescent banding.

U/Th analyses

The eleven coral samples dated using U/Th measurements analysed on the MC-ICP-MS returned dates of colonies between 105-381 years (Table 4.2). Samples were taken at the base of the 2003 cores for Seacliff A, Seacliff B, Edithburgh and Troubridge, further samples were taken from the 2005 cores at the end of the core or the point where the vertical growth axis was lost due to the coral turning or rolling. These samples were taken to obtain dates of a known position within the coral cores and establish the temporal veracity of the density bands.

Table 4.2: U/Th dates for four corals from Gulf St. Vincent and one coral from Spencer Gulf.

Specimen	***Sample distance (mm)***	***U (ppm)***	***230Th (ppt)***	***[230Th/238U] ± 2σ***	***[230Th/ 232Th]***	***Initial Delta 234U ± 2σ***	***Age (yr) ± 2σ***	***Detrital corrected U/Th age(*)***
Seacliff A 2003	160	2.6	0.06	0.00135 ± 0.00003	39	145.3 ± 1.1	129 ± 2	125 ± 6
Seacliff A 2005	325	2.4	0.09	0.00217 ± 0.00002	90	148.11 ± 0.8	206 ± 2	204 ± 5
Seacliff A 2005 (t)	410	2.6	0.17	0.00401 ± 0.00004	9	147.61 ± 1.1	381 ± 3	337 ± 28
Seacliff B 2003	500	2.1	0.03	0.00095 ± 0.00002	13	146.8 ± 1.4	90 ± 2	83 ± 8
Seacliff B 2003 (2)	500	2.2	0.04	0.00110 ± 0.00002	14	147.4 ± 2.1	105 ± 2	97 ± 8
Seacliff B 2005 (t)	560	2.3	0.05	0.00126 ± 0.00002	11	148.7 ± 0.7	120 ± 2	108 ± 10
Edithburgh 2003	275	2.9	0.03	0.00173 ± 0.00002	5	149.1 ± 0.7	164 ± 2	130 ± 21
Troubridge 2003	470	2.4	0.03	0.00073 ± 0.00002	58	149.7 ± 0.8	69 ± 2	68 ± 4
Troubridge 2003 (2)	480	2.3	0.05	0.00079 ± 0.00002	72	147.2 ± 1.4	75 ± 2	74 ± 4
Troubridge 2005 (t)	600	2.2	0.07	0.00110 ± 0.00002	86	145.1 ± 1.4	105 ± 3	109 ± 9
Taylors Island 2003	245	2.8	0.08	0.00159 ± 0.00003	83	146.5 ± 0.9	151 ± 2	149 ± 5

(2) Replicate sample from same core location

(t) Vertical growth axis was lost due to coral turning

(*) The following equation was used:

$[^{230}Th_{rad}/^{238}U] = [^{230}Th_{meas}/^{238}U] - [^{232}Th/^{238}U]\ [^{230}Th_{nr}/^{232}Th]\ \exp[-\lambda_{230}T]$

to determine the non-radiogenic ^{230}Th component ($^{230}Th_{rad}$) assuming $[^{230}Th_{nr}/^{232}Th] = 1 \pm 1$, making a conservative assumption of ±100% uncertainty in the correction

The initial delta ^{234}U was consistent with present day open-system seawater U values (Thompson & Goldstein 2005). Therefore, there was no indication of unusual seawater U concentrations or contamination issues in Gulf St. Vincent and Spencer Gulf. The ^{230}Th was minimal indicating that there was no issue with contamination from older Th samples. The corals used in this study were not subject to higher oceanic values of ^{230}Th which complicated the dating of deep-sea corals using this technique (Cheng et al. 2000).

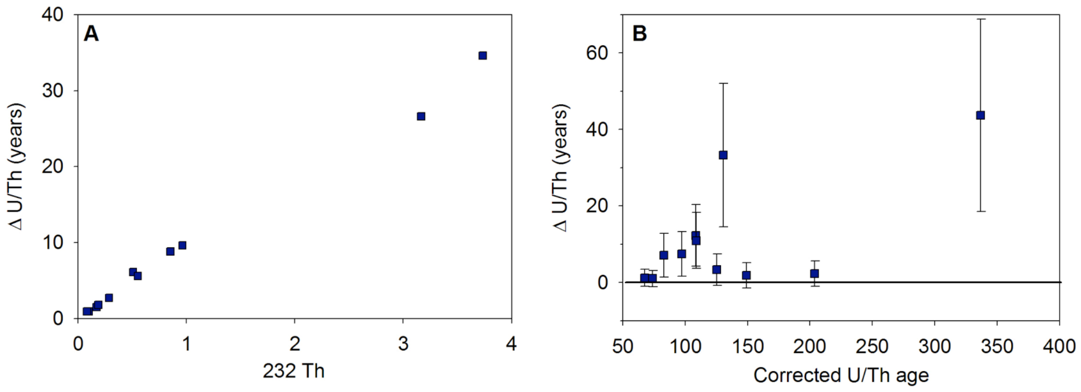

Figure 4.6: Change in the U/Th ages (ΔU/Th) after the correction for initial non-radiogenic ^{230}Th. (a) Higher amounts of ^{232}Th indicate the greatest age offset between corrected and non-corrected ages. The observed linear relationship in Figure 4.6A is due to the correction equation. (b) Distribution of non-radiogenic detrital corrections and error bars associated with the [$^{230}Th_{nr}/^{232}Th$] =1±1 assumption.

To assess the variability in the inherited [$^{230}Th_{non\ radiogenic}/^{232}Th$], we calculated the value of [$^{230}Th_{nr}/^{232}Th$] required to account for the difference between the detrital-corrected age and the age measured in the coral (after blank correction). The [$^{230}Th_{nr}/^{232}Th$] ratios range from 4.8 to 0.22 and do not correlate with concentration of ^{232}Th. We have corrected $^{230}Th_{rad}$ assuming [$^{230}Th_{nr}/^{232}Th$] =1±1, making the conservative assumption of ±100% uncertainty in the correction. The effect of inherited $^{230}Th_{nr}$ on the ages is shown in Figure 4.6 in a plot of the difference between the corrected age and the detrital contaminated age. The sample most sensitive to the correction is the oldest sample Seacliff A05 which has a concentration of ^{232}Th (3.73 ppb) and Edithburgh 03 (^{232}Th 3.17 ppb), resulting in a substantial age uncertainty of ± 33-43 years, or over ten times the blank corrected analytical error. However, for the majority of samples, with much lower ^{232}Th (i.e. < 1 ppb), the additional uncertainty introduced from ^{230}Th$_{nr}$ is approximately ± 2-3 years, of similar extent to the age uncertainty with blank corrections only. More rigorous procedures to exclude inherited ^{230}Th$_{nr}$ and the associated ^{232}Th would be necessary if precision at the sub-annual level was to be achieved.

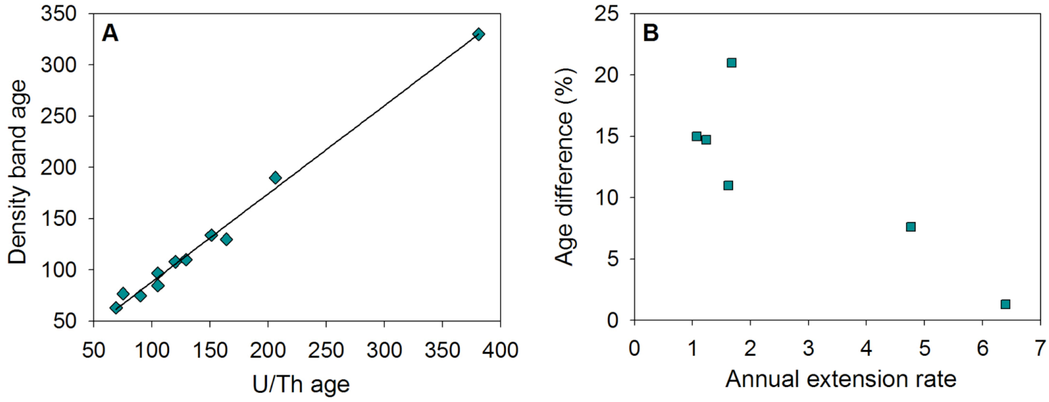

Figure 4.7:(a): Correlation regression of U/Th dates compared with density band ages, $r^2 = 0.98$, $p < 0.005$; (b) Comparison of annual extension rate with the percentage difference between the two age methods.

The U/Th dates were compared with the density band ages generated from x-rays (Figure 4.7a) and there was an overall underestimation of age via the band counting technique. A regression of the two different techniques provided a high correlation of $r^2 = 0.98$, $p < 0.001$. The underestimation of ages with the x-ray chronology technique of 2-19% depended on the annual growth rate of the colony, i.e. there was a lower accuracy with the denser, slow growing corals using the counting chronology technique (Figure 4.7b). However, for *Plesiastrea versipora* colonies with a moderate extension rate (> 3 mm) assigning chronology from x-rays was all within error of the U/Th analyses.

Discussion

During collection of *Plesiastrea versipora* core samples, a large variation in density between colonies was observed. The most conspicuous example of density variation was at Seacliff reef (GSV) where the two cores were collected < 5 m apart. Skeletal structure of one colony was fragile with thin septa and theca (Figure 4.3a), taking less than 10 min to drill 500 mm, whereas the second colony had a greater density and was difficult to drill using pneumatic equipment (> 1 hour for 500 mm core). There was a measurable difference in the thickness of interstitial aragonite (between corallites) between the two colonies, yet the environmental conditions for the two colonies are very similar.

Other workers have noted that density increases with water depth were related to increases in the spacing of polyps, that is, fewer polyps per unit area of the coral surface (Hughes & Jackson 1980). This study sees no correlation between numbers of polyps per unit area and bulk density, bandwidth or onshore offshore environmental trend. Under scanning electron microscopic examination there are striking physical differences in the robustness of skeletal elements between dense, high hydraulic energy setting corals and delicate less dense sheltered setting corals.

The Troubridge sample was the fastest growing colony at 105 ± 3 years for a 560 mm core, this coral would be considered to be living in ideal growing conditions, with relatively high light intensities (4 m water depth), and high nutrient potential, located on a sand bar towards the middle of Gulf St. Vincent. The next youngest core was the Seacliff B coral at 120 ± 2 years for a 540 mm core. As the density of the coral increases and the associated extension rate decreases using x-rays alone to establish a coral chronology becomes less accurate.

Although there was a high correlation between density bands ages and U/Th ages, the chronology derived from density band counting underestimated the age of corals, especially in colonies growing at less than 3 mm per year. Once growth bands become narrow there is not enough differentiation in the x-rays to determine the annual band couplets and years may not be recorded accurately in all parts of the colony. This led to a greater error between the U/Th dates and the density band chronology in the slow growing colonies of up to nineteen percent.

A comparison was made between four of the coral colonies to determine whether individual colonies responded to the same environmental conditions regardless of their growth rate (Figure 4.8). There was very little similarity in the average growth rate between the corals even on the same reef (Seacliff). Even during years when the temperature in South Australia was warmer in summer coinciding with El Niño events, the corals did not respond with increased extension rate.

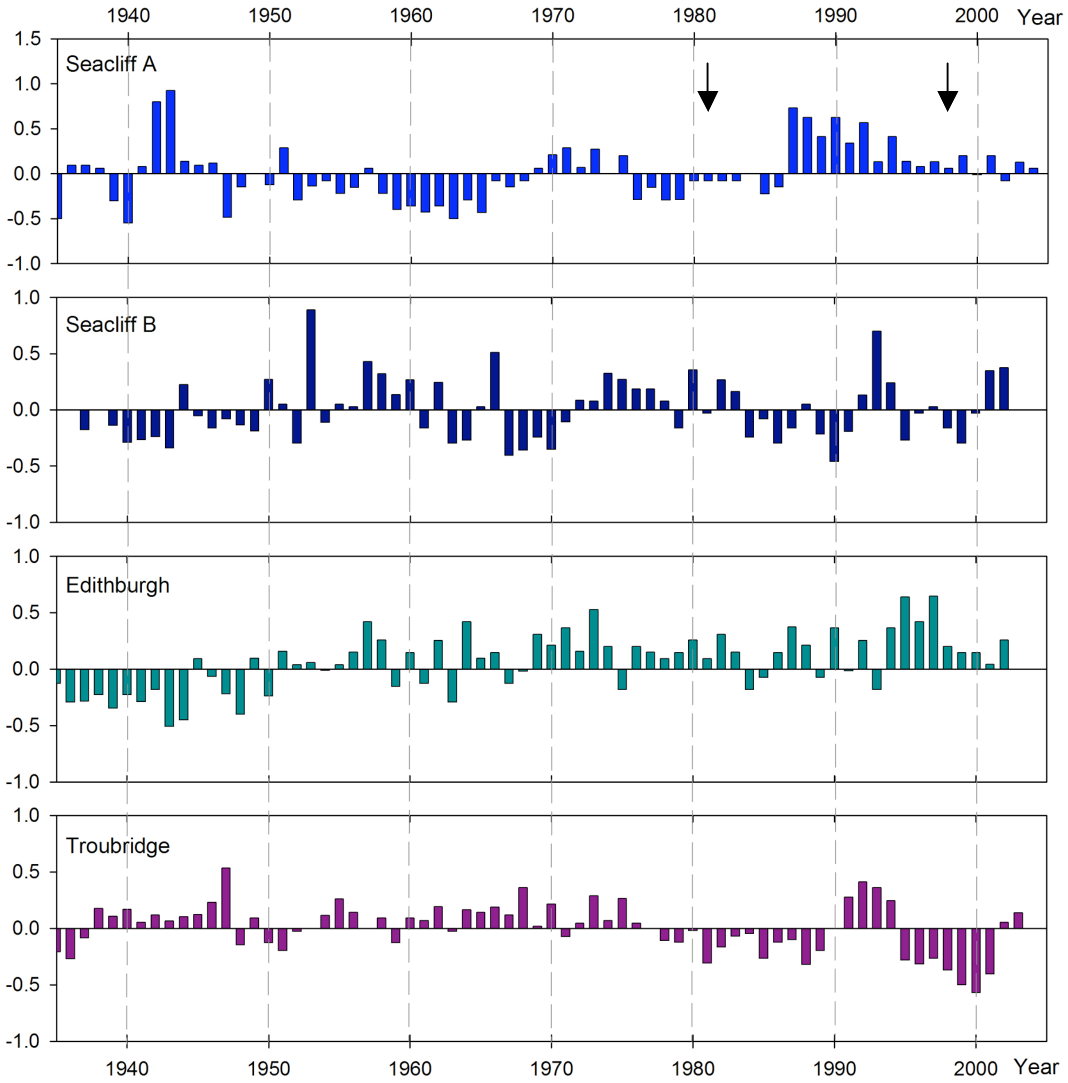

Figure 4.8: Variation about the colony specific mean extension rate for four corals (Seacliff A & B, Edithburgh and Troubridge) for the common period 1935-2003. Y axis units are the standard deviation for mean growth for each coral colony. Black arrows indicate strong El Niño events, however there is no correlation in coral mean annual growth with these events.

The Seacliff B coral is located on a metropolitan reef off the coast of Adelaide (pop: > 1,000,000) and may be influenced by local rivers (Onkaparinga and Torrens Rivers), which, although they have restricted flows and form water reservoirs, are likely to reflect the higher rainfall and terrestrial runoff (storm water) in winter. The luminescence bands may not be present in Seacliff A coral due to the slow growth rate, with the tissue zone acting as a smoothing function on the annual extension rate, effectively mitigating any periodic or infrequent temporal event.

Annual cycles in light and temperature are the most commonly proposed causative signals of annual density bands in massive corals (Barnes & Lough 1993). Seasonal changes in irradiance are greater at high latitudes than at the equator with light intensities reaching the corals being substantially reduced (Kevin & Hudson 1979; Kleypas et al. 1999). Populations of *Plesiastrea versipora* in high latitudes are exposed to highly fluctuating temperature and irradiance regimes varying by over 50% annually. Tropical coral species such as *Porites* can grow in high-latitude locations with winter minimums lower than 18˚C, but were surviving in this marginal environment by including a growth hiatus during the winter minimum temperatures (Fallon et al. 1999). However, *P. versipora* does not exhibit a growth hiatus during the winter temperature minimum albeit calcification rates slow during this period (Howe & Marshall 2002). Calcification rates in *Plesiastrea versipora* are considerably lower than in reef corals but indicate a similar pattern in temperature responses with a trend towards higher rates of calcification at approximately 18°C (Howe & Marshall 2002). Increased seasonality at high latitudes may result in a lower annual carbonate production, due to an abbreviated growing season with calcification/extension rates reduced during winter.

Plesiastrea versipora may be able to adapt to a range of environmental conditions by associating with symbionts with differing physiology adapted to particular latitudes, densities of these symbionts were amongst the highest reported in the literature (Rodriguez-Lanetty 2001). The growth rates of *P. versipora* determined during this study are among the slowest reported for hermatypic corals and the high-density colony growth rates of (~1 mm yr^{-1}) are comparable with deep-sea corals such as *Lophelia pertusa* (Mortensen & Rapp 1998) and *Desmophyllum dianthus* (Lazier et al. 1999).

The three larger colonies; Seacliff A, Seacliff B and Troubridge had also rolled, potentially during large storm events at separate times. Cores were not taken through the entire colonies since coring was stopped when it became obvious that the core was no longer aligned along the vertical growth axis. The high frequency of over turned corals in this study (4 corals), may be due to the colony size outgrowing the initial coral settlement on small shells or rocks and becoming unstable during large disturbances. Usual habitat for these corals included low rocky reef with a mixed algal/seagrass facies and a large amount of unconsolidated material. In comparison, tropical corals settling on stable calcareous reef platforms. To accurately assign a chronology for dense colonies with a lower extension rate, whole colonies would provide greater accuracy than bands from a core sample which were not always distinctive.

Summary

The ages derived from counting annual density bands and X-ray chronologies made it difficult to distinguish an accurate chronology for each coral especially for colonies with growth rates of < 3mm yr^{-1}. Density band width varied between neighbouring colonies on the same reef as well as between Gulf St. Vincent and Spencer Gulf. U/Th dating from MC-ICP-MS analyses provides a high-precision chemical technique to assess the annual nature of density bands and establish chronology in this coral. Using a second method to verify coral chronologies with low growth rates such as U/Th ages indicated that the X-rays varied from an 81-97% accuracy of annual extension for *Plesiastrea versipora*. Caution must be used when assigning chronologies to other high-latitude or cooler-environment corals with variable growth rates. Furthermore, using density and luminescent bands alone may not be a robust enough technique to determine changes in the environmental conditions impacting coral growth and extension rates.

The two aging techniques determined that *Plesiastrea versipora* deposits annual density bands. Therefore *P. versipora* has the potential to record environmental information in the annual layers of its skeleton and produce a paleoenvironmental archive for temperate-latitude environments where other high resolution archives do not occur.

Due to the large density variation occurring in neighbouring corals on the same reef, the extension rate is unlikely to be driven by environmental conditions. Possible hypotheses for explaining the extension rate differences between the Seacliff corals may include: genetic variation; different concentrations of zooxanthellae; different sub-species of zooxanthellae; or a different reliance on autotrophic versus heterotrophic feeding.

The colonies of *Plesiastrea versipora* examined in this study lived for several centuries and may be important in the local ecosystems of the South Australian gulfs. Coral abundance has been reduced in the last 40 years due to benthic trawling of soft sediment regions for prawn fisheries. Therefore, it is unknown if the loss of these long lived colonies has a detrimental effect to other facets of the marine ecosystem.

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Chapter 5:

Evaluating the Use of *Plesiastrea versipora* as a New Coral Archive of Temperate Paleoclimate

Chapter 5: Evaluating the use of *Plesiastrea versipora* as a new coral archive of temperate paleoclimate

Introduction

There is a general lack of long-term, high resolution records of past oceanic and climatic conditions in temperate latitudes of the Southern Hemisphere. Instrumental records only date back to the early 1900s for most locations. Some commonly used proxy records for temperate latitudes in the Australasian region include: speleothems (Treble et al. 2003; McDonald et al. 2004; Treble et al. 2005; Desmarchelier et al. 2006), tree rings (Cook 1995; D'Arrigo et al. 1996; Cook et al. 2000; Pearson et al. 2001), lake (Kotwicki & Allan 1998; Johnson et al. 1999; Magee et al. 2004; Gell et al. 2005; Johnson et al. 2005) and deep-sea sediment cores (Charles & Fairbanks 1992; Oppo & Rosenthal 1994; Goldstein et al. 2001; King & Howard 2004). However, these proxy archives are often at centennial-millennial scale or only represent part of the seasonal cycle (e.g. warm growing months for tree rings). Moreover, deep-sea sediment cores predominantly reflect the continental shelf environment which may be more stable than coastal sites over timescales of decades to centuries. New proxies from long-lived corals growing in temperate waters offer the opportunity to produce high-resolution geochemical records from the entire annual signal that may extend instrumental archives by several hundred years.

The chemistry of coral aragonitic skeletons has proved to be a useful tool in reconstructing various features of the ocean-atmosphere coupled system including sea-surface temperature (SST), sea-surface salinity (SSS), and nutrient cycling in seawater for example (Dunbar & Wellington 1981; Swart 1983; Wellington & Glynn 1983; Cole & Fairbanks 1990; Allison & Tudhope 1992; Shen et al. 1992; Urban et al. 2000; Montagna et al. 2006). Geochemical tracers can provide otherwise unavailable ground-truthed data needed to assess links between local climatic processes and global climate patterns. Seawater temperature has been linked to the relative concentrations of several elements incorporated into skeletal aragonite, including strontium, uranium, magnesium and boron (Smith et al. 1979; Mikkelsen et al. 1982; Beck et al. 1992; McCulloch et al. 1994; Min et al. 1995; Hart & Cohen 1996; McCulloch et al. 1996; Alibert & McCulloch 1997; Sinclair et al. 1998). Oceanic upwelling has been correlated with incorporation of barium and cadmium into the skeletal matrix (Lea et al. 1989; Shen et al. 1992; Druffel 1997). Barium has also been correlated with a terrestrial signature from flood plumes (Sinclair 1999; Alibert et al. 2003; McCulloch et al. 2003; Fleitmann et al. 2007). However, the mechanisms that control the incorporation of isotopes and trace elements into coral skeletons remain poorly understood. The incorporation of geochemical tracers is likely to be influenced by the ionic composition of the calcifying fluid, the calcification rate and water temperature (see Chapter 2 for further discussion). Many studies have established the advantages of analysing a suite of tracers from the same coral, allowing simultaneous determination of a range of environmental variables (Hendy et al. 2002; Quinn & Sampson 2002).

The scleractinian genus *Porites* has to date been the primary coral archive used to reconstruct paleoclimate, and is ideally suited to this task due to fast growth rates and ubiquitous nature in the tropics of the Pacific Ocean, Indian Ocean and Red Sea for example (Schneider & Smith 1982; Klein et al. 1993; Gagan et al. 1994; Kuhnert et al. 1999). *Porites* records are often temporally limited due to the size of the colonies to approximately 100-150 years (Boiseau et al. 1998; Linsley et al. 2000; Urban et al. 2000), however, some colonies can live for up to 300 years. This limitation in addressing climatic variability may be circumvented by stacking records (Hendy et al. 2002).

There have been several paleoclimate studies conducted using alternative coral genera including *Acropora* (Böhm et al. 2006; Gallup et al. 2006); *Diploastrea* (Watanabe et al. 2003; Bagnato et al. 2004); *Diploria* (Cardinal et al. 2001; Cohen et al. 2004; Goodkin et al. 2005; Hetzinger et al. 2006); *Montastrea* (Goreau 1977; Fairbanks & Dodge 1979; Leder et al. 1991; Swart et al. 2002; Watanabe et al. 2002; Reuer et al. 2003; Gischler & Oschmann 2005; Smith et al. 2006); *Pavona* (Shen et al. 1992; Wellington et al. 1996; Meibom et al. 2004); *Pocillopora* (Dunbar & Wellington 1981); *Siderastrea* (Guzman & Tudhope 1998; Reuer et al. 2003; Gischler & Oschmann 2005; Moses et al. 2006); *Solenastrea* (Swart et al. 1996a); and a high-latitude coral from the genus *Cladocora* (Silenzi et al. 2005; Montagna et al. 2007). Research with deep-sea corals for paleoclimate applications has included; *Desmophyllum* (Adkins 1998; Montagna et al. 2005; Montagna et al. 2006) and *Lophelia* (Mortensen & Rapp 1998; Spiro et al. 2000; Sinclair et al. 2006) and several other genera (Roark et al. 2005; Shirai et al. 2005).

This thesis provides the first geochemical investigation of *Plesiastrea versipora*, a long-lived massive coral with lower thermal tolerance, which enables it to live in cooler temperate latitudes. There have been several previous studies since the late 1970s on this species including aspects of its ecology, such as its: relationship with symbiotic zooxanthellae (Kevin & Hudson 1979; Rodriguez-Lanetty et al. 2001), phylogeography (Rodriguez-Lanetty 2001; Rodriguez-Lanetty & Hoegh-Guldberg 2002); metabolism and calcification (Howe & Marshall 2001; 2002) and nutritional status with the symbionts (Udy et al. 1993; Grant et al. 1998; Grant et al. 2003; Davy et al. 2006; Grant et al. 2006). However, much remains unknown about the ecology of this species including its reproductive ecology, plasticity in morphology and habitat preferences.

Aims

The objective of this chapter is to develop paleotemperature records including trace element (B/Ca, Mg/Ca, Sr/Ca, Ba/Ca U/Ca) and stable isotope ($\delta^{18}O$) proxies from *Plesiastrea versipora*. This coral species has not been evaluated as a paleoclimate archive before and no high resolution proxy records exist for the marine environment of southern Australia. The development of a new paleoclimate archive requires the establishment of a robust chronology (presented in Chapter 4) and an understanding of skeletal architecture as a basis for comparing temperature with geochemical records.

Further to this, the study aims to constrain the reproducibility of the SST seasonal cycle through multiple samples recorded by trace elements and to determine the growth rate dependent fractionation using corals with different annual extension rates. The SST proxy records contained within the temperate corals are compared to climate indices (such as the Southern Oscillation Index and Southern Annular Mode) to further constrain climate influences on this region.

Sampling and Analytical Methods

Regional Setting and Sampling

The coral sampling methods used in this thesis are described in Chapter 3 and 4. Coral cores were cut longitudinally into 7-8 mm slabs for X-ray and luminescence analysis to establish chronologies for each colony. Coral sections were X-rayed at a commercial X-ray medical facility, using an exposure of 55 kV and 5 mA for 15 sec with a Kodak CR500. Coral chronologies were established using a combination of the X-ray and U/Th dating techniques described in Chapter 4 and fine-tuned to SST proxy data generated by trace element analysis. Chronologies were established by correlating the high and low density bands with the maxima and minima SSTs and trace element/Ca minima and maxima respectively and linearly interpolating between these points.

Instrumental SST

The SST data used in this paper came from three sources. A fourteen year record (1992-2005) came from the jetty at Pt Stanvac, Gulf St Vincent (~ 5 km from Seacliff Reef), this was provided by the National Tidal Facility at Flinders University, now a component of the Australian Bureau of Meteorology (BOM). Two data loggers were placed *in situ* (next to the coral bommie) in May 2003 at Seacliff Reef and November 2003 at Troubridge Shoal, these loggers were collected in May 2005 and correlate well with the jetty SST data from the BOM. The IGOSS satellite-derived SST from 1° latitude (34.5°S and 35.5°S) x 1° longitude (139°E) grided cells (weekly from November 1981) was also compared with *in situ* data (Data source: http://iridl.ldeo.columbia.edu/SOURCES/.IGOSS/.nmc/.Reyn_SmithOIv2/.weekly/). The IGOSS data sets were not used for temperature calibrations as they did not correlate well with the SST data provided by BOM (Figure 5.1). The amplitude of the seasonal cycle in the IGOSS data is approximately 6°C, whereas the local temperature data set indicates a seasonal cycle with an amplitude of approximately 10-12°C displaying higher temperatures during known El Niño years (including 1998, 1999 and 2001). The IGOSS dataset indicates a variable seasonal amplitude during the length of the record and becomes more similar to the local temperature data from 1996 onwards. Therefore a 13 year temperature calibration dataset was used instead of the longer but less reliable satellite-derived data.

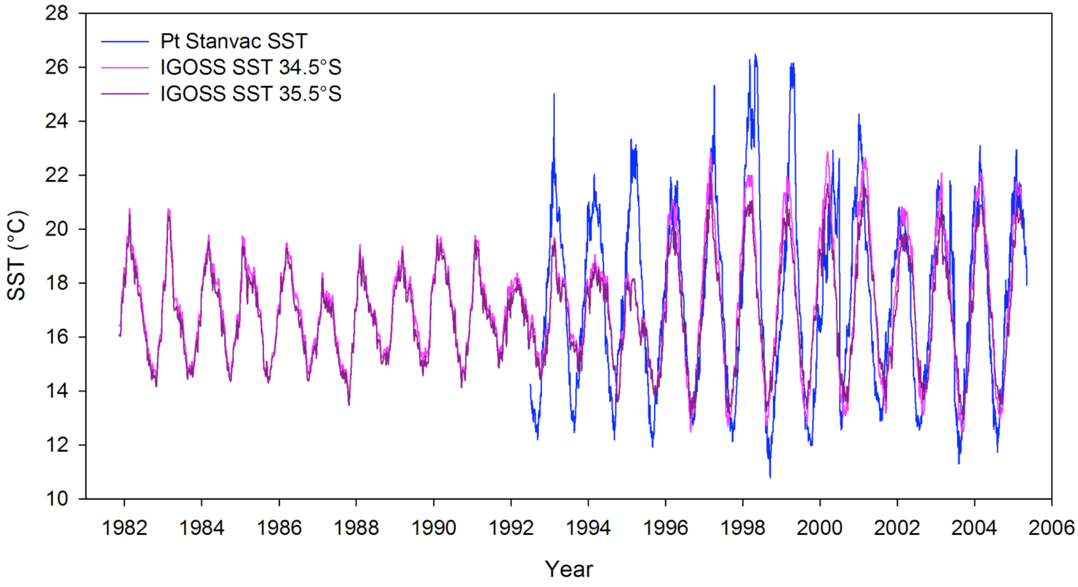

Figure 5.1: Comparison of IGOSS SST data with SST data from the National Tidal Facility at Port Stanvac.

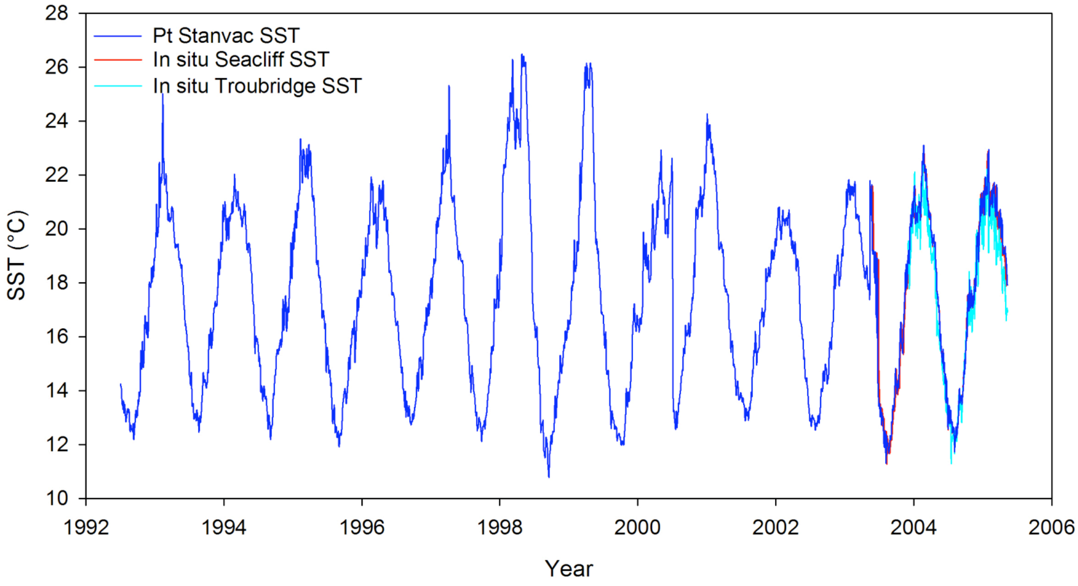

Figure 5.2: Comparison of SST data from Port Stanvac, with on site logger data from Seacliff Reef and Troubridge Shoals.

The fidelity of the *in situ* temperature records is displayed in Figure 5.2. The two logger records correlate very well with each other ($r^2 = 0.97$) and also with the jetty temperature record. There is greater temperature variability present in the summer maxima in the Troubridge shoals data than the Seacliff reef data because of the shallow depth of this site (4 m versus 14 m) with significant cooling occurring during the night.

Analytical Methods: Trace element LA-ICP-MS analysis

Laser ablation (LA) sampling requires very little sample preparation and allows rapid analysis of samples. Inductively coupled plasma mass spectrometry (ICP-MS) is able to simultaneously analyse a broad suite of trace elements with high sensitivity (Eggins et al. 1998; Sinclair et al. 1998). Therefore, LA-ICP-MS can be a valuable tool for extracting high-resolution environmental records from paleoclimate archives, specifically targeting seasonal variations such as upwelling and high-rainfall events that may be difficult to resolve using bulk sampling methods.

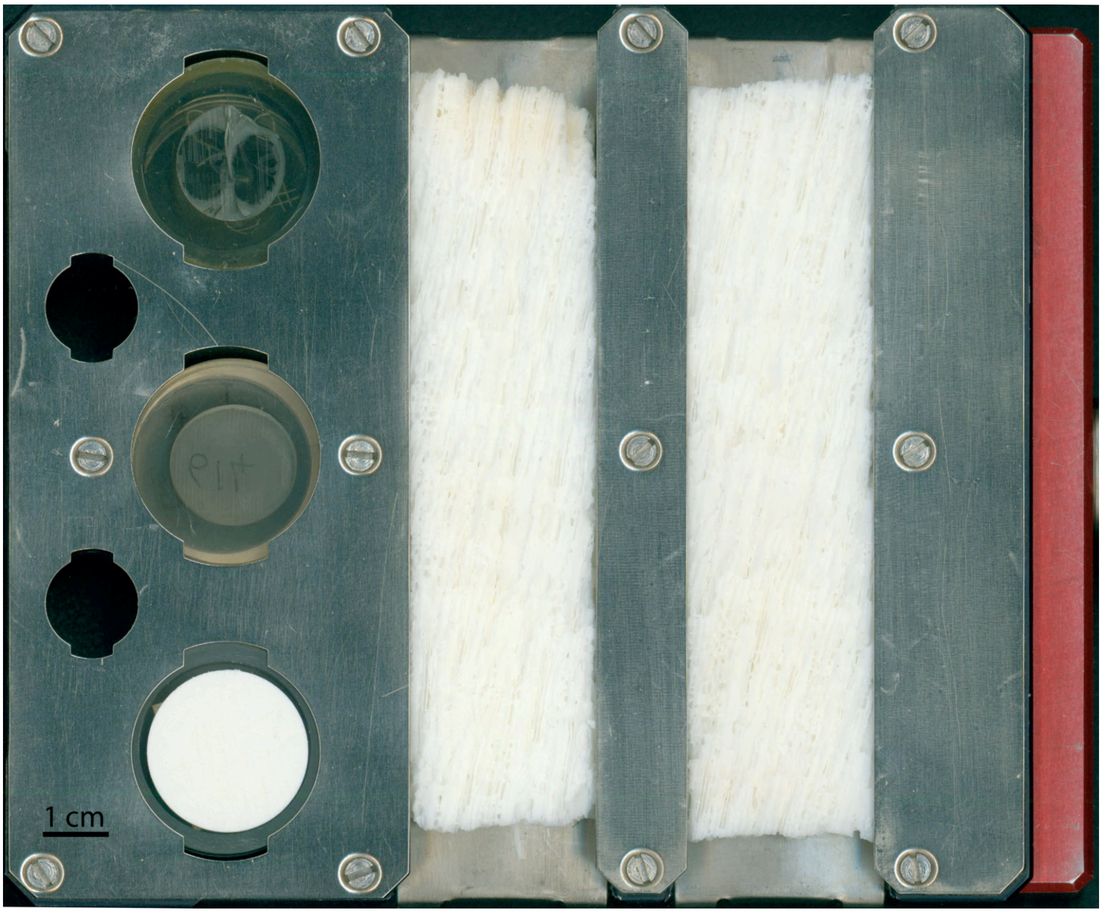

Figure 5.3: Laser cell containing two pieces of coral and the three standards, NIST 612 for calibrating the ICP-MS; NIST 614 for standardising the minor elements in the coral; CORAL – the *Porites* pressed powder in house coral standard from Davies Reef on the Great Barrier Reef and two pieces of Seacliff B05 coral – the top of the core and the second 90 mm piece.

Coral slabs were cut into smaller pieces (95 x 25 mm) parallel to the growth axis for laser ablation analysis and cleaned using a high-intensity ultra-sonic probe with ultrapurified 18 MΩ Milli-Q water. The probe was scanned slowly across the surface of the coral slab and the water renewed until no more carbonate particles were suspended. Two of the low density colonies (Seacliff and Troubridge) lost dissepiments and some septal material during probing, as observed when the cleaning method is applied to *Porites* (Gagan et al. 1994). These samples were also cleaned in an ultrasonic bath to dislodge other skeletal material from the large pore spaces in *Plesiastrea*. All samples were dried overnight in an oven at 35°C.

Coral samples were analysed using an ArF excimer laser (193 nm) with a sample cell (Eggins et al. 2005) connected to a VG Elemental PQ2 ICP-MS for analyses conducted in 2004/2005 and a Varian 820 ICP-MS for analyses conducted in 2006. Coral samples were loaded into the sample cell with three standards, two NIST glasses and a coral pressed-powder in-house standard (Figure 5.3). Three preablation scans were conducted at a frequency of 10 Hz, and energy of 50 mJ. The sample was scanned at a rate of 40 μm s^{-1} with the laser masked to produce a 50 x 500 μm rectangle to ensure the surface of the coral was very clean before sample collection. Samples were preablated using a larger masking slit (than sample collection) and the ablated material transported in a mixed stream of He and Ar to the ICP-MS (Eggins et al. 1998).

Sample sections were initially moved under the laser using analytical techniques designed for *Porites* and outlined in (Sinclair 1999; Fallon 2000) with a masking slit size of 200 μm x 50 μm at 5 Hz and 50 mJ for continuous profiling. However, due to the heterogeneity of the analyses a larger slit (to sample more architectural elements) was evaluated. Due to the larger calice size, compared with *Porites* and lack of columellar, compared with other large calice species such as *Diploastrea*, analysing different architectural components was unavoidable. Due to the architectural differences between *Porites* and *Plesiastrea*, analysis was trialled with several different masking slit and spot sizes. The rectangular slit was preferred over the spot to enable an average ablation over a larger area of coral skeleton (Figure 5.4). Smaller spot sizes were evaluated but these produced a high level of heterogeneity in the element analysis. Various operating conditions were evaluated (including both spot size and laser pulse rate) to establish a balance between spatial resolution, count rate and reproducibility. A traverse of the coral sample was mapped out using a 'chain of points' to follow a particular growth element and reduce the variation of skeletal architecture in the laser pathway (Figure 5.4). It was determined that ablating predominantly thecal material produced greater reproducibility than ablating septal material, where more three-dimensional heterogeneity was present. The trace element analysis was conducted parallel to the growth axis and scanned at a rate of 20 µm s^{-1}. Approximately 4 ml min^{-1} He was included in the cell gas mixture to increase sensitivity, reduce oxide production and elemental fractionation (Eggins et al. 1998).

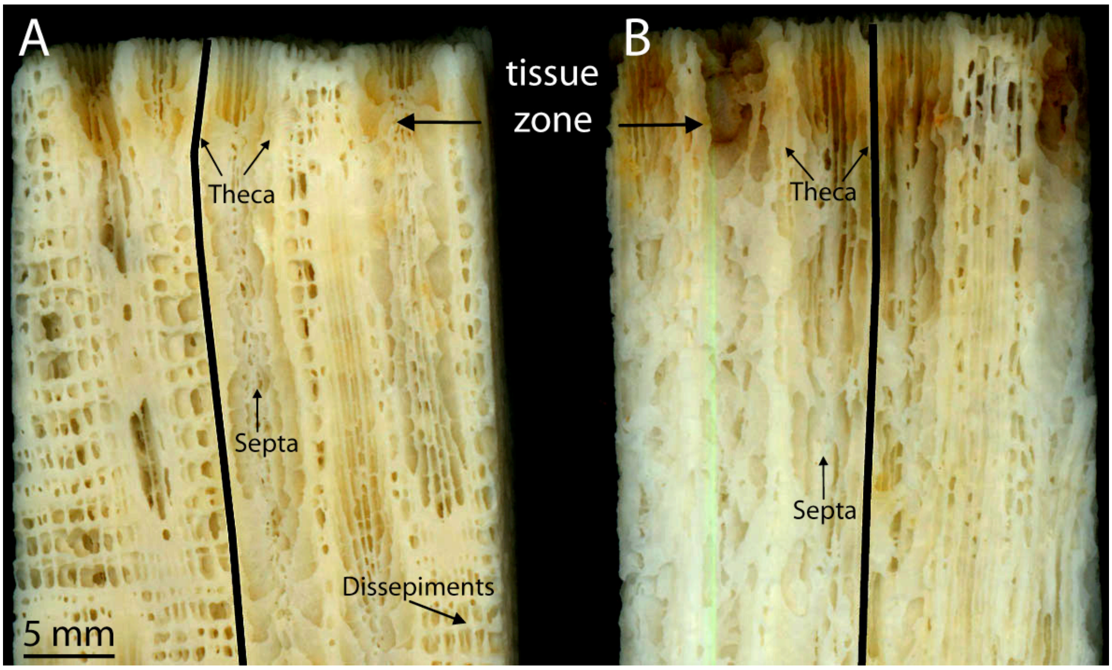

Figure 5.4: Magnified view of the upper portion of two pieces of coral with the lowest and highest extension rates (A) Seacliff A; (B) Troubridge. The tissue zone is the same depth 4 mm in both corals. Architectural components septa and theca are labelled; laser tracks were mostly confined to the theca as the septal region indicated greater variability in analyses. Black rectangle indicates size of sample ablation and track down corallite. Scale bar is 5 mm.

The major elements (B, Mg, Sr, Ba, U) were analysed during two traverses of the coral piece to ensure no analytical drift. The final laser conditions ablated a 40 x 400 μm rectangle on the sample at a rate of 5 Hz and energy of 50 mJ. Two analyses for minor elements were conducted at 10 Hz and 50 mJ after the ICP-MS had been conditioned for several hours to reduce contamination in the instrumental background concnetrations. Isotope backgrounds and standards were measured before and after sample analysis to correct for instrument drift. The atomic masses monitored during analysis included ^{7}Li, ^{11}B, ^{25}Mg, ^{31}P, ^{43}Ca, ^{46}Ca, ^{51}V, ^{55}Mn, ^{57}Fe, ^{59}Cu, ^{66}Zn, ^{84}Sr, ^{89}Y, ^{90}Zr, ^{91}Zr, ^{98}Mo, ^{111}Cd, ^{120}Sn, ^{137}Ba, ^{139}La, ^{140}Ce, ^{141}Pr, ^{146}Nd, ^{208}Pb and ^{238}U. The standards used for element calibration included a pressed coral powder standard for 'major elements' B, Mg, Sr, Ba and U calibrated by isotope-dilution ICP-MS and TIMS analysis at ANU (Fallon et al. 1999; Fallon 2000) and a NIST 614 silicate glass for 'minor elements' (Li, P, V, Mn, Fe, Cu, Zn, Y, Zr, Zr, Mo, Cd, Sn, La, Ce, Pr, Nd, and Pb using concentrations reported in (Horn et al. 1997). All elements were normalised to ^{43}Ca for 'major elements' or ^{46}Ca for 'minor elements' to act as an internal standard and correct for variations in count rate resulting from changes in coral porosity and ICP-MS efficiency.

Data processing involved determining the instrument background and standards at the beginning and conclusion of an analytical run. Figure 5.5 displays the procedure for data processing including: A: average background counts were collected at the beginning and end of each analysis for approximately 60 s bracketing the coral sample. B: Background was linearly interpolated and subtracted from sample count rate. C: Normalisation of all elemental counts to ^{43}Ca or ^{46}Ca to act as an internal standard before calibration against a linearly interpolated value between Coral and NIST standards collected for 240 s bracketing analysis. D: Concentration of elements in coral sample were calculated assuming a constant concentration of Ca of 10 mol kgCaCO$_3^{-1}$. All data were converted from ppm to mmol/mol or μmol/mol. Data was smoothed using an 11-point average for corals with growth rates > 5 mm providing a resolution of 225-230 μm which represents approximately fortnightly growth. Slower growing corals (Seacliff A, Taylors Island, Edithburgh, Whyalla and Dutton Bay) were smoothed with a 5 point average to a sampling resolution 100 μm which correlated to approximately 2-3 weeks. Although there is still some high-frequency variability in the data that can not be linked to temperature or other known environmental factors, further reducing the data would mean short term environmental events recorded in the coral may not be apparent.

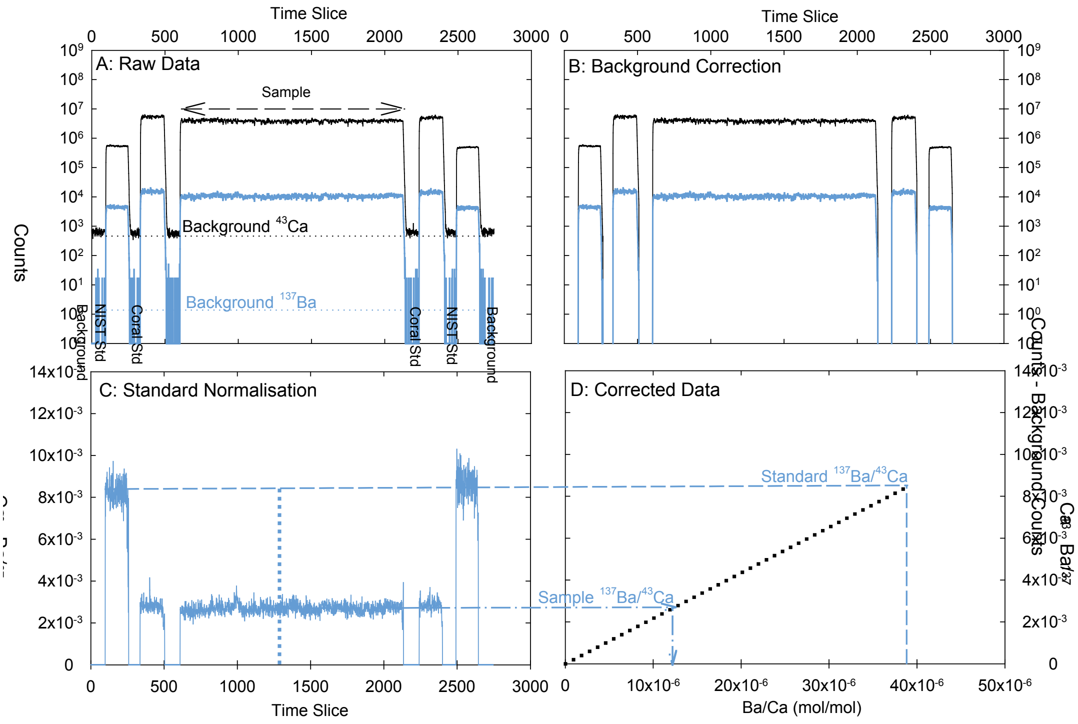

Figure 5.5: Laser data processing first with background levels removed then normalised to ^{43}Ca and the in-house coral standard. A. Backgrounds and standards measured at the beginning and end of the analysis were averaged and instrumental precision assessed. B. Background subtracted using a value linearly interpolated between the initial and final background after analysis. C. Internal standardisation using ^{43}Ca for all elements (example of Ba/Ca displayed). D. Calibration with the relevant standard (CORAL or NIST 614) using a value linearly interpolated between the standard measured before and after analysis. Absolute concentrations of all elements were calculated assuming a constant Ca concentration of 10 molkg^{-1}.

The more modern ICP-MS (Varian) enabled a larger suite of elements to be analysed (^{51}V, ^{57}Fe, ^{59}Cu, ^{90}Zr, ^{91}Zr, ^{98}Mo, ^{139}La, ^{140}Ce, ^{141}Pr, and ^{146}Nd,) than was previously available on the PQ2. The Varian has significant improvements over the PQ2 including more efficient cycling allowing a longer dwell time on each element, greater sensitivity and a lower machine background.

Analytical Methods: Stable isotope analysis

Carbonate samples were milled at a resolution of monthly to five yearly increments (200 µm – 6 mm) along the growth axis of coral cores. Milling techniques are similar to those described in Gagan et al. (1994). Individual powdered samples were analysed for $\delta^{18}O$ and $\delta^{13}C$ in an automated individual carbonate-reaction Kiel (III) device coupled with a Finnigan Mat-251 mass spectrometer at the Research School of Earth Sciences, The Australian National University. Powdered coral samples weighing 180-220 µg were reacted with two drops of 103% phosphoric acid at 90°C. The resulting H_2O-CO_2 gas was purified by freezing with liquid nitrogen removing the water, vaporising the CO_2 and trapping it in a cold trap system. The purified CO_2 is then passed through to the inlet system of the mass spectrometer for measurement. All isotopic data are measured relative to the National Bureau of Standards NBS-19 ($\delta^{18}O$ =-2.20‰; $\delta^{13}C$ =1.94‰) reported as per mil (‰) relative to Vienna Peedee Belemnite standard (VPDB). Analytical precision for replicate measurements (n = 115) of $\delta^{13}C$ in NBS-19 was ± 0.02‰ (2σ). The National Bureau of Standards NBS-18 is also run weekly for instrumental precision ($\delta^{18}O$ = -23‰; $\delta^{13}C$ = -5.0‰) reported as per mil (‰VPDB).

The trace element analyses were conducted down the centre of the coral Seacliff B03 parallel to the major growth axis and the $\delta^{18}O$ analyses were milled approximately 8 mm away from the laser analyses on the edge of the coral piece. As well as the sampling offset on different corallites, there is a difference in sampling resolution between the two techniques. The trace elements are ablated at a rate of 16 µm sec $^{-1}$ then smoothed to remove the high frequency variability combining an average of 5 sec of analytical rime. The smoothed data results in an effective resolution of ~ 250 µm which corresponds to approximately fortnightly resolution, where as the $\delta^{18}O$ were milled using a sampling resolution of ~ 200 µm, also approximately fortnightly resolution (but with a larger amount of carbonate used in analysis).

There is a significant difference in the sample volume analysed between bulk sampling of $\delta^{18}O$ and trace elements by LA-ICP-MS. The laser sampling rectangle is ~ 400 x 40 µm x ~ 1 µm per pulse depth, which corresponds to 16,000 µm^3 per pulse or ~ 20 ng of sample per pulse. The laser data is averaged to an approximate resolution of 250 µm, therefore the total sample ablated per data point is ~ 160 ng (assuming 50% coral porosity). The $\delta^{18}O$ samples are milled at ~ 200 µm x 2500 µm x 3000 µm which equates to 1.5 mm^3 or around 2000 µg of sample, of which a 200 µg sub-sample is analysed.

Results and Discussion

Comparison of LA-ICP-MS systems

When assessing the potential of a new paleoenvironmental archive it is important to assess the quality of data reproducibility, and this study provided an ideal opportunity with the replacement of the PQ2 ICP-MS during the course of the project. Although previous studies have conducted comparisons between different ICP-MS, they have been confounded by other complicating factors such as non-uniform sample ablation (different laser-ablation systems or aspirated samples) (Munksgaard et al. 2004).

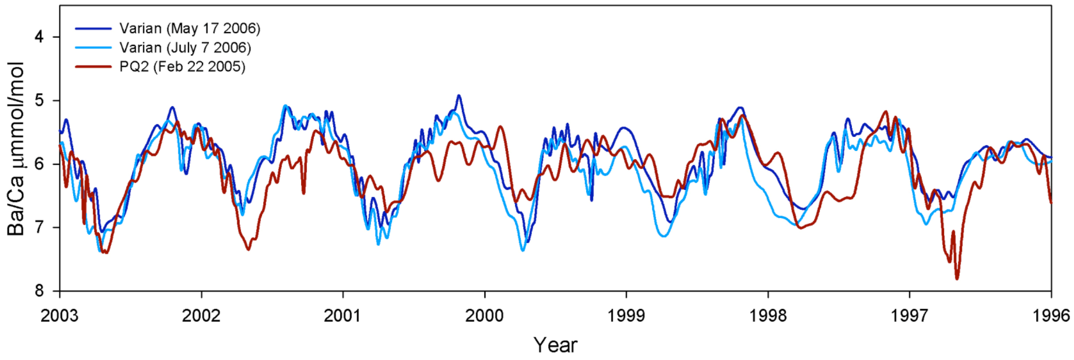

Figure 5.6: Comparison of data collected on two different ICP-MS within the Earth Environment Mass Spectrometry Laboratory, ANU. The data were run on parallel tracks approximately 18 months apart. In February 2005 for the PQ2 analyses and May/July 2006 for the Varian analyses.

This study has combined the use of two ICP-MS from the same laboratory at ANU connected to the same 193 nm Excimer Compex Laser and demonstrates high reproducibility between the two instruments. To check reproducibility, analyses were conducted on a piece of coral from Seacliff colony (Seacliff B03 - collected in 2003) and run on the PQ2 and the Varian ICP-MS over an 18 month period (Figure 5.6). The three analyses were conducted on neighbouring calices on the same piece of coral and indicate a similar annual temperature cycle. Some of the disparity between the amplitude of the temperature cycle in neighbouring calices, reflect variations in coral architecture and calice geometry.

A direct comparison on the same laser track between the two ICP-MS was not possible because the track run on the PQ2 was not marked. Due to the three-dimensional structure of *Plesiastrea* (compared with *Porites*) the laser tracks are not visible under ultra-violet light. Therefore the differences in Ba/Ca concentration between the PQ2 analysis and the Varian analyses in Figure 5.6 are likely to reflect coral heterogeneity in architecture, rather than instrumental differences as the measured concentrations of Ba are well above detection limits.

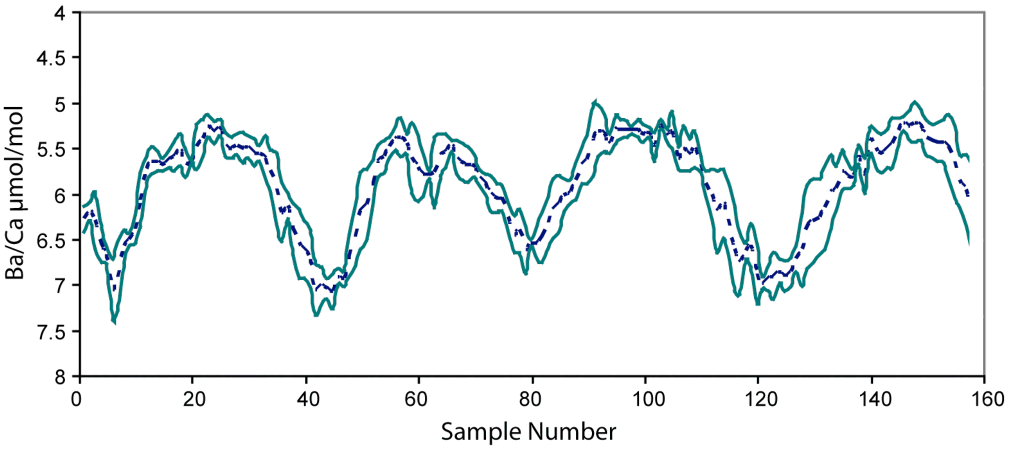

Figure 5.7: Data reproducibility from the Varian ICP-MS on the same track run seven times over three months with Ba/Ca on Seacliff B05. Dashed blue line is the mean for the seven analyses and green lines are ± 1σ.

Reproducibility on the same track from Seacliff B05 (collected in 2005) with seven Varian analyses over a three month period was excellent (1σ = 0.2 µmol/mol) (Figure 5.7). There is more heterogeneity observed between the peaks rather than at trace element concentration maxima and minima. A potential cause for this discrepancy may be due to the way the laser ablates the coral skeleton on different skeletal components. The majority of the trace element (TE) proxy data presented in this chapter was generated on the Varian rather than the PQ2 because of a higher level of precision obtained and more efficient cycling allowed a longer dwell time on each atomic mass. A comparison between the two ICP-MS was made for calibration of one of the coral colonies (Seacliff B) for cores collected in 2003 and 2005.

Overview case study: Seacliff B colony

An initial evaluation of the independent paleotemperature proxies δ^{18}O and the trace elements Ba/Ca, Sr/Ca, U/Ca and Mg/Ca indicate systematic variations over the 22 mm of coral skeleton (Figure 5.8).

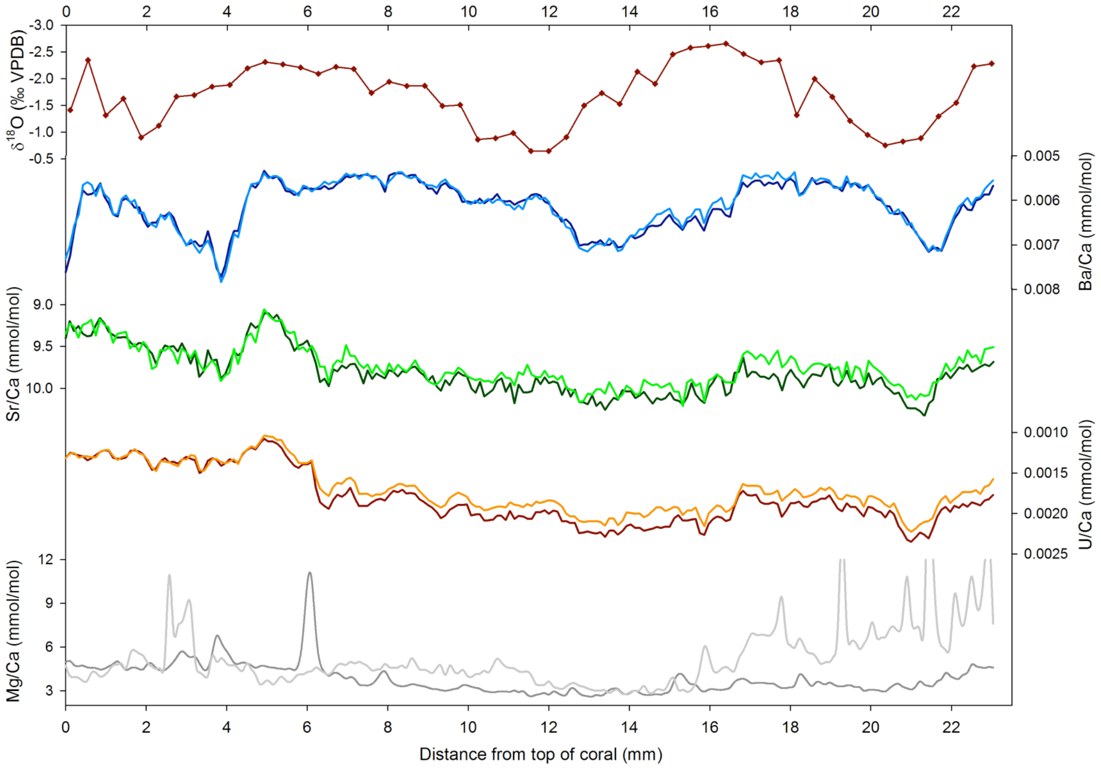

Figure 5.8: Data reproducibility between □^{18}O analyses and trace metal ICP-MS analyses on Seacliff B 03. The lighter colour used for Ba/Ca, Sr/Ca and U/Ca and Mg/Ca indicated the second analyses on the same laser track.

The average extension for this section of the Seacliff B core is 9 mm yr^{-1}, therefore the 22 mm section represents 2 ½ years of growth. Distinct annual variation occurs in all elements except Mg/Ca, with the greatest amplitude in concentrations in δ^{18}O and Ba/Ca concentrations. There was a small seasonal variation in Mg/Ca concentrations but this signal was overwhelmed by large spikes of concentrations three times usual coral values, that were not present on second analytical run on the same laser track.

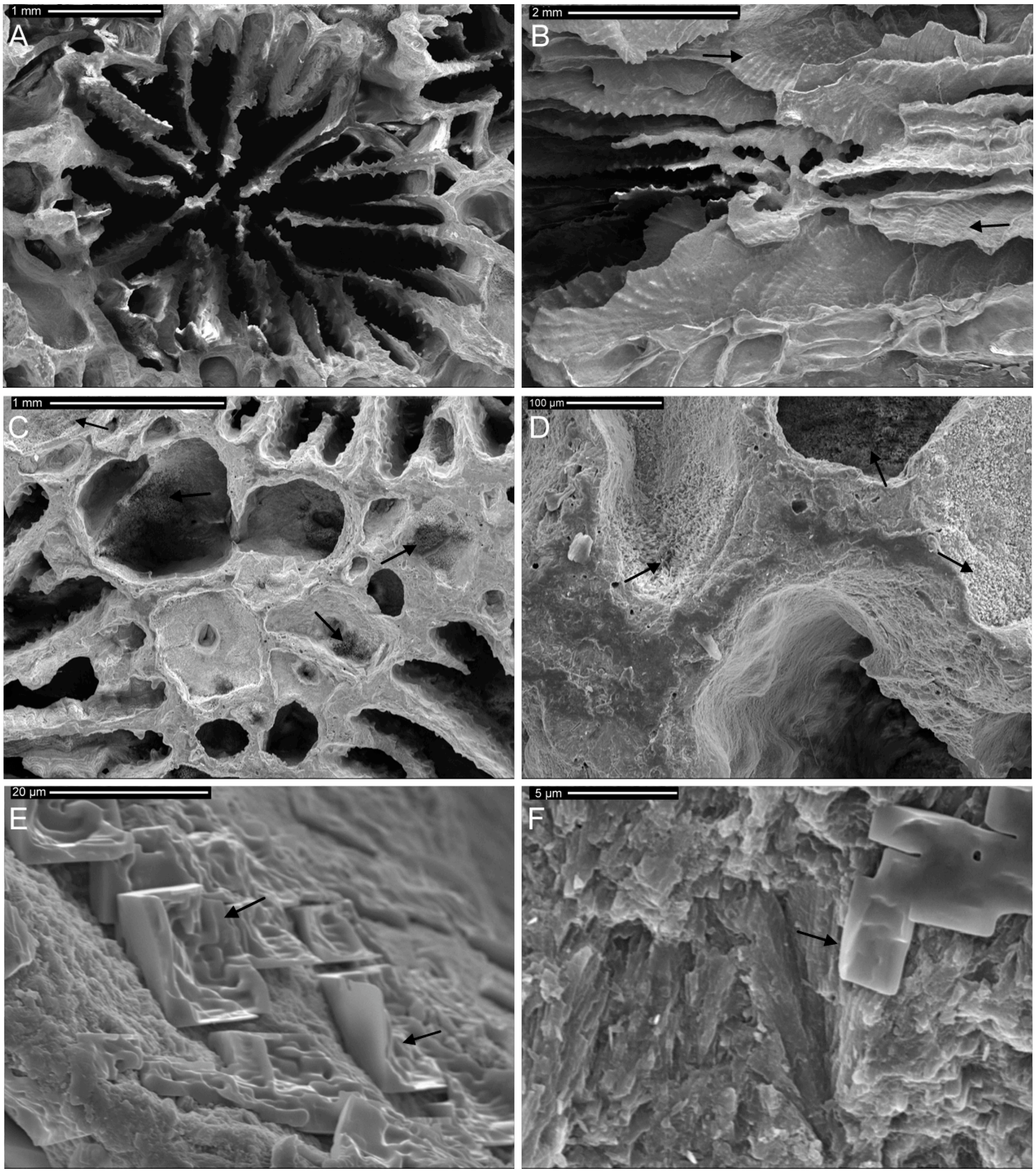

Figure 5.9: Scanning electron micrographs of *Plesiastrea versipora*. (A): Individual corallite of Seacliff B; (B): Longitudinal section of septa from Seacliff B displaying micro-crenulations of ~ 15-20 µm, potentially daily growth bands indicated by black arrows; (C): Arrows point to secondary aragonite in pore spaces in colony Seacliff A, none were found on septal surfaces; (D): Magnified section of secondary precipitate needles from Seacliff A; (E) and (F): Examples of rhombic crystals that are suggested to be high-magnesium calcite from Seacliff A (E) and Troubridge (F).

Ba/Ca and $\delta^{18}O$ produce a similar signal with winter minima offset between Ba/Ca and $\delta^{18}O$ due to growth rate differences between the different corallites analysed. The Sr/Ca and U/Ca data indicate very similar trends but do not appear to capture the three winters in the 22 mm section as coherently as $\delta^{18}O$ or Ba/Ca. The Ba/Ca concentrations were more reproducible over the same laser track than Sr/Ca and U/Ca, which in turn were more reproducible than Mg/Ca.

Mg/Ca was also collected during LA-ICP-MS analyses; however, the data indicated a high level of contamination with high-frequency spikes in the laser data which were not reproducible (Figure 5.8). There was negligible correlation between Mg/Ca and other trace element temperature proxies and $\delta^{18}O$, therefore it was interpreted that there was minimal temperature control on Mg incorporation into *Plesiastrea versipora*. The high-resolution nature of laser-ablation ICP-MS may enhance the heterogeneity of trace element signals including Mg/Ca, this has been observed in other LA studies (Sinclair 1999; Fallon 2000), and ion microprobe analyses (Allison & Tudhope 1992; Allison 1996b). Lower temporal resolution sampling (monthly) does not record heterogeneity in Mg/Ca and indicates a high correlation with SST (Mitsuguchi et al. 1996).

The anomalous Mg spikes occur most frequently when the laser samples aragonite next to a pore space or hole in the skeletal matrix. Potential sources of contamination masking a possible SST signal include diagenesis (McGregor & Gagan 2003) and secondary precipitates including high-Mg calcite. Secondary precipitates were revealed during scanning electron microscope examination, including secondary precipitates (Figure 5.9: C & D) and also potentially high-Mg calcite rhombs (Figure 5.9: E & F). No evidence of biological high-Mg crystals was observed, such as bacterially-derived brucite, which has been observed in tropical coral skeletons (Nothdurft et al. 2005). Concentrations for Mg/Ca have not been included in the rest of the chapter, as they were assessed to be reflections of contamination in the coral skeleton including secondary precipitates (Figure 5.9) rather than primary Mg/Ca in the coral aragonite lattice.

Calibrating Trace Element Records to SST

To accurately compare the laser ablation analyses with in situ SST, the laser data set has to be translated from distance to time. This is achieved by first smoothing the SST data which was averaged from daily to fortnightly, followed by resampling the laser data using a time-series analysis software package. The software Analyseries (Paillard et al. 1996) uses linear interpolation to resample a dataset using fixed points. The SST data and Ba/Ca laser data were 'peak matched' with 2 points per year using summer maxima (February) and winter minima (August). Only two marker points were used to interpolate the trace element data even though it cannot be assumed that linear growth occurred between the summer and winter marker points due to the differences in width of the high and low density bands. An example of the distance-time conversion of laser data is displayed in Figure 5.10. This figure describes the sampling of a coral core for laser ablation and stable isotope samples, followed by the translation of distance-time by peak matching a trace element record with SST.

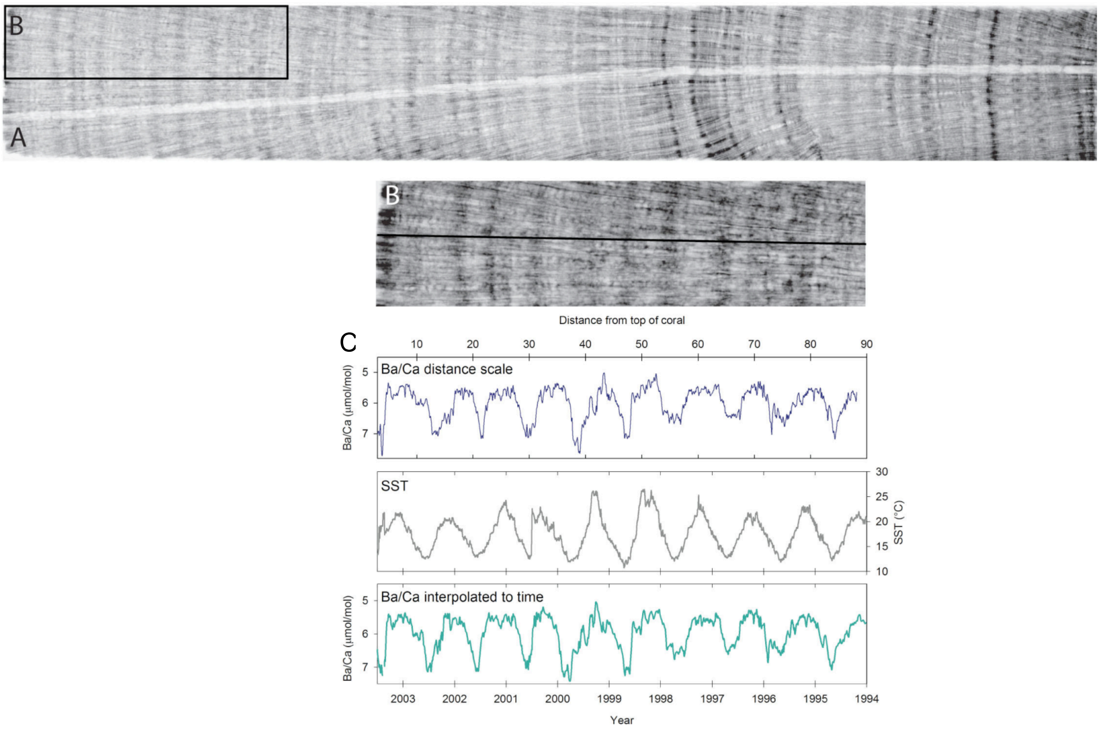

Figure 5.10: Distance to time translation for trace element analyses. (A): X-ray of Seacliff B indicating 40 years of growth and transect of milled samples for δ^{18}O analyses and inset B 9 cm piece of coral core for LA-ICP-MS analyses. (B): Laser piece for the top of core Seacliff B03, black line indicates laser track. (C): Ba/Ca analyses for Seacliff B03_1 (inset B) plotted as distance down coral core (blue curve), Ba/Ca axis is inverted. This data is peak matched to in situ SST data (grey curve) and linearly interpolated between peaks to convert distance scale to time scale on x axis (green curve).

Previous studies have reported that artificially fixing the time series between the peaks and troughs can incorporate greater error into your time translation (Sinclair 1999). After the laser data had been interpolated, the peak shape was different due to the greater extension and higher amount of calcification in summer, all trace element concentrations have a broad summer and sharper winter trough (Figure 5.10 (A)). Other studies have observed a similar asymmetry in trace element seasonal cycles, suggesting that growth is not constant throughout the year at a range of latitudes and extension rates and calcification vary seasonally (Fallon et al. 1999; Cardinal et al. 2001; Cohen et al. 2004; Montagna 2004). Other high-latitude studies conducted on both tropical (Fallon et al. 1999) and non-tropical (Montagna et al. 2007) coral species have concluded that the coral reaches a certain temperature threshold and stops growing, however this was not observed in the *Plesiastrea versipora* colonies from Gulf St. Vincent or Spencer Gulf. Studies on the calcification of *Plesiastrea versipora* colonies from Port Phillip Bay (Victoria) with similar temperature ranges to the South Australian gulfs concluded that massive forms of *Plesiastrea* continue to calcify at low temperatures (Howe & Marshall 2002). Howe and Marshall (2001) observed considerable variation in skeletal deposition between individual corallites with reduced crystal organisation in skeletal material deposited at 10°C.

Five of the *Plesiastrea versipora* cores collected in this study were calibrated for a 10-12 year period (12 years for cores collected in 2005) with a composite SST dataset from 1992-2005 (Figures 5.11-5.16) including *in situ* logger data from two coral colony locations and the National Tidal Facility data from Port Stanvac (Gulf St. Vincent). Seasonal cycles of both Sr/Ca and Ba/Ca were used to construct time series for all corals. Ba/Ca concentrations displayed the most regular seasonal cycle. However, because Ba/Ca is known to be influenced by other environmental factors including upwelling and river discharge (Lea et al. 1989; Sinclair 1999), Sr/Ca was also used to verify the regularity of the seasonal cycle. The seasonal cycles in the laser data were also compared to density bands in the skeleton, and summer peaks (or low concentrations) in the Ba/Ca data corresponded to low density bands in the coral core.

To assess the reproducibility within a coral colony, SST calibrations were conducted for two cores from Seacliff B; collected in 2003 and 2005. The SST/coral calibration comparison conducted on Seacliff B03: PQ2 (Figure 5.11) and Seacliff B05: Varian (Figure 5.12) yielded better correlations between the trace element proxy and SST for the Varian analyses. The difference in SST calibrations between Figure 5.10B and Figure 5.11B may be predominantly a function of differences in individual corallites between the 2003 and 2005 cores.

In contrast to the Seacliff B cores, the Troubridge coral (Figure 5.13) has lower Ba/Ca concentrations, the summer peaks are at a similar concentration of 5 μmol/mol, however the winter troughs are 6.4 μmol/mol compared with 6.8-7 μmol/mol. This corresponds to a lower slope in the Ba/Ca SST calibration than Seacliff B coral. The seasonal cycle is not clear in concentrations of Sr/Ca and U/Ca throughout the calibration period and change from 2003-2005 with higher concentrations. This feature in the trace element data produces a bimodal distribution in the calibration regressions for Sr/Ca and U/Ca in Figure 5.13B.

The denser corals with much slower extension rates, Seacliff A, Edithburgh and Taylors Island (Figures 5.14-5.16) did not exhibit an obvious seasonal cycle in Sr/Ca and U/Ca for part of the calibration period, when compared with coral colonies with a more rapid extension rate such as Seacliff B and Troubridge (Figures 5.12-5.13). None of the coral colonies exhibited a very strong temperature dependency for B/Ca although the r^2 values indicate a correlation with SST of greater than 50%, the slope of the calibration is very low for all corals. The lack of temperature dependence driving the B/Ca concentrations is reflected in the trace element derived temperature values producing anomalous results.

The El Niño year in 1998 corresponds to lower concentrations in Ba/Ca, Sr/Ca and U/Ca (reflecting warmer temperatures) for Seacliff A and B corals. The Sr/Ca and U/Ca concentrations did not display clear seasonal cycles for three years after the El Niño in Seacliff B. A similar response was observed following the 2002 El Niño, however, no reduction in skeletal extension was observed during or after El Niño years (Figure 4.8) discussed in Chapter 4.

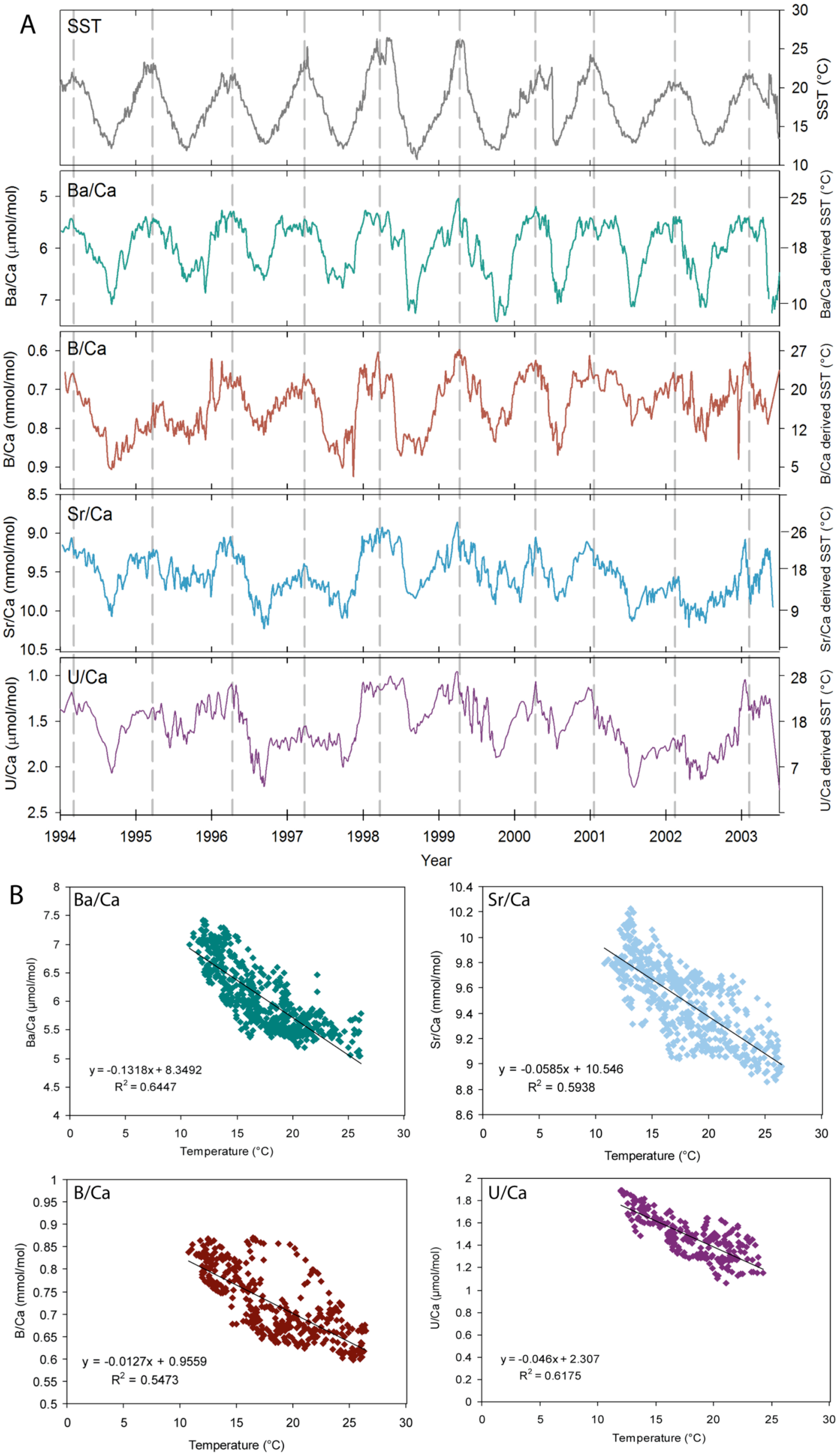

Figure 5.11 (A): Seacliff B03 comparison with *in situ* SST from Pt Stanvac. Average extension rate of Seacliff B03 is 6 mm yr^{-1}. Data collected on the PQ2. Grey lines indicate SST maxima in February each year and corresponding low density bands. (B): Regressions of the trace element ratios with *in situ* SST from Port Stanvac.

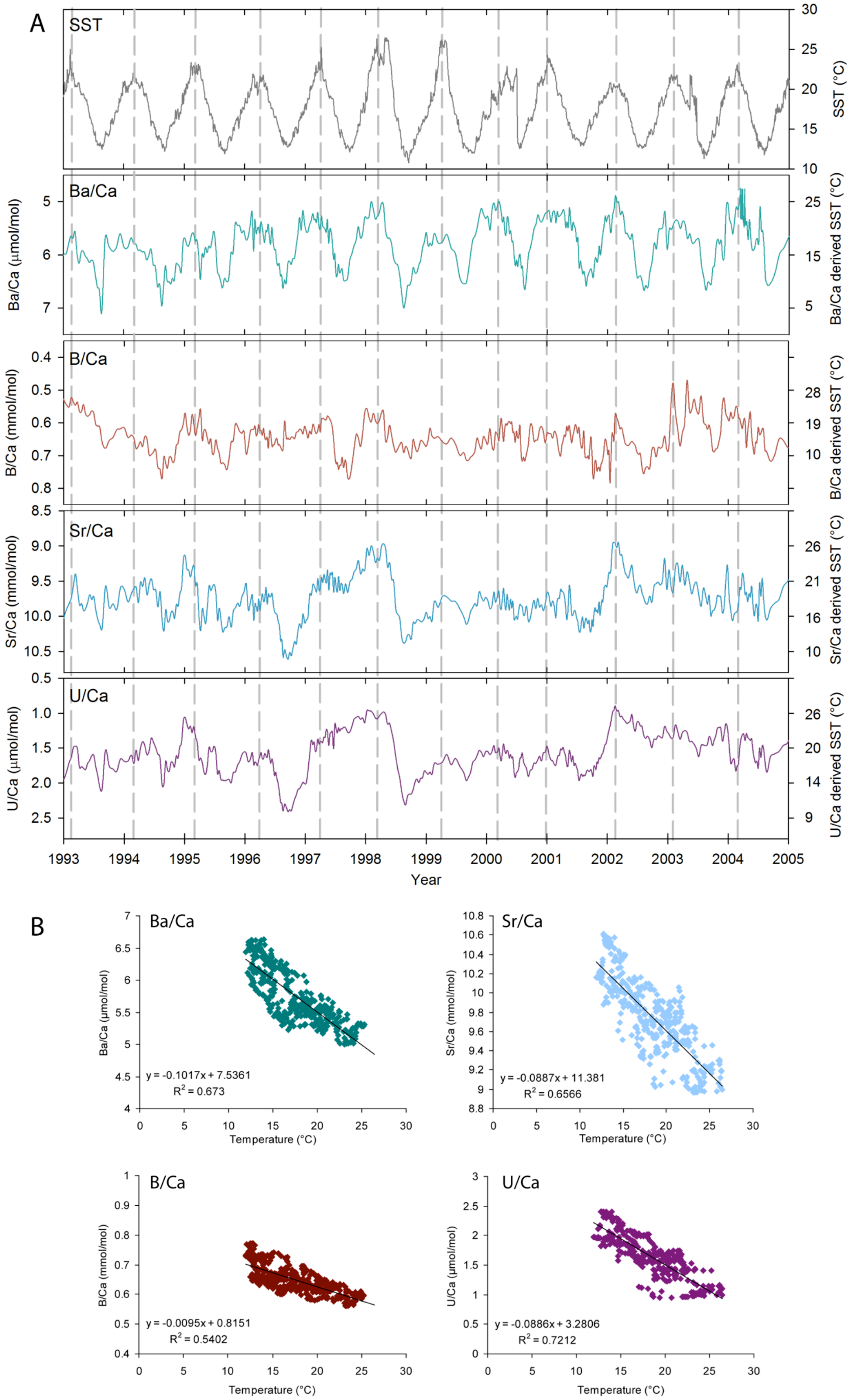

Figure 5.12 (A): Seacliff B 05 comparison with *in situ* SST from Pt Stanvac. Average extension rate of Seacliff B05 is 6 mm yr^{-1}. Data collected on the Varian. (B): Regressions of the trace element ratios with *in situ* SST.

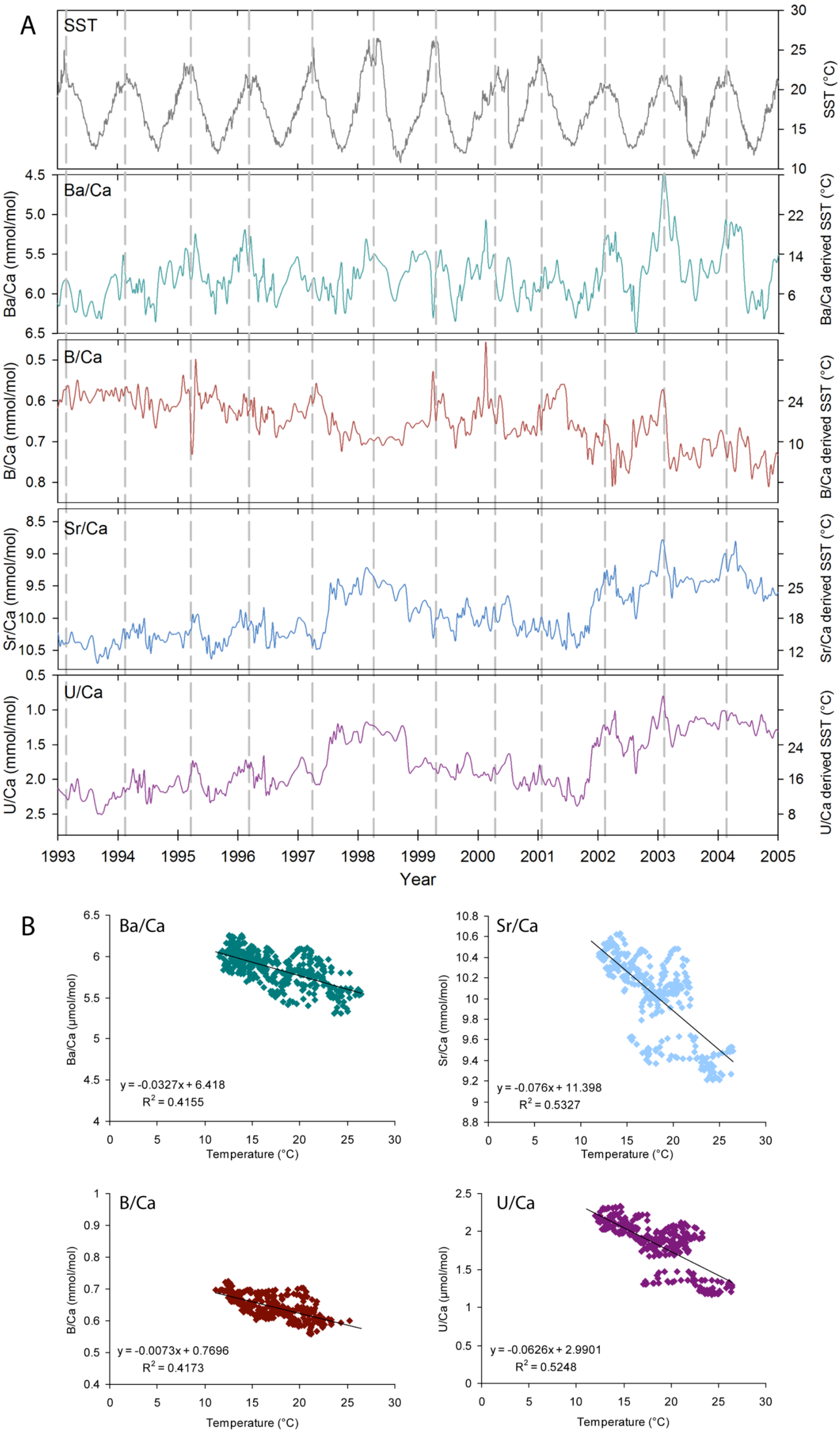

Figure 5.13 (A): Troubridge 05 comparison with *in situ* SST from Pt Stanvac. Average extension rate of Troubridge 05 is 8 mm yr^{-1}. (B): Regressions of the trace element ratios with *in situ* SST.

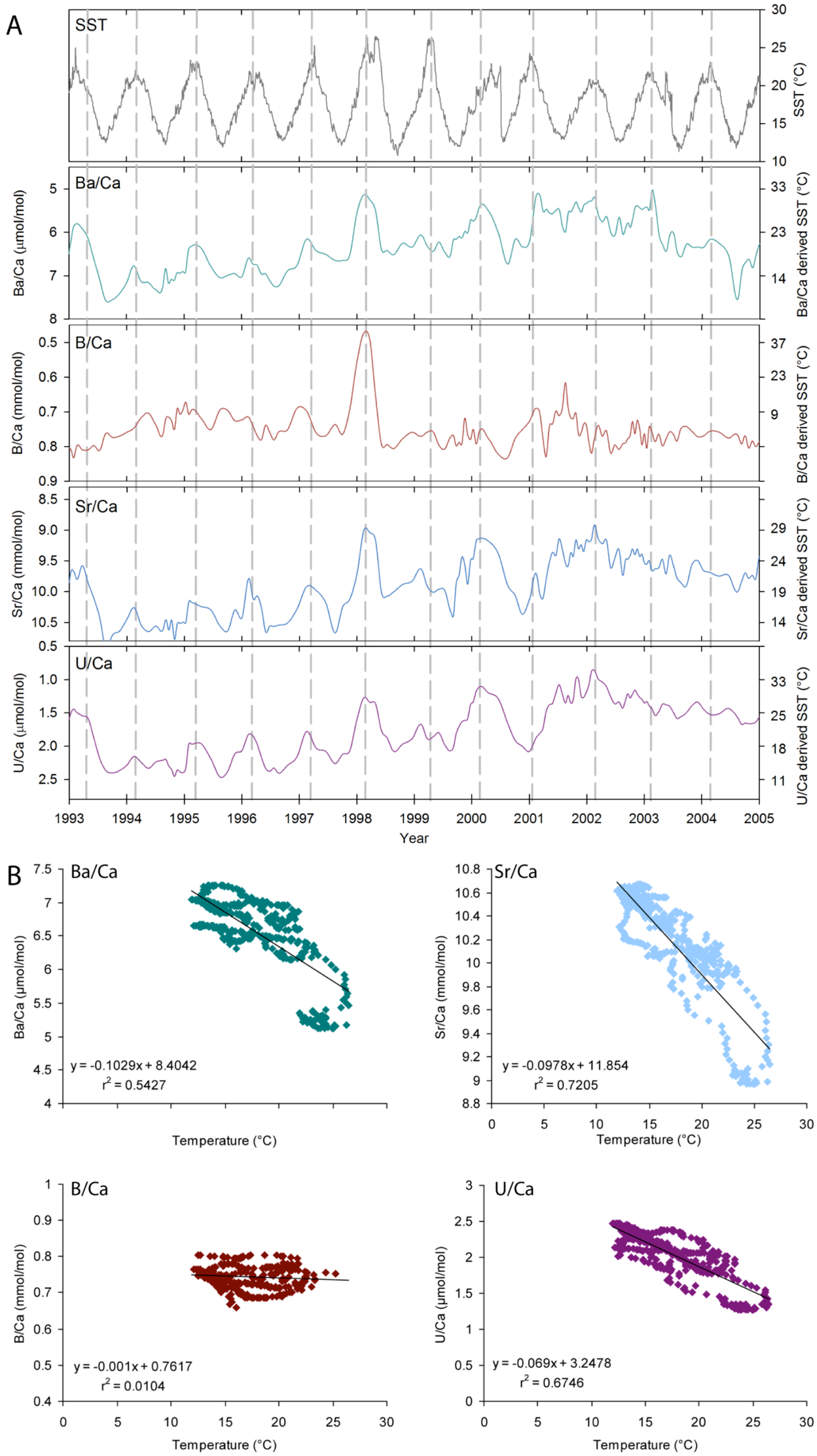

Figure 5.14 (A): Seacliff A05 comparison with *in situ* SST from Pt Stanvac. Average extension rate of Seacliff A05 is 2 mm yr^{-1}. (B): Regressions of the trace element ratios with *in situ* SST.

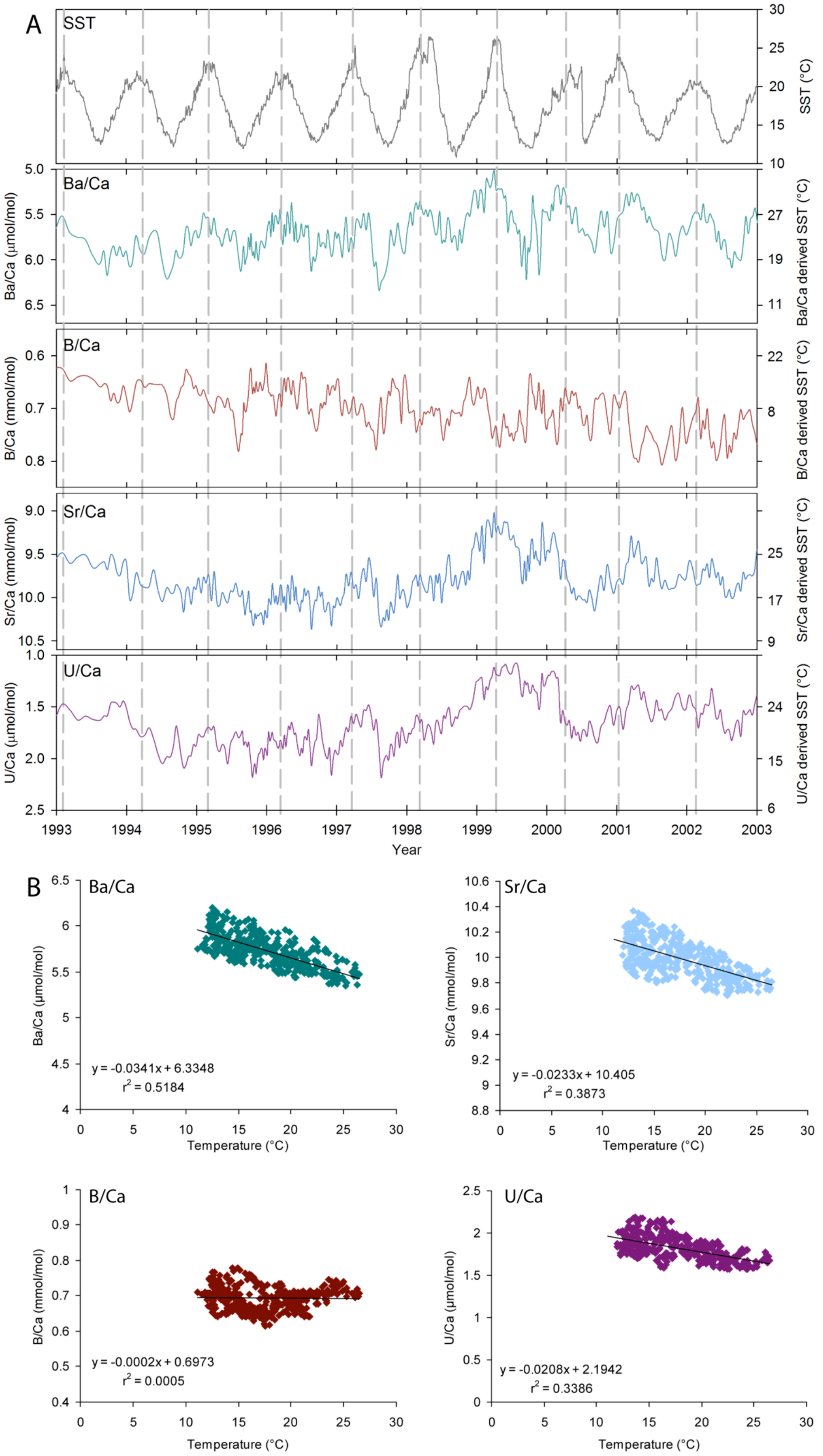

Figure 5.15 (A): Edithburgh 03 comparison with *in situ* SST from Pt Stanvac. Average extension rate of Edithburgh 03 is 2 mm yr^{-1}. (B): Regressions of the trace element ratios with *in situ* SST.

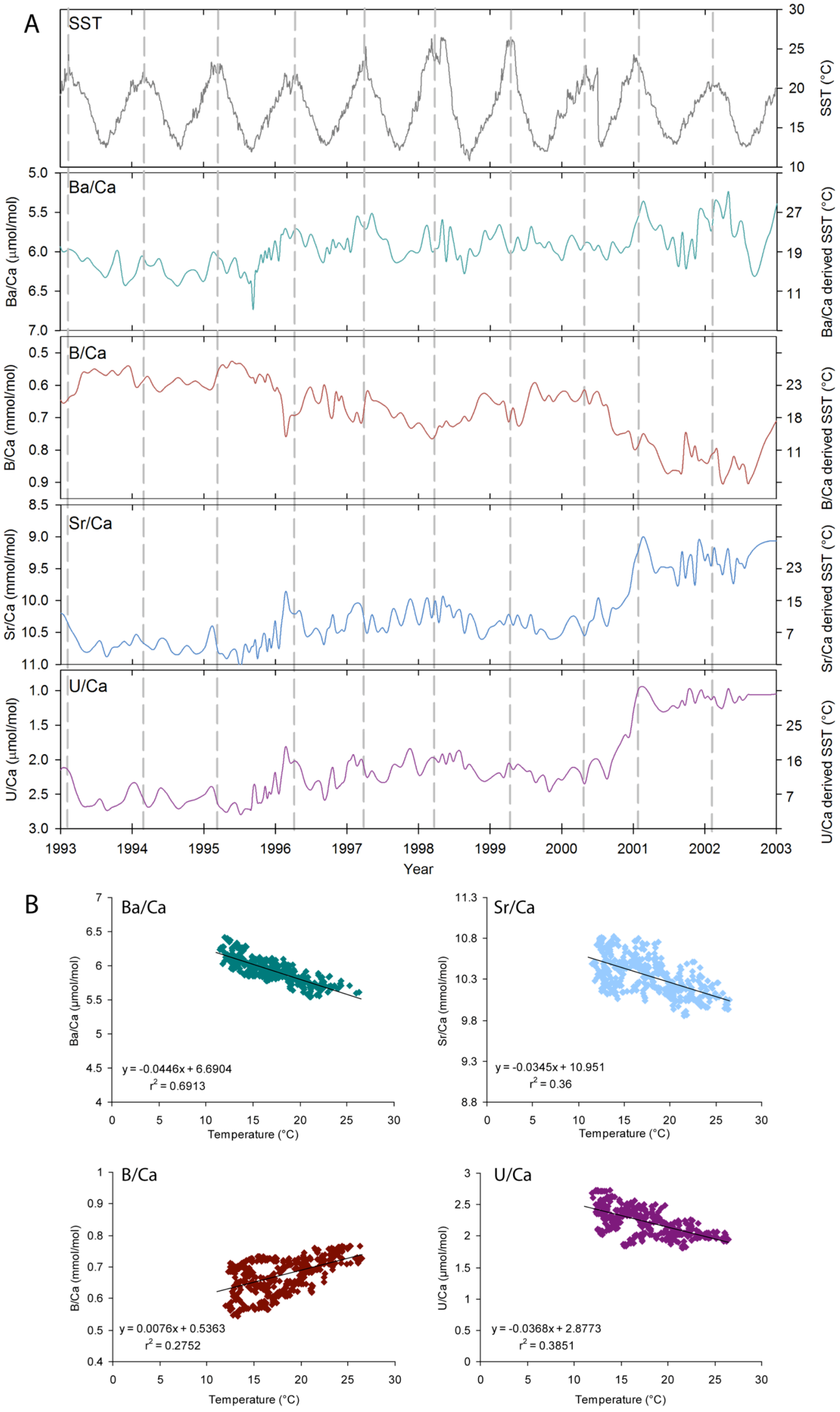

Figure 5.16 (A): Taylors Island A03 comparison with *in situ* SST from Pt Stanvac. Average extension rate of Taylors Island A03 is 1.5 mm yr^{-1}. (B): Regressions of the trace element ratios with *in situ* SST.

The remaining *Plesiastrea versipora* SST calibrations in Figures 5.14-5.16 are from corals growing less than 3 mm yr^{-1} and do not indicate clear seasonal cycles in any of the trace element concentrations. Although some of the SST calibrations have a reasonably good r^2 value, this may be due to the data clustering tightly and therefore appearing to artificially correlate with temperature, without any direct role of SST in the concentration of Sr/Ca or U/Ca in the coral skeleton. Previous studies have observed ambiguous seasonal cycles, despite a variable temperature range indicating a sinusoidal cycle (Marshall & McCulloch 2001).

Table 5.1: Trace element/SST transfer functions for five *Plesiastrea versipora* cores.

	B/Ca (mmol/mol)			Sr/Ca (mmol/mol)		
	a	b	r^2	a	b	r^2
Seacliff B03 PQ2	0.96	-0.013	0.55	10.55	-0.059	0.59
Seacliff B05 Varian	0.81	-0.011	0.54	11.38	-0.089	0.66
Seacliff A05	0.76	-0.001	0.01	11.85	-0.099	0.72
Troubridge 05	0.77	-0.007	0.41	11.40	-0.076	0.53
Edithburgh 03	0.70	-0.0002	0.0005	10.41	-0.023	0.39
Taylors Island A03	0.54	0.008	0.28	10.95	-0.035	0.36
MEAN	0.76	-0.0067		11.09	-0.0635	

	Ba/Ca (µmol/mol)			U/Ca (µmol/mol)		
	a	b	r^2	a	b	r^2
Seacliff B03 PQ2	8.35	-0.132	0.64	2.31	-0.046	0.62
Seacliff B05 Varian	7.54	-0.101	0.67	3.28	-0.089	0.72
Seacliff A05	8.40	-0.103	0.54	3.25	-0.069	0.67
Troubridge 05	6.40	-0.033	0.42	2.99	-0.063	0.52
Edithburgh 03	6.33	-0.034	0.52	2.19	-0.021	0.34
Taylors Island A03	6.69	-0.045	0.69	2.88	-0.037	0.39
MEAN	7.23	-0.0637		2.81	-0.0542	

* Using the transfer function $y = a + b*SST(°C)$, r^2 is the correlation coefficient using a least squares regression. Seacliff B regression equations are generated from the 2003 core using the PQ2 ICP-MS and the 2005 core using the Varian ICP-MS

The corals with the fastest growth rates such as Seacliff B and Troubridge appear to record seasonal variation with the most consistency, whereas the slower growing corals (Seacliff A, Edithburgh and Taylors Island; Figure 5.14-5.16) do not accurately resolve the seasonal cycle and may calcify too slowly to record the large SST range (10-26°C) of the South Australian gulfs in their skeleton. All *Plesiastrea versipora* colonies did not display a coherent seasonal cycle in B/Ca, Sr/Ca and U/Ca in the last two years of growth, this may be related to smoothing associated with the tissue zone, although Seacliff B and Troubridge are growing at a rate of twice the tissue thickness (~ 4 mm) per year. The potential tissue smoothing effect was also observed in Ba/Ca for the slow growing corals as the slope is reduced for colines with lower extension rates.

Ba/Ca exhibited a less ambiguous seasonal cycle than B/Ca, Sr/Ca and U/Ca for all corals analysed even though the 'degree of fit' in the trace element – SST correlations were similar. The transfer functions associated with SST/coral calibrations are listed in Table 5.1, although there is a high degree of variability in the slope of the transfer function (b values from table), this has been observed in previous review studies (Correge 2006) and temperature calibration equations from other published studies listed in appendix A.

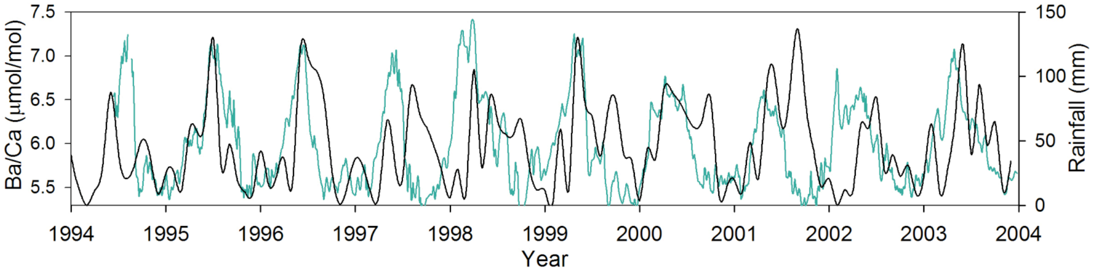

Figure 5.17: Comparison of Ba/Ca (blue) record from Seacliff B05 with rainfall record (black) from Kent Town, Adelaide. Rainfall data provided by the Bureau of Meteorology.

Other environmental factors were examined to see if they contributed to the incorporation of Ba into the coral skeleton. Rainfall (measured in Adelaide) was compared with one of the metropolitan coastal corals and only described 28% of the annual variability (Figure 5.17). The high Ba/Ca winter peak often lags the rainfall peaks by several months, and where a correlation does occur between the two variables, this may be explained by the time of year, with rainfall predominantly occurring in winter and more Ba incorporated with cooler seawater temperatures. The concentrations of Ba/Ca in both the coastal and open gulf *Plesiastrea versipora* colonies were comparable, and the open gulf corals could not be influenced by rainfall or higher Ba from river discharge, suggesting the Ba concentration is stable throughout the gulfs. Recent studies examining Ba/Ca concentrations in fish otoliths in temperate Australian waters have suggested that Ba/Ca is a conservative tracer of fish movement, and ambient Ba in coastal waters is 5-6 g L^{-1} compared with Ba enriched estuarine sites of > 10 µg L^{-1} (Elsdon & Gillanders 2003; Hamer et al. 2006).

Sr/Ca has been the most studied paleotemperature proxy apart from $\delta^{18}O$ (Swart & Grottoli 2003; Correge 2006). A wide range exists between published Sr/Ca-SST calibrations, with equivalent Sr/Ca concentrations deriving temperature differences of 2-4°C for example (Beck et al. 1992; McCulloch et al. 1994; Shen et al. 1996; Alibert & McCulloch 1997; Gagan et al. 1998), see Appendix A for a more complete list of Sr/Ca-SST calibrations. Several hypotheses have been suggested to explain the variability in Sr/Ca calibrations, including; coral species collection, seawater concentrations, sampling size, instrumental variability and inter-laboratory spikes (Gagan et al. 2000). The slopes of the Sr/Ca calibrations in this study for corals with extension rates greater than 3 mm yr^{-1} and the % change per °C are comparable to published studies. However, the error associated with the LA-ICP-MS technique corresponds to approximately 2°C, implying that calibrations generated in this study have an error too great for precise paleotemperature reconstructions, but are adequate to compare this species of coral with calibrations derived from tropical corals.

The calibrations for the five corals between trace element/Ca-SST described in Table 5.1 are similar to the range of published literature calibrations (Appendix A). Temperature dependence of Sr/Ca for *Plesiastrea versipora* at 0.06 mmol/mol/°C has been observed both in *Porites* and other species (Smith et al. 1979; de Villiers et al. 1994; McCulloch et al. 1999; Fallon et al. 2003). The U/Ca was also comparable to published calibrations 0.05 µmol/mol/°C (Min et al. 1995; Fallon et al. 1999; Fallon et al. 2003). Very little temperature dependence was observed in B/Ca although a previous laser-ablation study by Fallon et al. (2003) observed similar slopes. The Ba/Ca ratio measured on *Plesiastrea versipora* ranged from 4.5µmol – 7.3 µmol, a greater range than ranges observed in Caribbean and East Pacific corals (Shen & Boyle 1988; Lea et al. 1989; Shen et al. 1992), this may be due to the lower temperatures experienced in the South Australian gulfs. A study conducted on a high-latitude faviid coral from the Mediterranean also observed a large range in Ba/Ca concentrations and has a comparable large annual temperature range of over 15°C (Montagna 2004).

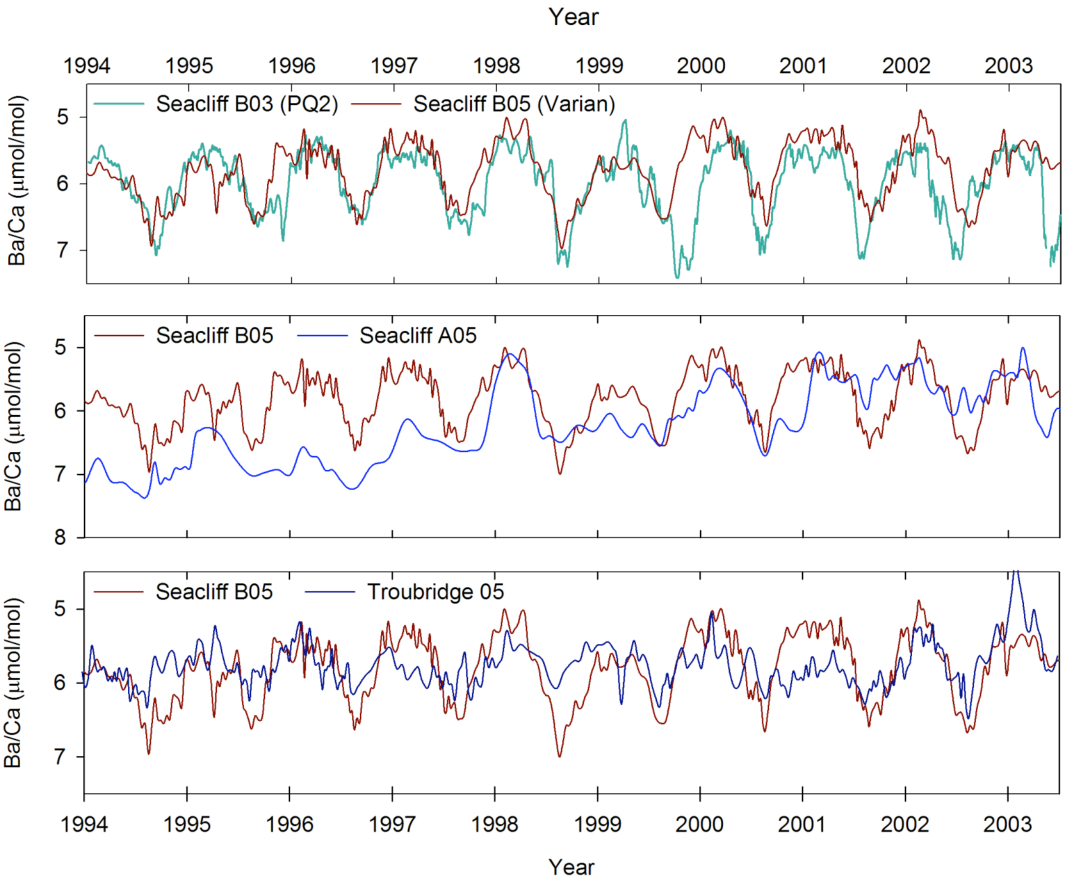

Figure 5.18: Comparison of Ba/Ca records from three corals. The first panel compares the Seacliff B cores from 2003 and 2005; the second panel compares Seacliff B05 with Seacliff A05 and the third panel compares Seacliff B05 with Troubridge 05.

Figure 5.18 compares the reproducibility between the two Seacliff B cores from 2003 and 2005. Although there is a high coherency between the two records, there are differences in the expression of the winter minima, due to differences in individual calice growth. Therefore, a linear regression between the two records results in a low correlation, due to the differences in seasonal amplitude in some years. A comparison of Seacliff B and Seacliff A clearly demonstrates the reduced seasonal cycle recorded by Seacliff A. The comparison between the two colonies with comparable extension rates, Seacliff B and Troubridge record a similar amplitude in the seasonal cycle but indicate variability in sub-seasonal scale Ba/Ca concentrations.

The SST calibrations indicate that *Plesiastrea versipora* does record seasonal variability using the well established trace element proxies Sr/Ca and U/Ca. In addition, Ba/Ca, shows a strong correlation with SST, which was first hypothesised to have a temperature control on elemental substitution in the skeleton by Lea et al. (1989) and subsequently observed in experimental studies (Dietzel et al. 2004). The *Plesiastrea versipora* colonies growing at less than 3 mmyr^{-1} have low temperature dependence in Sr/Ca, U/Ca and B/Ca concentrations and converting concentrations to temperature using the equations for each coral from Table 5.1 does not result in realistic temperatures. The SST correlations calculated in this study indicate that temperature does play a significant role in the trace element variation in *Plesiastrea versipora* colonies growing at > 3 mmyr^{-1}, although there are also other factors such as vital effects which are influencing the trace element chemistry (Gaetani & Cohen 2006; Sinclair et al. 2006).

Trace Element Intercorrelation

Sr/Ca and U/Ca exhibited a strong linear correlation when regressed together for all corals examined (Figure 5.19). Most corals were very significantly correlated ($r^2 > 0.93$) (see Tables 5.2-6), and the lowest correlation between the two elements was for the Whyalla and Dutton Bay coral ($r^2 = 0.85$ (Table 5.7) and $r^2 = 0.88$ (Table 5.8)). One important observation is that Sr/Ca and U/Ca always appear to correlate on both an intra- and inter annual time scale regardless of the elemental ability to track temperature. The relationship between these two elements appears more robust between sites than other elemental correlations (Figure 5.19). There was also a significant correlation observed between Sr/Ca and Ba/Ca, however, the scatter plot comparison between Ba/Ca and U/Ca indicate more variability in the data. The relationship between these three elements suggests a degree of temperature control on skeletal incorporation.

The tight coupling between Sr/Ca and U/Ca for all *Plesiastrea versipora* colonies may be indicative of similar incorporation mechanisms for these two elements. A brief review of calcification models was described in Chapter 2, and the model thought to describe calcification in *Plesiastrea versipora* most accurately is based on a membrane bound pocket of supersaturated fluid (Howe & Marshall 2002). The composition of the calcifying fluid is thought to be actively controlled by the coral polyp, with the chemistry of the seawater modified by transport of ions across the basal epithelium (Cohen et al. 2006; Gaetani & Cohen 2006). One hypothesis to describe the difference in the correlations between the elements may be that Sr and U enter the calcification fluid through the same chemical pathway and are therefore subject to a similar partition coefficient.

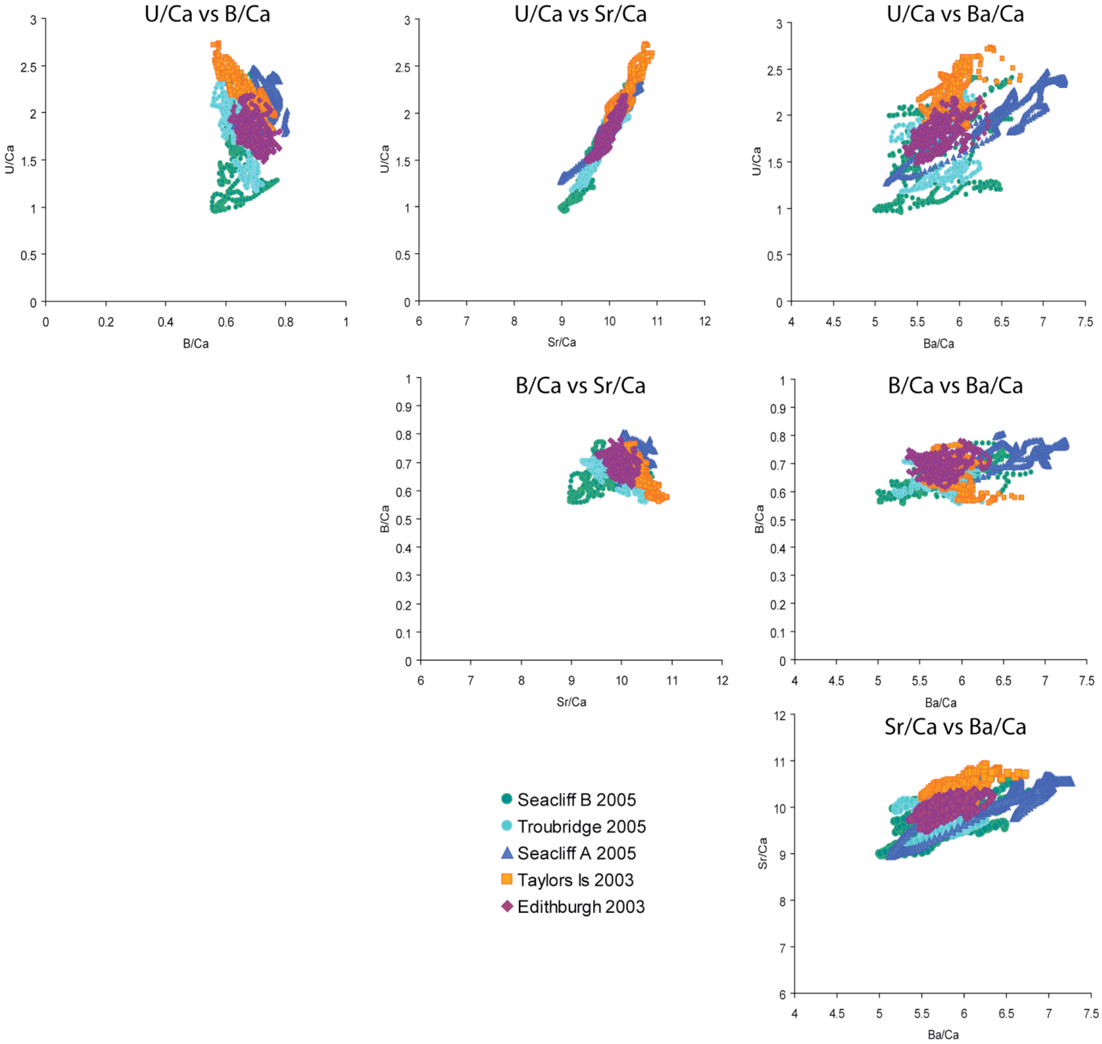

Figure 5.19: Correlations between B/Ca, Sr/Ca, Ba/Ca and U/Ca for five *Plesiastrea* colonies. The different colours represent different coral cores. Units for B/Ca and Sr/Ca are mmol/mol; units for Ba/Ca and U/Ca are μmol/mol. B/Ca shows the least temperature dependence and least similarity with other trace metal paleothermometers.

By contrast Ba may enter the calcification pore space through a different chemical pathway to Sr and U. Even though all three elements substitute for Ca^{2+} and produce an isomorph of aragonite (witherite ($BaCO_3$) (Speer 1983; Lea et al. 1989); strontianite ($SrCO_3$) (Kinsman 1969; Amiel et al. 1973a; Cross & Cross 1983; Speer 1983); rutherfordine (UO_2CO_3) (Christ et al. 1955; Amiel et al. 1973b; Min et al. 1995)). Although temperature has been known to play an important role in the partitioning of boron into aragonite (Ichikuni & Kikuchi 1972) the boron species $B(OH)_4^-$ most likely substitutes for the CO_3^{2-} site (Hemming & Hanson 1992) and therefore may be more dependent on the pH of the calcification fluid rather than SST. B/Ca does not show a strong correlation with SST in *Plesiastrea* compared with previous studies (Hart & Cohen 1996; Sinclair et al. 1998; Fallon et al. 1999; Montagna et al. 2006).

A recent study by Sinclair et al. (2006) suggested that an inverse relationship between U/Ca and Mg/Ca was a universal feature of all corals. It is not surprising that Mg/Ca has an inverse relationship with other trace elements as it has a positive correlation with SST compared with B/Ca, Sr/Ca and U/Ca which have a negative correlation with SST. The negative correlation suggests that in warmer temperatures it is harder for cations to replace Ca^{2+} and therefore have lower concentrations. The Mg/U relationship observed by Sinclair et al. (2006) in one shallow water species and three deep-water or azooxanthellate species is not supported by the results of this study. All *Plesiastrea versipora* colonies analysed indicated anomalous spikes in Mg that could not be correlated to a seasonal cycle. Mg/Ca has been shown to be more complex than other trace elements due to different concentrations of Mg in different carbonate lattice structures (Allison 1996a; 1996b). The coherency between Sr/Ca and U/Ca observed in *Plesiastrea versipora* was higher than the anti correlation between U and Mg observed by Sinclair et al. (2006). These authors also suggest that there is a single chemical process fractionating trace elements which can be influenced by environmental parameters such as SST but is dominantly controlled by physiological parameters (Sinclair 2005). The trace element behaviour observed in *Plesiastrea versipora* suggests that there is biological control influencing the temperature dependent fractionation, however not all trace elements are subject to the same level of physiological fractionation, possibly due to different ionic pathways into the calcification fluid.

All corals can calcify different shaped aragonitic crystals depending on a range of environmental conditions including temperature and daylight (Coles & Jokiel 1978; Kleypas et al. 1999). A thorough investigation of the calcification in *Plesiastrea versipora* was conducted by Howe and Marshall (2002), and three dominant crystal forms were observed in a temperature dependent diel pattern. These forms included two forms during daytime light calcification, small spheroid crystals and at higher temperatures small needle-shaped crystals (Howe & Marshall 2002). The dark calcification deposition was described as an amorphous sheet-like cementation (Howe & Marshall 2002) and it is likely that these three forms of crystal structure have different abilities to substitute other cations for Ca^{2+}.

Long Timescale Trace Element Records – Fast Growing Corals

The differences in trace element systematics observed between the *Plesiastrea versipora* colonies with fast extension rates (> 4 mm yr^{-1}) and those with slow extension rates (< 3 mm yr^{-1}) will be discussed separately in different sections. The trace element analyses presented in this section are shorter than the length of the coral core extracted (determined in Chapter 4), due to the loss of the primary growth axis. As described in the methods, LA-ICP-MS analyses are conducted down the main growth axis to provide the most reproducible concentrations (Sinclair 1999; Fallon 2000). Trace element data not collected on the main growth axis displays an irregular or skewed seasonal cycle and has not been presented here.

To examine the long term temperature changes recorded in the *Plesiastrea versipora* cores a combination of Ba/Ca and Sr/Ca ratios were used. Ba/Ca was chosen because it indicated the most coherent seasonal cycle and has a greater percentage change per °C than U/Ca. A linear trend was fitted to the length of each of the *P. versipora* records to assess the change through time in the temperature record and whether any obvious trends could be determined.

The high coherency between Sr/Ca and U/Ca was observed throughout the long records of all coral cores. The Seacliff B record (Figure 5.20) extends for 63 years before the primary growth axis was lost. The Ba/Ca record displayed variable amplitude over the seasonal cycle on a multi-year scale. Greater variation was observed with the winter minima than summer maxima. The B/Ca record indicated a shift in the mean value in ~ 1978, however given the low coherency of B/Ca with SST, this may be a vital effect or an artefact in changing calcification rather than a real environmental signal. The Sr/Ca and U/Ca records did not display an apparent seasonal cycle for all years. The Seacliff B coral indicated a temperature increase of 1°C over the last 53 years in the Ba/Ca and Sr/Ca signals.

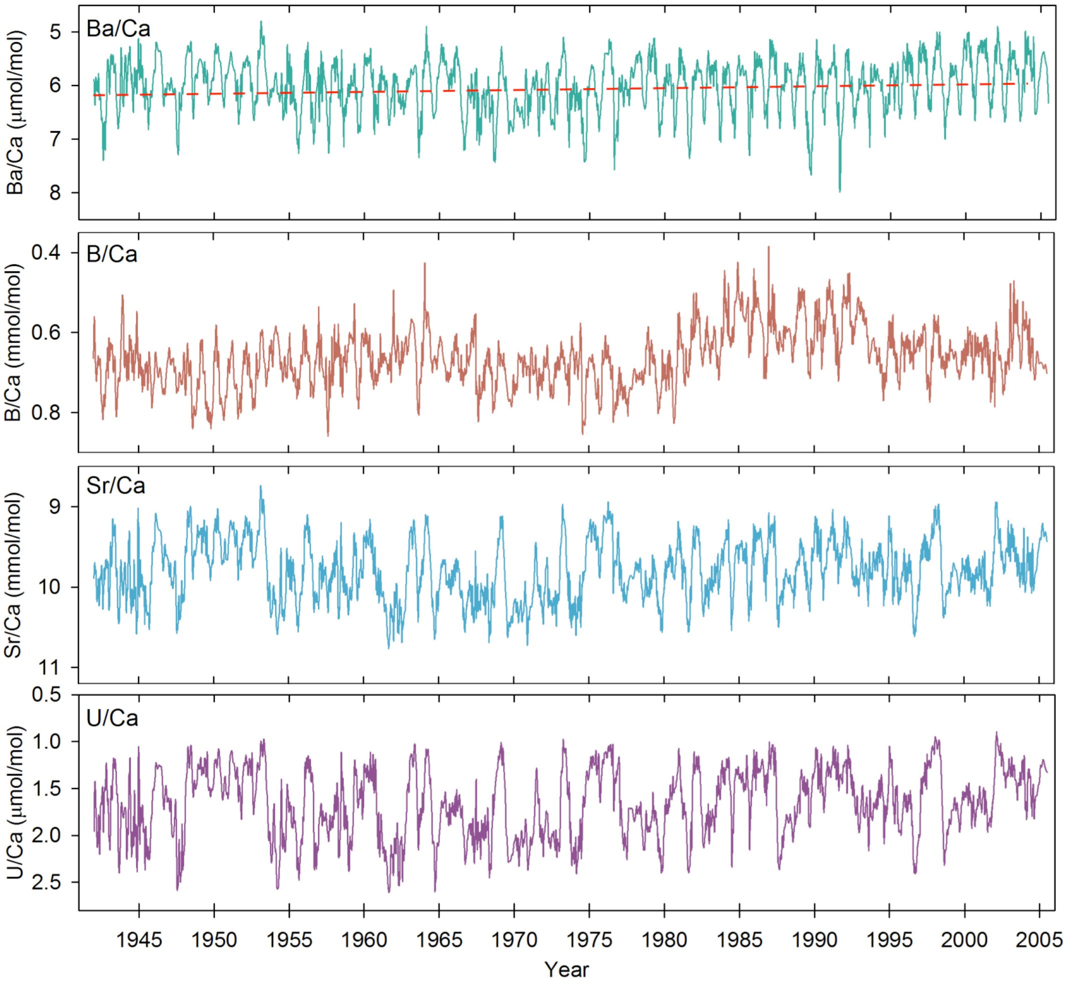

Figure 5.20: Trace element profiles for Seacliff B05 from Seacliff Reef, Gulf St Vincent. Average extension rate of Seacliff B05 is 7 mm yr^{-1}. Resolution of running average is approximately fortnightly (250 µm).

Table 5.2: Correlation coefficients of Seacliff B05 coral at 250 μm resolution ($p < 0.001$)

	B/Ca	Sr/Ca	Ba/Ca
Sr/Ca	0.29		
Ba/Ca	0.46	0.59	
U/Ca	0.27	0.94	0.45

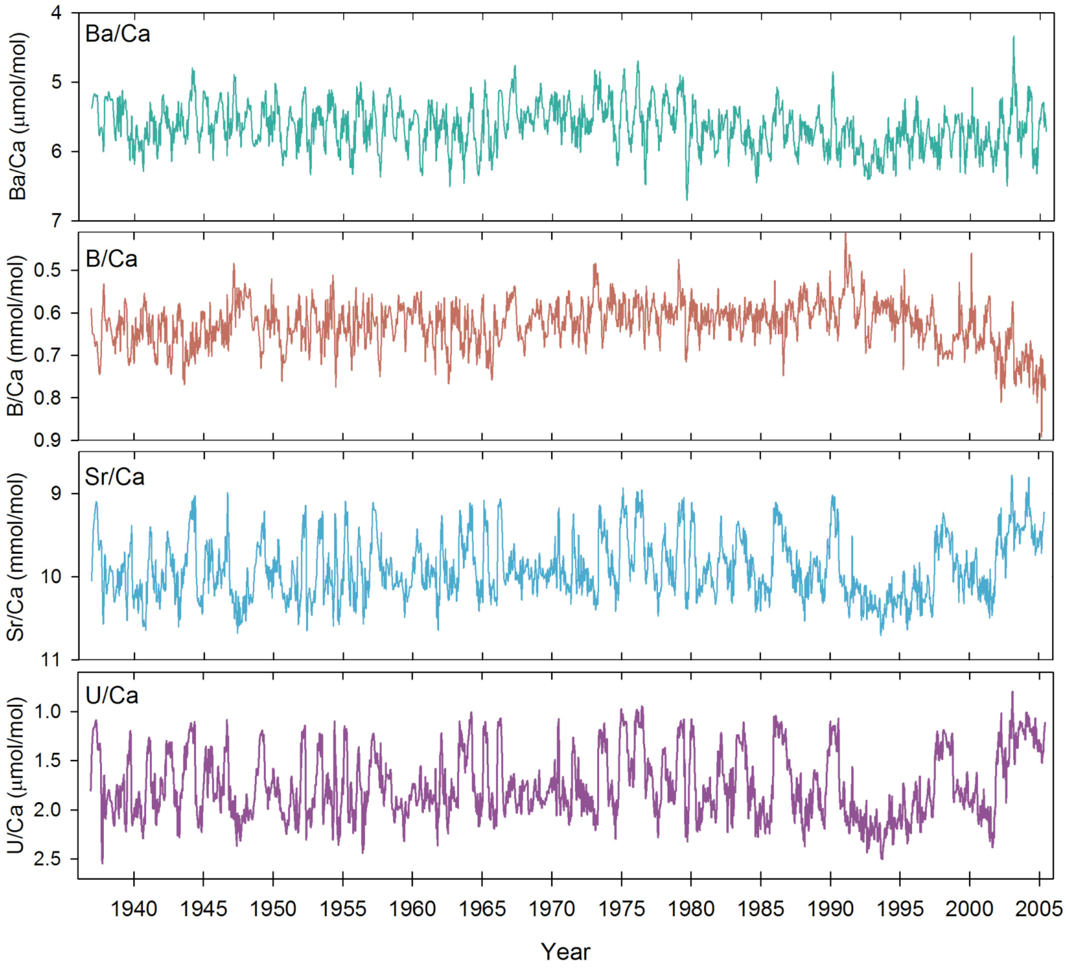

Figure 5.21: Trace element profiles for Troubridge 05, Gulf St Vincent. Average extension rate of Troubridge 05 is 7 mm yr^{-1}. Resolution of running average is approximately fortnightly (250 μm).

Table 5.3: Correlation coefficients of Troubridge coral ($p < 0.001$).

	B/Ca	Sr/Ca	Ba/Ca
Sr/Ca	-0.25		
Ba/Ca	0.29	0.46	
U/Ca	-0.28	0.95	0.42

The record from the Troubridge coral (Figure 5.21) spans 69 years and the Ba/Ca signal displays a variable amplitude to the seasonal signal throughout the record. B/Ca displays a decreasing trend from the early 1990s. The Sr/Ca and U/Ca have the lowest concentrations in the tissue zone and do not display a coherent seasonal cycle.

The Troubridge coral (Figure 5.21) indicated a larger temperature change over the length of the core compared with Seacliff B of 3-4°C. This colony also displays a slight cooling trend over the 1950-1960s and the 1980s. The temperature trend may be unreliable due to the low concentration change per °C in the trace element-SST calibrations or the SST data set from Port Stanvac may not be accurate in recording seasonal maxima and minima.

Long Timescale Trace Element Records – Slow Growing Corals

The longest trace element record for the South Australian gulfs generated in this study was approximately 200 years and was from the coral Seacliff A (1818-2005; Figure 5.22); the second longest record was from the Taylors Island coral in Spencer Gulf (1874-2003; Figure 5.23). All three of the long slow growing coral cores (Seacliff A, Edithburgh (Figure 5.24) and Taylors Island) and 2 shorter colonies from Whyalla (Figure 5.25) and Dutton Bay (Figure 5.26) display a bimodal distribution in the trace elements. The bimodal behaviour in Sr/Ca and U/Ca was reproducible down the same laser track, and also between neighbouring tracks on different calices with an offset when concentrations changed, but with a similar magnitude. Potential mechanisms to explain the trace element behaviour will be discussed below.

The Ba/Ca signal in Seacliff A (Figure 5.22) also displays a certain degree of bimodal behaviour, with large shifts occurring throughout the record. This is reflected in stronger correlations between Ba/Ca, Sr/Ca and U/Ca. If the temperature calibration was precise then these shifts would correlate to a temperature shift of almost 20°C. The amplitude of the seasonal cycle in all trace elements is reduced to what would be expected with a temperature range of 12°C throughout the year. It is apparent that the trace elements in Seacliff A are not accurately recording SST and are reflecting a calcification/precipitation process that is physiologically controlled by the coral polyp rather than external environmental conditions.

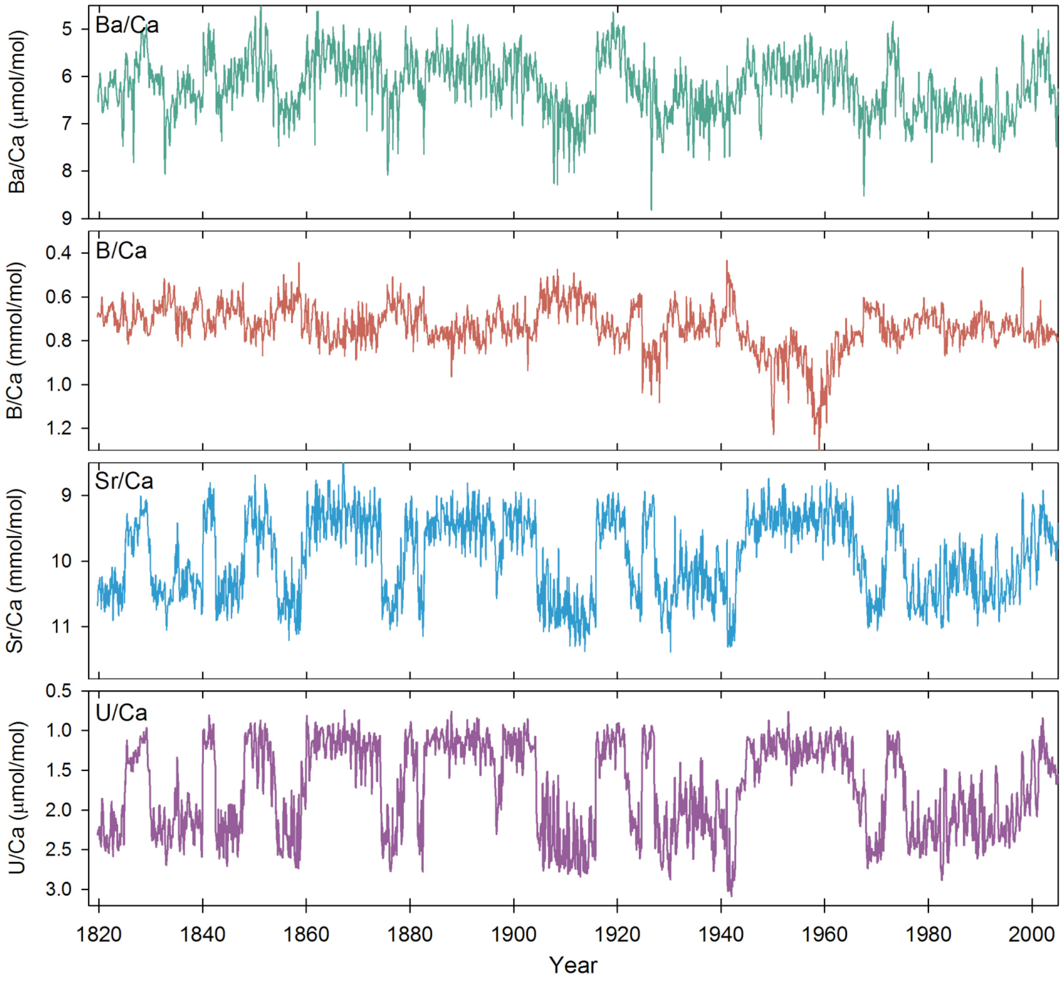

Figure 5.22: Trace element profiles for Seacliff A05 from Seacliff Reef, Gulf St Vincent. Average extension rate of Seacliff A05 is 2 mm yr^{-1}. Resolution of running average is approximately fortnightly (100 µm).

Table 5.4: Correlation coefficients of Seacliff A05 coral

	B/Ca	Sr/Ca	Ba/Ca
Sr/Ca	-0.55		
Ba/Ca	-0.29	0.77	
U/Ca	-0.54	0.97	0.73

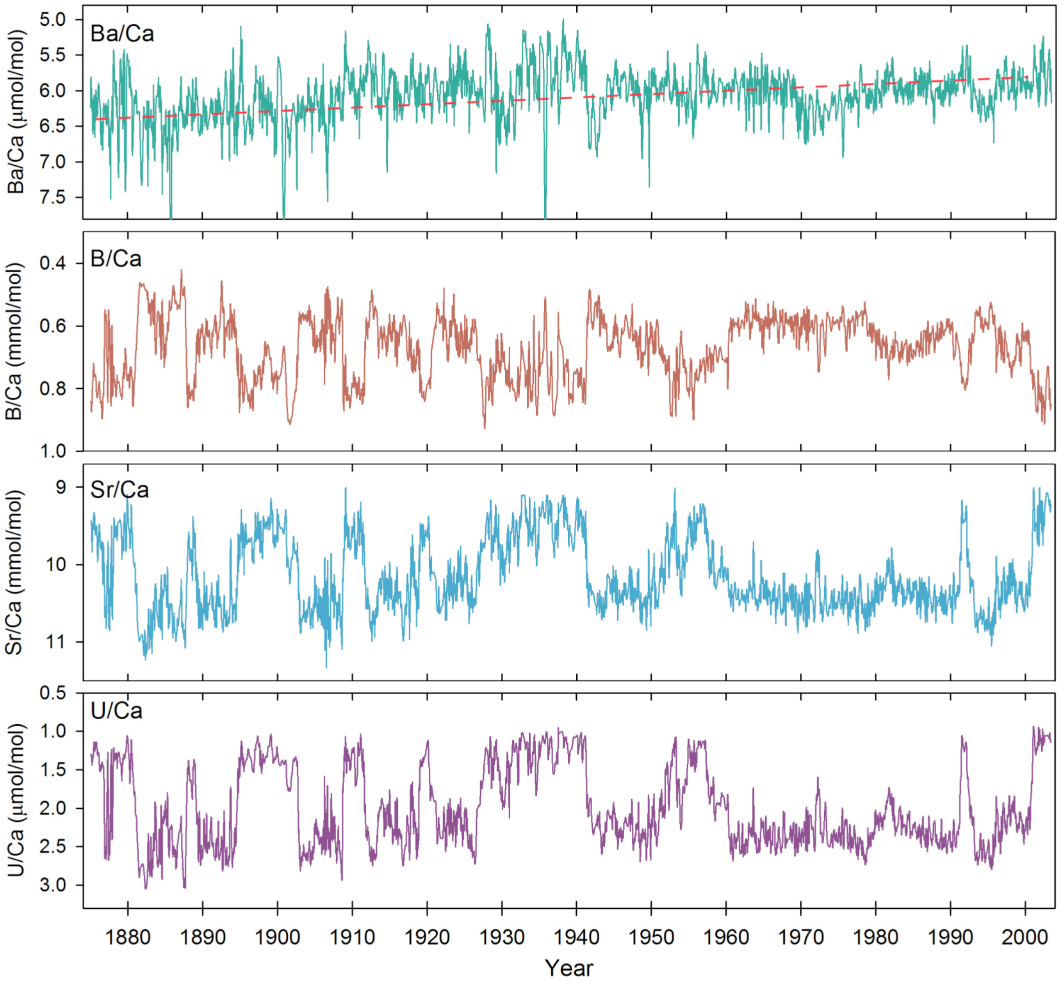

Figure 5.23: Trace element profiles for Taylors Island A03, Spencer Gulf. Average extension rate of Taylors Island A03 is 1.5 mm yr^{-1}. Resolution of running average is approximately fortnightly (100 µm).

Table 5.5: Correlation coefficients of Taylors Island coral at 100 µm resolution.

	B/Ca	Sr/Ca	Ba/Ca
Sr/Ca	-0.79		
Ba/Ca	-0.24	0.36	
U/Ca	-0.82	0.96	0.25

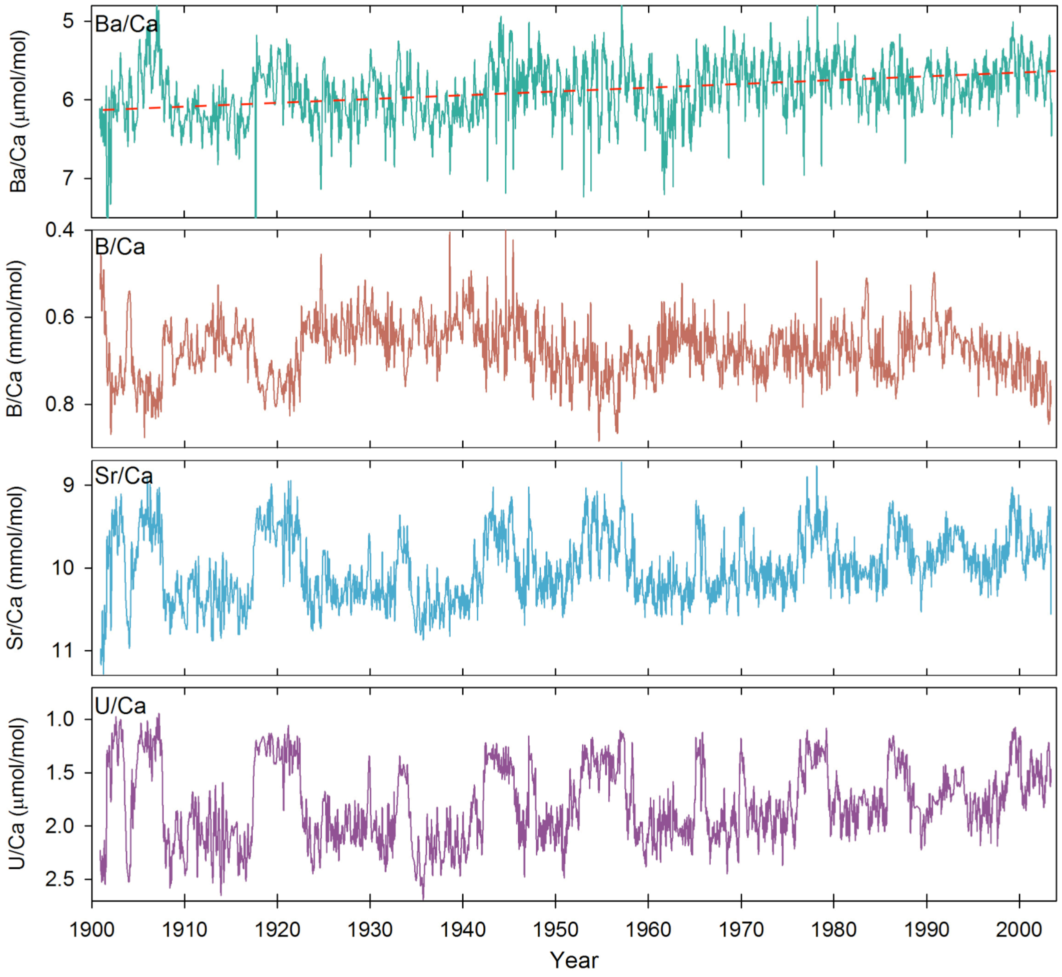

Figure 5.24: Trace element profiles for Edithburgh 03 from Edithburgh, Gulf St. Vincent. Average extension rate of Edithburgh 03 is 2.5 mm yr^{-1}. Resolution of running average is approximately fortnightly (100 µm).

Table 5.6: Correlation coefficients of Edithburgh coral at 100 µm resolution

	B/Ca	Sr/Ca	Ba/Ca
Sr/Ca	-0.41		
Ba/Ca	-0.17	0.57	
U/Ca	-0.45	0.93	0.44

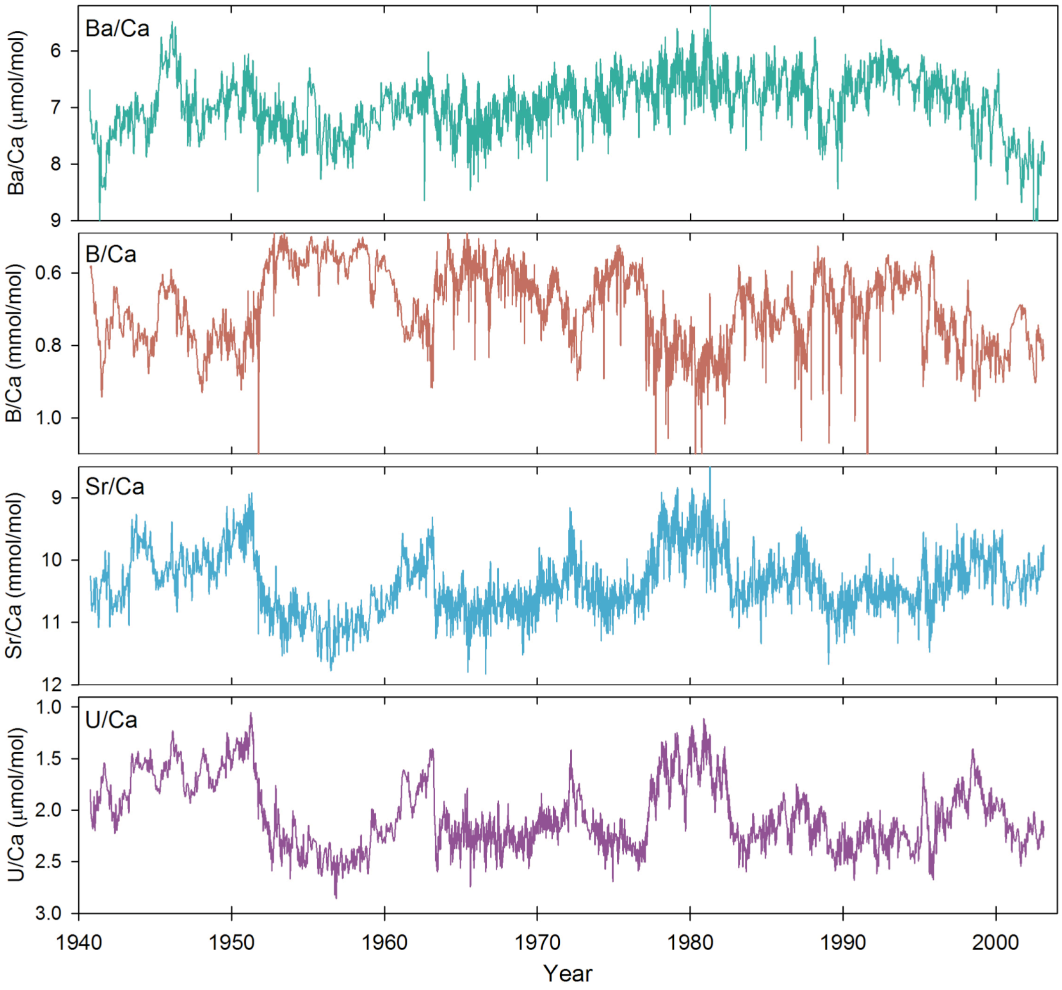

Figure 5.25: Trace element profiles for Whyalla A03 from Point Lowly, Whyalla, Spencer Gulf. Average extension rate of Whyalla A03 is 1.2 mm yr^{-1}. Resolution of running average is approximately fortnightly (100 µm).

Table 5.7: Correlation coefficients of Whyalla A03 coral at 100 µm resolution

	B/Ca	Sr/Ca	Ba/Ca
Sr/Ca	-0.69		
Ba/Ca	-0.14	0.48	
U/Ca	-0.67	0.86	0.35

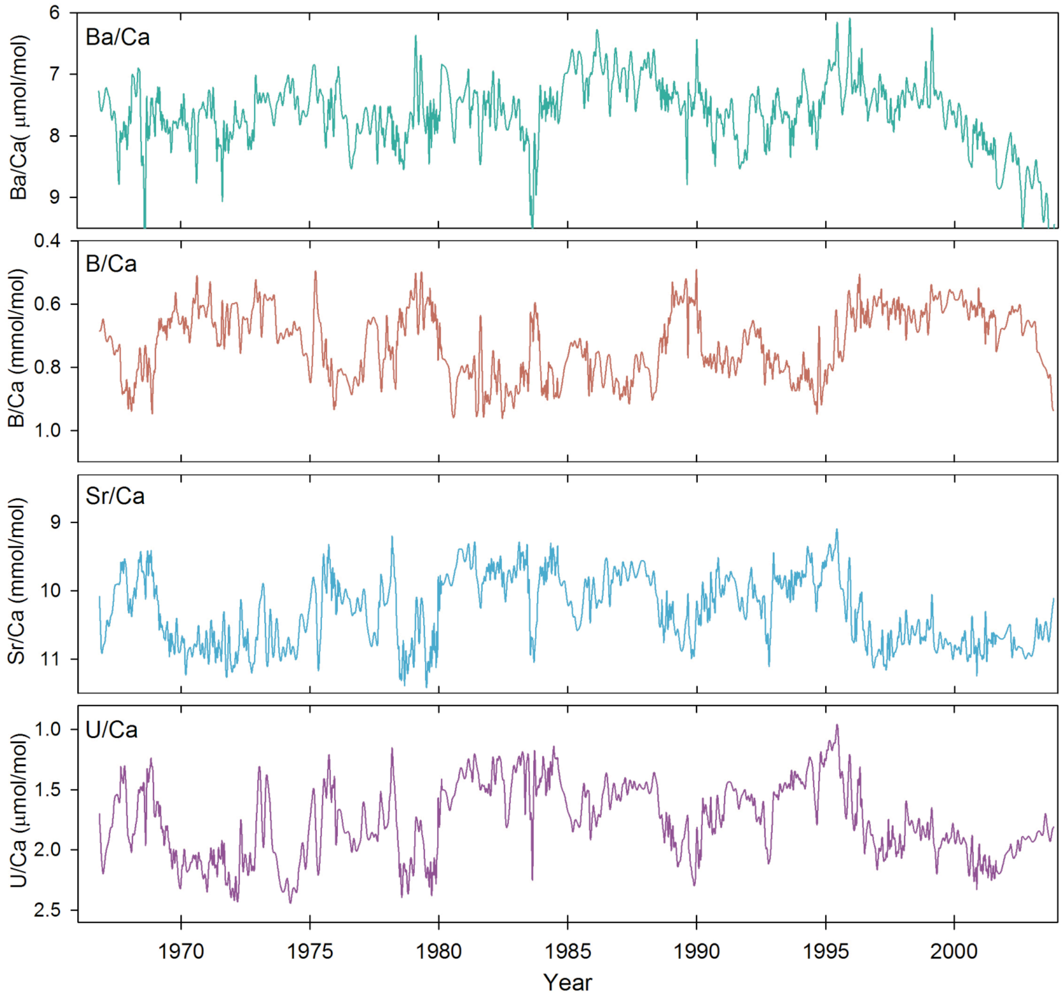

Figure 5.26: Trace element profiles for Dutton Bay A03 from Dutton Bay, Coffin Bay. Average extension rate of Dutton Bay A03 is 3 mm yr^{-1}. Resolution of running average is approximately fortnightly (150 μm).

Table 5.8: Correlation coefficients of Dutton Bay A03 coral at 150 μm resolution

	B/Ca	Sr/Ca	Ba/Ca
Sr/Ca	-0.69		
Ba/Ca	0.077	0.29	
U/Ca	-0.58	0.89	0.28

The Taylors Island trace element data spans 125 years. The Ba/Ca record in Taylors Island (Figure 5.23) indicates several extremely cool winters in the early part of the record. Using the temperature calibration derived in Figure 5.15 implies these winters were much lower than the SST in this region in modern times and the signal is unlikely to be related to an environmental or temperature record alone. The trace element data becomes more stable from 1940, with fewer fluctuations in Ba/Ca, Sr/Ca and U/Ca. It is unknown why the coral calcification changed during that period. The overall trend for the Ba/Ca data indicates gradual warming over the length of the record. However, as the calibration for this coral is not considered to be primarily influenced by SST, it may be a vital effect rather than due to environmental change.

The Edithburgh record (Figure 5.24) spans 105 years and is similar to the other slow growing corals, with a bimodal distribution in Sr/Ca and U/Ca. The Ba/Ca record for this coral indicates a variable amplitude in the height of the seasonal cycle, with more cool winters than warmer summers. The trend from Ba/Ca in this coral is of gradual warming of ~ 2°C, with a mean Ba/Ca derived temperature of 17.5°C at the start of the coral record increasing to 19.5°C. This correlates to 2°C above the modern mean SST at Port Stanvac of 17.5°C.

The Whyalla (Figure 5.25) and Dutton Bay (Figure 5.26) records span 62 and 39 years respectively. Both of these corals are from shallow sites with large fluctuations in salinity throughout the year. Calibrations were not conducted for these corals because the temperature dependence of Ba/Ca, Sr/Ca and U/Ca suggested very low concentration change per °C and therefore little temperature dependence on the incorporation of these trace elements. This hypothesis was supported by the long trace element records which indicate a variable average concentration of trace elements and little apparent seasonal cycle.

The slow growing corals gave evidence of different trace element behaviour to the *Plesiastrea versipora* cores growing at greater than 3 mm yr^{-1}. Corals with more rapid extension rates display regular seasonal variation, and calibrations for Sr/Ca and U/Ca are comparable to published trace element-SST calibrations. However, several of the slow growing corals do not display a high degree of temperature dependence in their trace element fluctuations on a seasonal time scale. Variations in the fidelity of corals with different growth rates to accurately record SST has been observed in other high-latitude, slow-growing corals (Cardinal et al. 2001). However, previous authors have suggested that complete resolution of the entire amplitude of the annual cycle is not necessary to determine interannual to interdecadal climate variations (Quinn et al. 1996b; Bagnato et al. 2004).

Such extreme disparity between the trace element calibrations for colonies of *Plesiastrea versipora* growing within the same reef, or under similar environmental conditions in the same gulf, cannot be neglected when assessing the reliability of fossil colonies. The seasonal amplitude reduction observed in the trace element concentrations in the slow growing corals may be a function of growth rate dependent fractionation combined with seasonally variable growth rate. The effects of growth rate on trace elements values is well known (de Villiers et al. 1994), and the distortion of the sinusoidal shape of trace element records is also well-established (Barnes et al. 1995), but the combined effect of these two factors on the amplitude of trace element concentrations over a seasonal cycle is not well understood (Cardinal et al. 2001).

Bimodal Trace Element Behaviour

The ‘bimodal’ or ‘stepped’ trace element behaviour is reproducible both over the same track and on nearby tracks in neighbouring corallites and is a distinctive feature of the coral lattice in the slow growing *Plesiastrea versipora* colonies.

Unfortunately, the mechanisms driving the trace element behaviour in the slow growing corals was not able to be determined during the course of this study. The bimodal behaviour in Sr/Ca and U/Ca is considered to be driven by the coral rather than any external environmental influences because there is no correlation in the ‘mode-switching’ from high to low concentrations between corals in different sites.

A frequency analysis conducted on four *Plesiastrea versipora* cores including Seacliff B, Seacliff A, Taylors Island and Edithburgh displays the bimodal distribution of Sr/Ca and U/Ca clearly in Seacliff A and Taylors Island (Figure 5.27). The Seacliff B coral has a ‘normal’ trace element distribution in a bell curve which centres on the mean SST value of 17.5°C. The Edithburgh core indicates a slight bimodal distribution, but it is not as coherent as the behaviour of Sr/Ca and U/Ca observed in Seacliff A or Taylors Island.

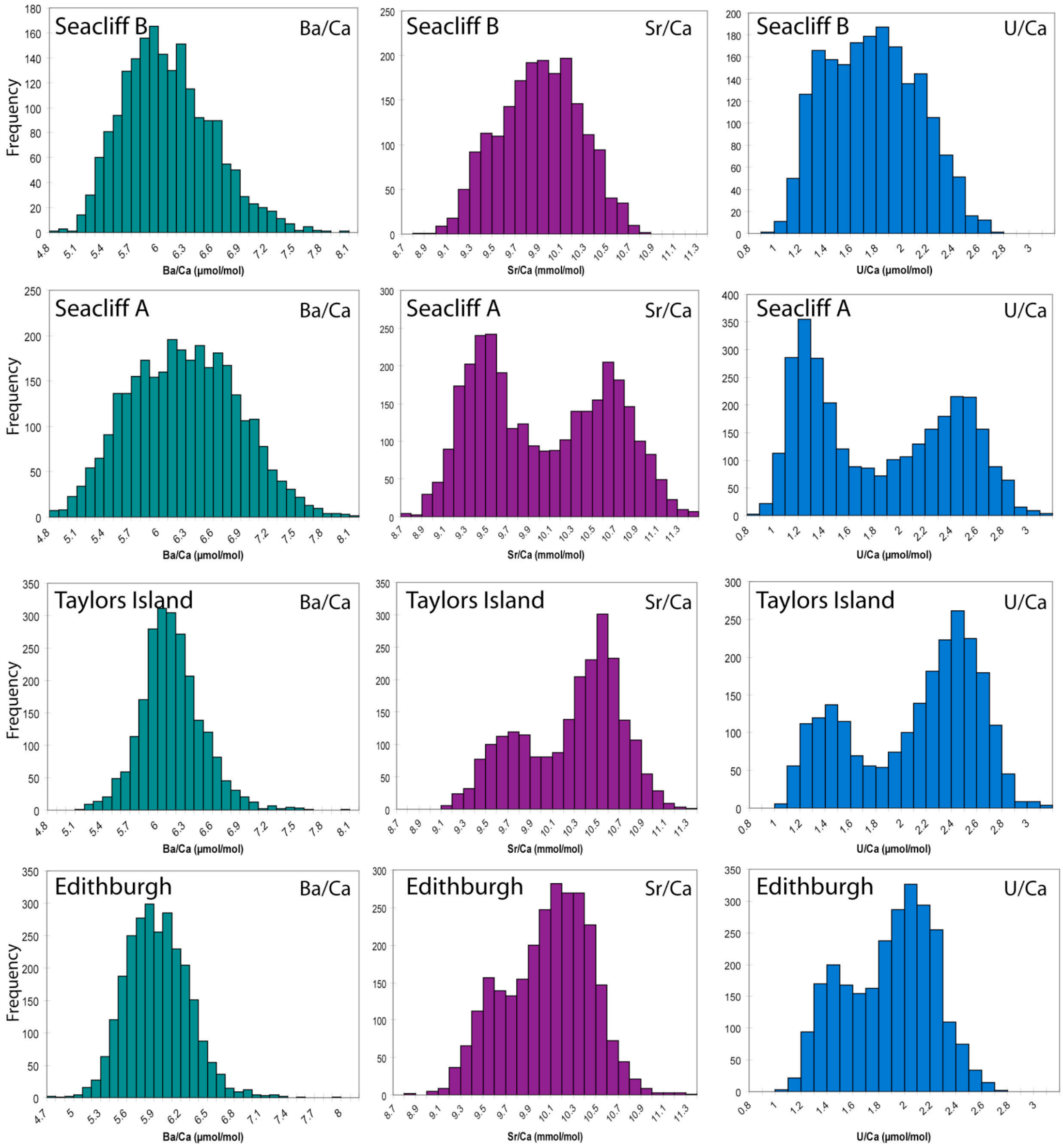

Figure 5.27 Frequency distribution of Ba/Ca, Sr/Ca and U/Ca for four corals; Seacliff B, Seacliff A, Taylors Island and Edithburgh. Bimodal distribution of trace elements is apparent in Sr/Ca and U/Ca concentrations in Seacliff A and Taylors Island corals.

One potential hypothesis for this variation is Edithburgh may be on the verge of the threshold for slow growing versus fast growing trace element incorporation behaviour. The average extension rate of Edithburgh is between 2-3 mm yr^{-1}; where as both Seacliff A and Taylors Island are less than 2 mm yr^{-1}. The most probable explanation for the different behaviour of Ba/Ca compared with Sr/Ca and U/Ca in the slow growing cores is that it enters the calcification fluid in a different ion transport pathway. If this hypothesis is correct then the Ba ion transport pathway may be subject to a different level of biological control from the coral polyp.

There was no observed correlation between analysing different skeletal elements and jumps in the Sr or U concentrations in the ICP-MS while viewing the laser scanning on the video monitor. A visual correlation between skeletal elements and data would be difficult to determine during analysis as data is collected on a log scale on the ICP-MS, so observing shifts of 1-2 mmol/mol or μmol/mol is unlikely. However, the differences in skeletal structure between the slow growing corals and the fast growing corals (Figure 4.3; Figure 5.4) would suggest that a laser track is likely to encounter more architectural elements on the fast growing corals than on the slow growing corals. There was no correlation observed between the bimodal behaviour of Sr/Ca and U/Ca with minor trace elements in the slow growing corals (data presented in Chapter 6). An examination of the slow growing corals using other micro-analytical techniques such as nano-SIMS may be able to establish the influence of different architectural components of the coral skeleton.

It is unlikely that the bimodal distribution of elements is due to slow coral calcification. Calcification only at certain times of the year would bias the temperature recorded in the skeleton, and this feature would be consistent between different coral colonies. A study conducted by Howe and Marshall (2002) determined that *Plesiastrea versipora* from Victoria continued growing throughout the year, but given the large differences in extension rate in the South Australian corals, not all colonies may continue calcifying throughout the year.

The incorporation of trace elements into coral aragonite is not a simple reaction only controlled by temperature. At the crystal scale, trace elements such as Sr may not be distributed homogenously (Hart & Cohen 1996; Greegor et al. 1997; Allison et al. 2001). During the biomineralisation process, trace element fractionation can be effected by a number of mechanisms (a more detailed description is in Chapter 2) related to coral growth rate (de Villiers et al. 1995), degree of autotrophy or heterotrophy, or environmental parameters including sea water salinity and alkalinity

(Shen & Dunbar 1995). A recent study examining trace elements on a nanometre scale concluded that biological processes drive trace element incorporation into coral skeletons and seasonal variations in trace elements that correlate with SST are indicative of a secondary process (Meibom et al. 2007).

Recent discussions in the literature (Allison et al. 2005; Sinclair et al. 2006; Meibom et al. 2007) suggest that the majority of micro-scale analytical studies have observed a strong biological influence over small spatial scales. When the high frequency heterogeneity is smoothed, which is usual practice with high resolution studies such as LA-ICP-MS, the correlation with several trace elements and SST becomes apparent. The observation that on a seasonal time scale trace elements and stable isotopes correlate with environmental factors such as SST, but on a micro-structural scale there is no correlation due to high-frequency 'noise' implies that seasonal variations in environmental conditions are not the only mechanism controlling trace element incorporation into coral skeletons. The pathways that transport different chemical elements into coral skeletons may take place across protein mediated pathways (Cohen & McConnaughey 2003) that may also be sensitive to temperature.

Stable Isotopes

Stable isotopes were analysed in three colonies of *Plesiastrea versipora*, Seacliff A, Seacliff B and Edithburgh to assess the paleoenvironmental archive recorded by δ^{18}O and δ^{13}C. This section assesses δ^{18}O and its potential as a paleothermometer in *Plesiastrea versipora*; the δ^{13}C data is presented in Chapter 7. One of the first observations from the stable isotope data was the large spread in the δ^{13}C data (Figure 5.28) compared with other coral studies. The Seacliff A colony displayed a range in δ^{18}O values from -1.8 to 0.8‰, the Seacliff B colony had δ^{18}O values ranging from -2.3 to -1.3‰ and the Edithburgh colony had δ^{18}O values ranging between -2.4 to -1.4‰. The difference in δ^{18}O values between the two Seacliff colonies may be related to growth rate dependent fractionation (McConnaughey 1989). The difference in δ^{18}O values between the Seacliff corals and the Edithburgh coral cannot be explained by this mechanism, as the growth rate of Edithburgh coral is ~ 3 mm yr^{-1} and situated between the growth rates of the two Seacliff corals.

However, the Edithburgh colony is located on the western side of Gulf St. Vincent and may have different zooxanthellae species or symbiont concentrations in the coral polyps, which could change the metabolic fractionation of the stable isotopes (Grottoli & Wellington 1999).

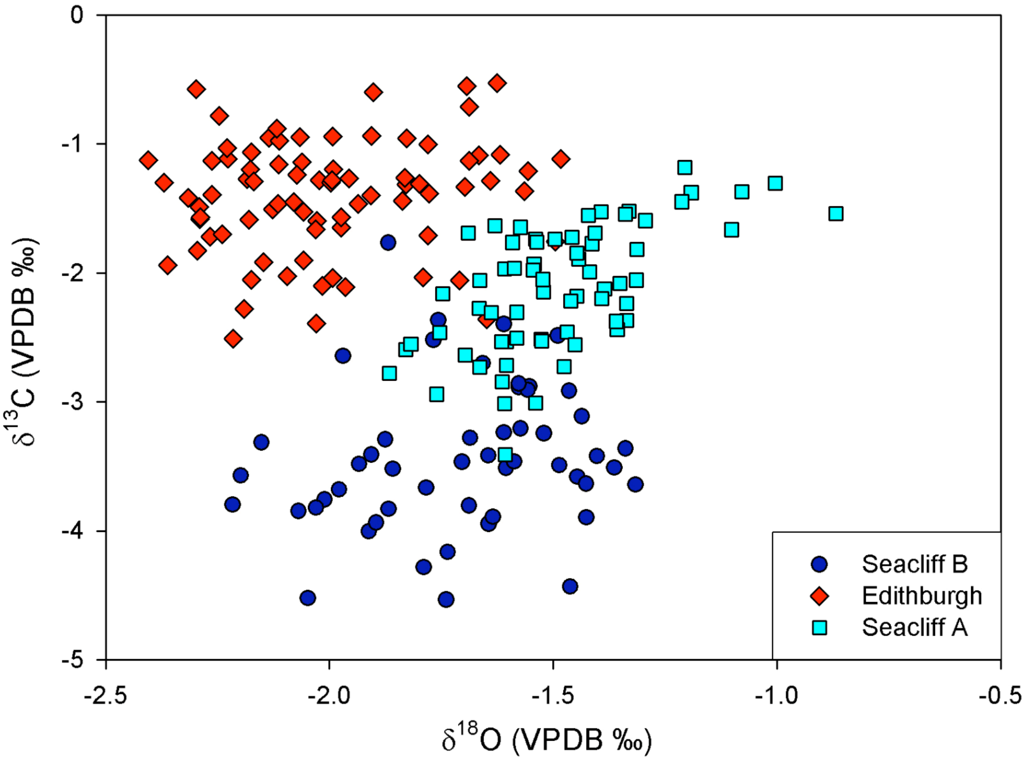

Figure 5.28: Cross plot of $\delta^{13}C$ and $\delta^{18}O$ for the three corals analysed. Seacliff B is dark blue circles; Seacliff A is aqua squares and Edithburgh is red diamonds. The Edithburgh coral is situated on the western coastline of Gulf St. Vincent at ~ 4 m water depth, whereas the Seacliff corals are on the eastern coastline of Gulf St. Vincent at ~ 14 m water depth.

The $\delta^{18}O$ values were significantly more enriched compared with tropical coral values (Weber & Woodhead 1972; Gagan & Chivas 1995). One possible explanation for the variability in the stable isotope values may be related to the difference in extension rate and skeletal density between the three corals (discussed in Chapter 4). Both amount of light and growth-rate dependent isotopic fractionation are known to influence isotopic composition of coral skeletons (McConnaughey 1989; Swart et al. 1996b). McConnaughey (1989) demonstrated a distinct spatial structure in the equilibrium offsets from inorganic aragonite in coral skeletons. This offset is referred to as a ‘vital effect’ and may be related to both metabolic and kinetic fractionation in coral skeletons.

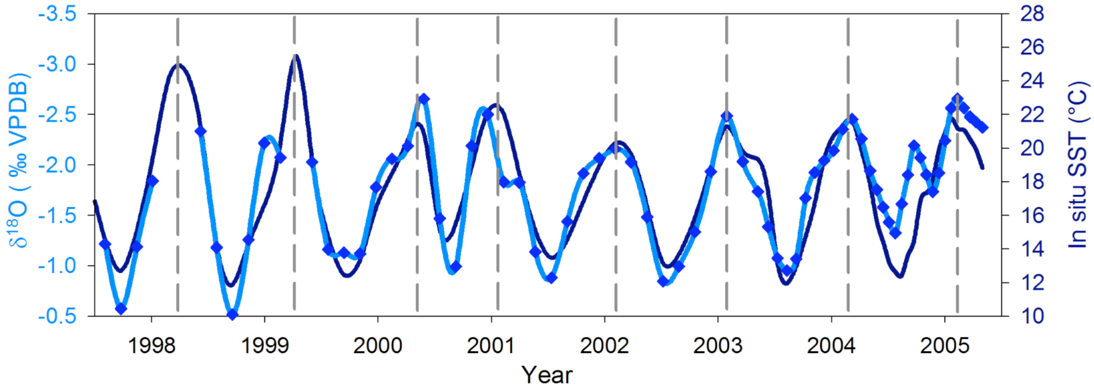

Figure 5.29: Comparison of $\delta^{18}O$ analyses from Seacliff B for an 8 year calibration period with *in situ* SST from Pt Stanvac. Extension rate for Seacliff B is 6 mm yr^{-1}.

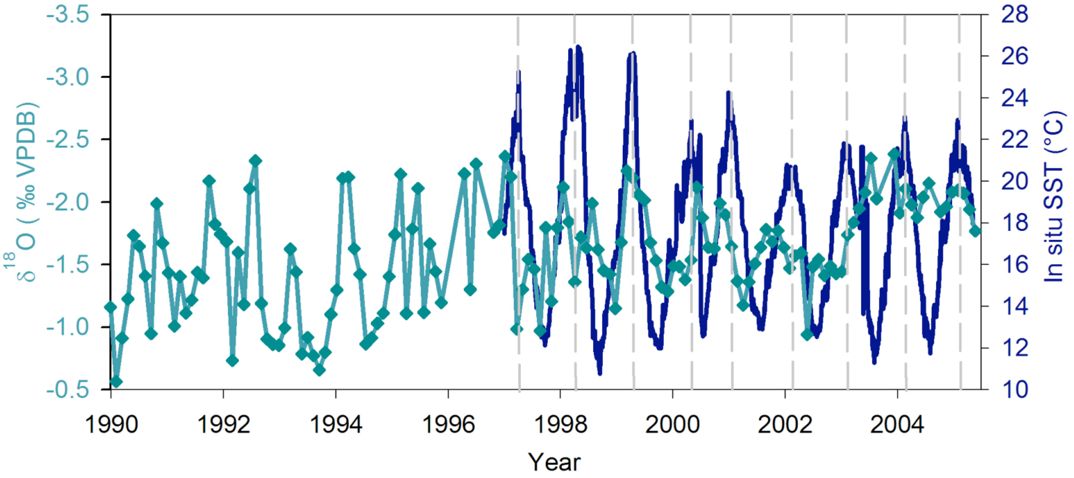

Figure 5.30: Comparison of $\delta^{18}O$ analyses from Seacliff A for a 14 year calibration period with *in situ* SST from Pt Stanvac. Extension rate for Seacliff A is 2 mm yr^{-1}.

The relationship between $\delta^{18}O$ and SST is illustrated for the two Seacliff corals in Figure 5.29 and 5.30. Isotopic samples were milled every 100 μm down the growth axis for both colonies. The sampling resolution for Seacliff B was 400 μm (every fourth sample analysed) to achieve approximately fortnightly resolution. The sampling resolution for Seacliff A was 100 µm which equated to one sample every two-three weeks. The coral chronology was established by correlating SST maxima and minima with $\delta^{18}O$ minima and maxima, respectively, and linearly interpolating between these points. The seasonal cycle of Seacliff B shows a good correlation with SST (Figure 5.29) but Seacliff A only displays approximately half the seasonal amplitude you would expect from this site (Figure 5.30).

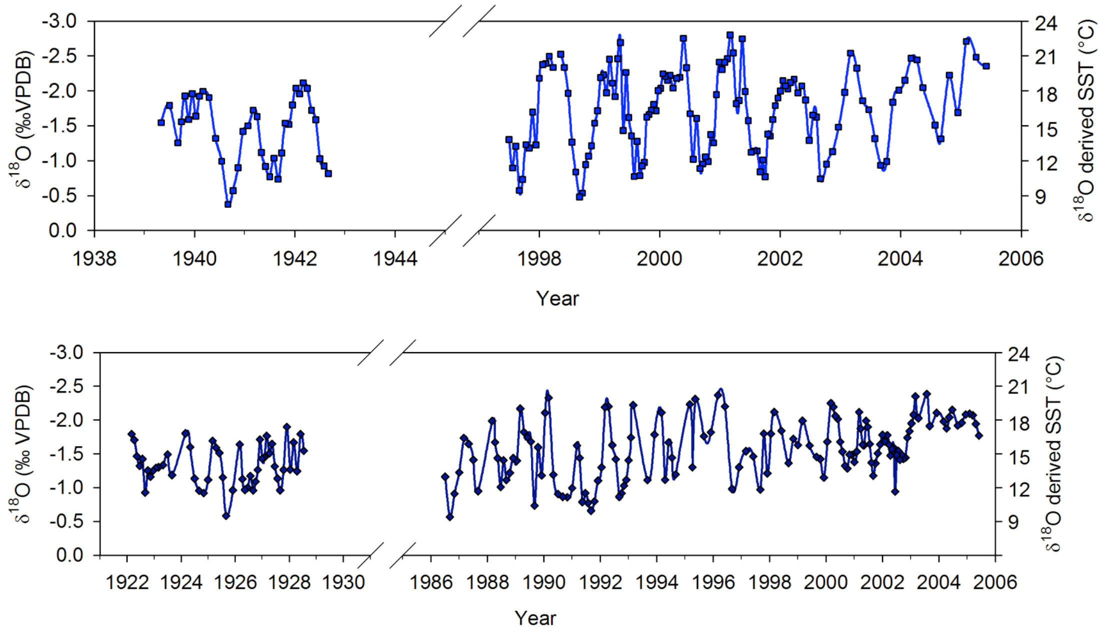

Figure 5.31: Fortnightly-monthly resolution $\delta^{18}O$ analyses for two periods in the Seacliff corals. The upper panel is Seacliff B and the lower panel is Seacliff A.

The reduced amplitude in the seasonal cycle expressed by the $\delta^{18}O$ values in Seacliff A is similar to the reduced amplitude observed in trace element concentrations in this coral. Figure 5.30 indicates a greatly reduced seasonal amplitude in the first three years of sampling near the top of the coral and this reduced signal was also apparent in the trace element data and was suggested to be a function of tissue zone smoothing.

A $\delta^{18}O$ – SST calibration equation was developed using regression analysis on the Seacliff B coral to calibrate the $\delta^{18}O$ paleothermometer for this coral. The Seacliff A colony was not used for the calibration because it did not record the complete seasonal cycle.

The calibration equation is:

$$\delta^{18}O = -0.9 - 0.16 \times SST°C$$

The calibration equation for *Plesiastrea versipora* has a lower slope than many calibrations for *Porites* in tropical regions (Gagan et al. 2000), but is comparable to mid-latitude *Porites* studies (Quinn et al. 1996a; Suzuki et al. 1999) and shows a higher slope than other mid-latitude studies (Mitsuguchi et al. 1996; Ayling et al. 2006).

The general arch-shape of the $\delta^{18}O$ seasonal profiles mimics the results of the trace element profiles presented earlier in this chapter. This seasonal shape is in agreement with numerical models of skeletal growth with variable inter-annual extension rates (Taylor et al. 1993; Barnes et al. 1995; Taylor et al. 1995). The calibration equation derived from the Seacliff B $\delta^{18}O$ analyses was applied to $\delta^{18}O$ values from Seacliff A and Edithburgh to assess temperature/salinity variations over longer records through time. However, because the calibration has been derived from only one coral; applying the transfer function to $\delta^{18}O$ values from the two other corals will increase the error in interpreting $\delta^{18}O$ derived temperature variations over time.

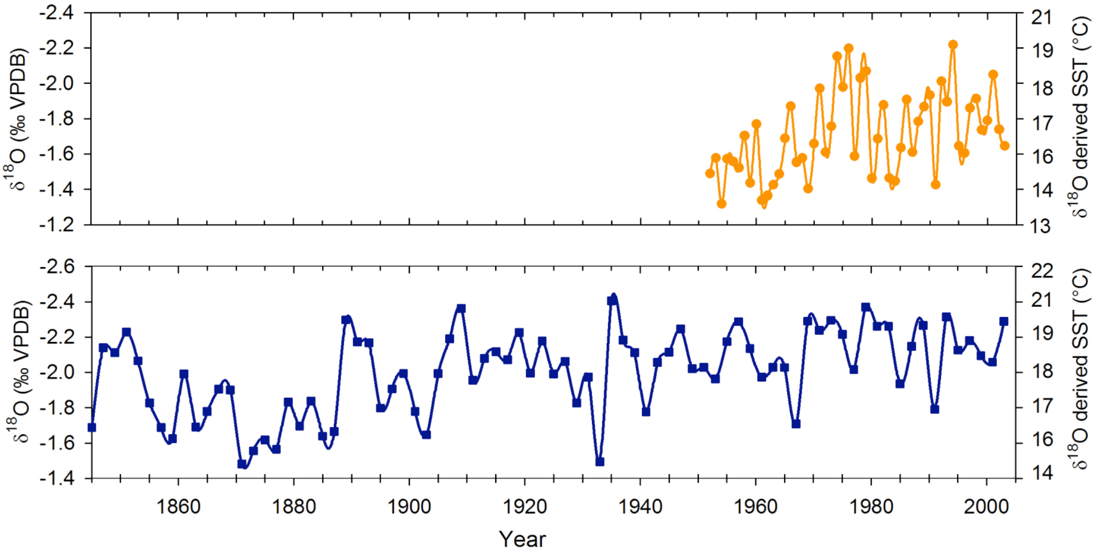

Figure 5.32: Low resolution $\delta^{18}O$ analyses for Seacliff B (annual samples - orange) and Edithburgh (biennial samples - blue).

The mean of the δ^{18}O values for the low resolution analyses in all three corals is similar to the average SST in Gulf St. Vincent of 17.5°C at the start of the three low resolution records. Both the high-resolution sampling for the two Seacliff corals (Figure 5.31) and the annual-biannual sampling for two corals (Figure 5.32) from Gulf St. Vincent indicate gradual warming in the gulf over the last 150 years. Using the calibration equation (above) the warming suggested by Seacliff B is approximately 1.8°C and Edithburgh is 1.5°C. This trend in seawater warming is very similar to the trend suggested by the trace element data. The large shifts between analyses in the three long records are likely to be an artefact of not obtaining a homogenous sub-sample for the annual/biannual sample, rather than real environmental variations. An example of this feature is in Figure 5.32, between 1930-1935 the Edithburgh δ^{18}O values suggest a shift of 6°C – which may be a combination of salinity and temperature changes, but it is more likely to be an artefact of sampling. Due to instrumental usage constraints, more replicate analyses to establish the heterogeneity in the record were not possible.

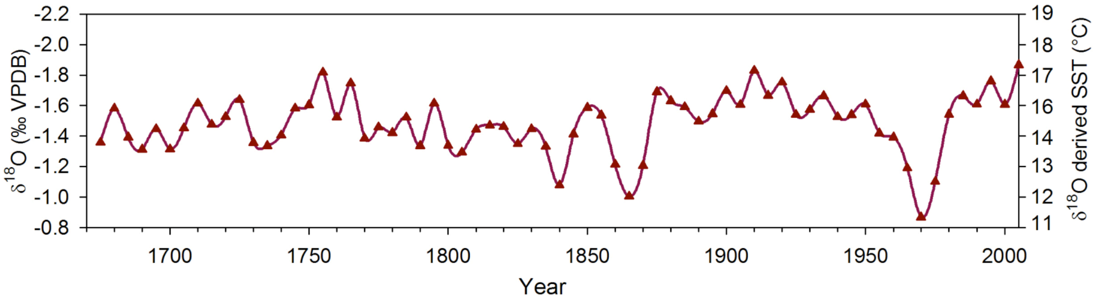

Figure 5.33: Three hundred year record of δ^{18}O analyses for the *Plesiastrea versipora* colony Seacliff A. Samples were the equivalent of 5 years of growth.

The long-term isotopic record from Seacliff A generated by 5-year samples (Figure 5.33) does not suggest the same degree of warming as the shorter records. This 300 year record suggests a more stable temperature with cooling during the late 1700s/early 1800s and also in the 1970s. However, the high resolution samples from this colony did not reflect the full seasonal amplitude so it is likely that there are biological or vital effects confounding the temperature signal recorded in this colony. Interestingly, cool periods were observed in both the Seacliff A and the Edithburgh

δ^{18}O records during the late 1850s and the 1970s. Other cooler periods expressed in the Edithburgh coral during the late 1800s and 1930s was not observed in the Seacliff A record. Variation in salinity in Gulf St. Vincent over the last century may also contribute to the trends observed in Figure 5.32 and 5.33. There was not time during the analytical component of this thesis to analyse bulk samples of Ba/Ca or Sr/Ca to establish the salinity signal from temperature in the δ^{18}O records.

A tale of two corals from Seacliff: Variable growth rates impacting proxy calibrations

The current understanding of coral skeletal structure suggests that errors in the interpretation of environmental proxies may arise as a result of the complex architecture of coral skeletons (Taylor et al. 1993; Lough & Barnes 1997). Individual corallites can reflect large variations in the environmental record due to different calcification rates (McConnaughey 1989; de Villiers et al. 1995), variation within skeletal elements (Patzold et al. 1992), colony topography (Alibert & McCulloch 1997; Cohen & Hart 1997) and sampling resolution (Leder et al. 1996). Variables which have been invoked as controlling influences on skeletogenesis include light intensity and duration (Marshall & Wright 1998; Reynaud et al. 2007), temperature (Cohen & McConnaughey 2003; Marshall & Clode 2004), sedimentary suspension (Shen et al. 1996), turbidity, hydraulic energy (Cohen & Hart 1997) and nutrients (Meibom et al. 2007).

Coral samples that include multiple skeletal elements formed at different times may obscure the reconstructed environmental proxy. Previous studies on corals with large corallites have focused on one skeletal element such as the columella (Watanabe et al. 2003) to overcome this problem. It was not possible to focus on one skeletal element in *Plesiastrea versipora* for either the high-resolution LA-ICP-MS sampling or the milled stable isotope samples due to the architectural complexity of the skeleton and the different densities between colonies. The approach used in this study was to determine the robustness of new coral proxy using independent paleothermometers prior to paleoclimate reconstructions. This may have introduced error in the ability to capture the full amplitude of the seasonal cycle. Previous studies have observed that the theca, columellar and septa grow at different times and contain a different temporal record (Watanabe et al. 2003), whereas other studies on the same species observed no variation in the temporal record between different architectural elements (Bagnato et al. 2004).

A study examining the effect of extension rate on $\delta^{18}O$, indicated a significant impact on SST correlations when the extension rate was below a threshold of 6 mm per year (Felis et al. 2003). Uptake of Sr^{2+} has been shown to be dependent on growth rate as well as temperature and light conditions (Reynaud-Vaganay et al. 2001). The amount of smoothing which occurs during coral calcification is not well understood.

A recent study on the slow growing coral *Diploria labyrinthiformis* from Bermuda, with extension rates of 2-6 mm yr^{-1} evaluated a multi-coral calibration method to determine a universal Sr/Ca-SST calibration equation (Goodkin et al. 2007). Goodkin et al. (2007) suggest that using a multiple-colony calibration yields greater precision and accuracy relative to instrumental SST datasets than single colony calibrations to enable higher confidence when extrapolating to fossil coral reconstructions. The *Diploria* study combined three colonies for their Sr/Ca-SST calibration with growth rates of 3.2-4.2 mm yr^{-1} and discard Sr/Ca information from one colony with an extension rate of 2 mm yr^{-1} (Goodkin et al. 2007). Given the results of the present study examining corals with very different growth rates and consequently very different Sr/Ca-SST (or other trace element-SST calibrations) it appears unlikely that combining calibrations from several different colonies would improve the accuracy of trace element-SST calibrations. Until more is understood about the processes involved in calcification including: 1). how cations are incorporated into coralline aragonite; 2). what control the polyp has in determining rates of cation substitution for Ca^{2+}; 3). concentration variability in seawater over temporal and spatial scales, combining calibrations derived from colonies with different growth rates may not improve precision.

Two corals presented in this thesis, Seacliff A and Seacliff B are from the same reef and the same depth, are located very close together (less than 10 m), on a spatial scale with minimal variability in environmental conditions, yet not only do they display very different extension rates (2mm yr^{-1} versus 7 mm yr^{-1}), the calibrations derived from both trace elements and stable isotopes are very different. The concentrations of trace metal incorporation is also different, this is discussed further in Chapter 6.

There is only one recorded species of *Plesiastrea* in the Indo-Pacific region (Veron 1986), however, there may be differences in the zooxanthellae clades (Rodriguez-Lanetty & Hoegh-Guldberg 2003) which can impact the rate of calcification. Genetic differences between colonies cannot be discounted, but was not within the scope of this thesis to determine. The level of autotrophy compared with heterotrophy is also not well understood in temperate corals. Howe & Marshall (2001) suggested that *Plesiastrea versipora* may be dependent on heterotrophic feeding, but this may also be variable between different colonies.

Correlations between Independent Proxies

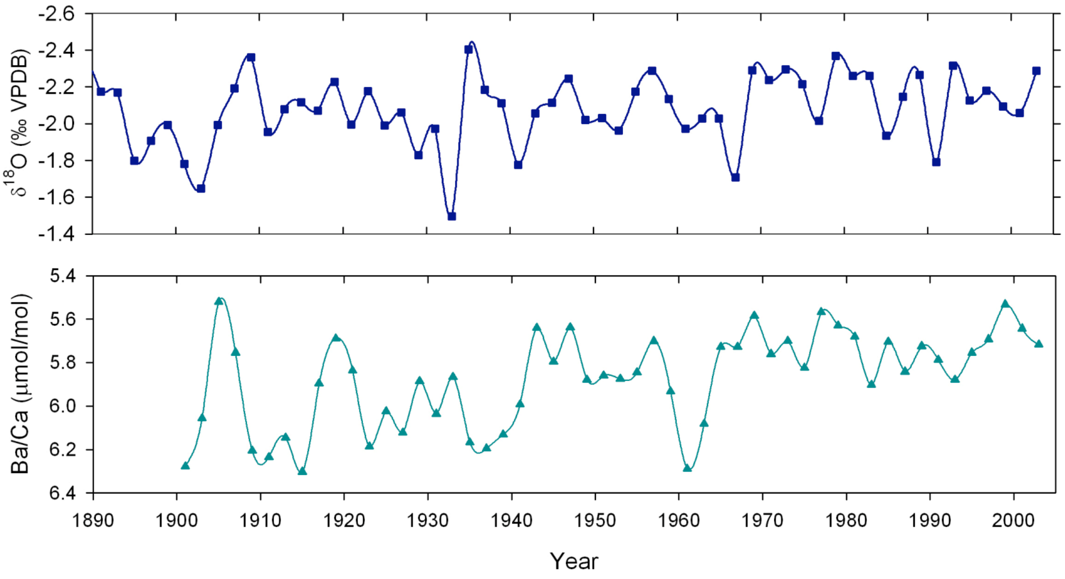

Figure 5.34: Comparison of Ba/Ca and $\delta^{18}O$ analyses for Edithburgh. Ba/Ca analyses were binned to a two year average. A four year lag is present between the two proxy records, this may be due to incorrect smoothing of Ba/Ca and the variation in initial sample size between the two techniques.

Similar warming trends were observed between Ba/Ca concentrations and $\delta^{18}O$ analyses in two *Plesiastrea versipora* colonies, Seacliff B and Edithburgh. The Edithburgh colony indicated a warming trend of 1.5°C over the last 150 years. Other coral studies have observed warming trends of a similar magnitude (Kuhnert et al. 1999; Cole et al. 2000). Direct comparisons between the laser ablation ICP-MS trace element records and stable isotope analyses are difficult due to the difference in initial sample size. To circumvent the sample resolution issue, the trace element data from the Edithburgh colony was smoothed to an average biennial value to compare with the $\delta^{18}O$ record from the same coral. This comparison (Figure 5.34) produced interesting results. Deviations from the mean value observed in the $\delta^{18}O$ record were also observed in the Ba/Ca record. These deviations around the mean in both proxy records represent similar temperature variations. Although there was an offset between the two proxy records, with Ba/Ca leading $\delta^{18}O$ by approximately three years, this is likely to be due to inaccuracies in the smoothing of the Ba/Ca. A more accurate comparison would be to conduct isotope dilution ICP-MS analyses on the same milled samples that the stable isotope analyses were conducted; however, this was not possible during the time frame of this thesis. The cyclicity observed in both proxy records should be subject to further exploration and future investigations using frequency analysis may be able to establish fluctuations in regional climate influences present in these records.

Climate Events Manifested in Plesiastrea versipora Proxy-records

The southern coastline of Australia is influenced by large-scale climate systems from three ocean basins. Therefore El Niño Southern Oscillation, Indian Ocean Dipole, Pacific Decadal Oscillation and the Southern Annular Mode may play an influential role on regional climate in South Australia and be recorded in paleoenvironmental proxies derived from *Plesiastrea versipora*. Due to the complexities in the trace element and $\delta^{18}O$ records from *Plesiastrea versipora*, it was difficult to ascertain regional climate forcing in the coral records with any degree of certainty.

Tree ring studies based on Huon Pine from Tasmania have found significant multi-decadal and centennial time scale variability in the warm-season temperature reconstruction that may be related to slow changes in ocean circulation dynamics in the southern Indian Ocean (Cook et al. 2006). A robust ENSO signal has been observed in New Zealand kauri ring-width chronologies, suggesting New Zealand also experiences large-scale SST variability associated with ENSO from the tropical Pacific (Fowler et al. 2004; Cook et al. 2006). However, it is not understood whether ENSO paleoreconstructions based on one proxy or archive calibrated to a single component of ENSO such as SST would be sufficient to fully characterise the intensity and duration of the ENSO event (Gergis et al. 2006).

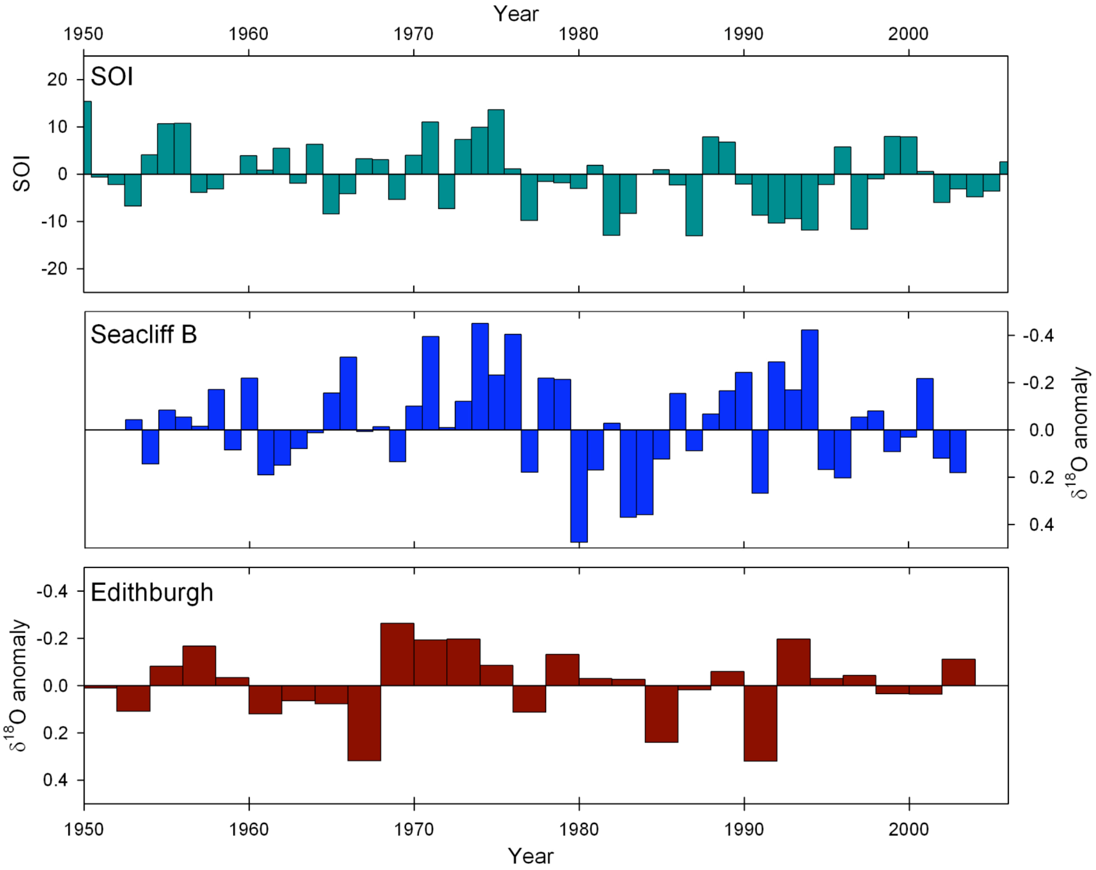

Figure 5.35: Comparison of the Southern Oscillation Index with $\delta^{18}O$ records from Seacliff B and Edithburgh. All data has been normalised and presented as anomaly data. SOI index from http://www.bom.gov.au/climate/current/soi2.shtml and coral records were normalised using the period 1975-2005.

An initial evaluation of the Southern Oscillation Index and $\delta^{18}O$ records from Seacliff B and Edithburgh corals (Figure 5.35) indicated coherence over parts of the record. The $\delta^{18}O$ records are presented as anomaly data and were normalised relative to a twenty year period in the modern part of the record. El Niño events were observed in several *Plesiastrea versipora* cores in the trace element temperature proxies, Ba/Ca, Sr/Ca and U/Ca. The El Niño events during 1970, 1982 and1998 were represented by a warmer summer, usually followed by a reduced winter minimum the next year. The correlation between SOI and the South Australian corals is reduced during the 1990s.

Summary

The results of this chapter demonstrate that colonies of *Plesiastrea versipora* with extension rates greater than 2 mm yr^{-1} may be useful as a paleoclimate archive in temperate Australian waters. Ba/Ca was evaluated to be the most reliable paleotemperature trace element measured in these corals, and may be useful in other high-latitude environments where upwelling and terrestrial influences do not effect Ba/Ca concentrations.

Unfortunately, the colonies with higher extension rates suitable for climate reconstruction on a sub-annual scale do not have a columellar or architecture suitable for analysing a single component of the skeleton, which may reduce the ability to capture the full amplitude of a seasonal cycle. Both the stable isotope and trace element SST proxies indicated a high level of reproducibility when moving over different regions of the coral architecture but remaining in a single calice.

The colonies with very low extension rates have skeletal components with enough aragonite to analyse a single component (theca), but only record approximately 50% of the seasonal SST range due to growth related fractionation and tissue smoothing. The colonies with growth rates lower than the width of the tissue zone (< 4 mm) are unsuitable for seasonal-scale reconstructions, and are more useful for decadal and centennial scale climate reconstructions. However, these colonies displayed ‘bimodal’ distributions in Sr/Ca and U/Ca which suggests a complex biologically mediated incorporation into coralline aragonite.

The length of the paleoclimate reconstruction was not fully realised compared with the size of the colonies due to colonies rolling and losing their primary growth axis during storm events. This issue is related to the temperate coral habitat and the fact that colonies attach to small rocks and shells on rocky reefs rather than securely cement on carbonate reef platforms.

This species presents a valuable new paleoclimate archive in a range of temperate environments, as the geographical range of *Plesiastrea versipora* is extensive throughout the Pacific and Indian Oceans in both the Northern and Southern Hemisphere.

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Chapter 6:

Evaluating Anthropogenic Signals from *Plesiastrea versipora*

Chapter 6: Evaluating anthropogenic signals from *Plesiastrea versipora*

Introduction

Urban, industrial and agricultural developments may significantly alter the marine environment. Such mechanisms may include increased sediment runoff though land use changes and waterways modification. For example, increased sediment in the coastal zone has the potential to cause ecological shifts from species requiring high light intensities such as corals to species able to cope with reduced water quality such as algae. Reduced water quality from suspended sediments also contains higher nutrient levels causing regime shifts from carbonate reefs to algal dominated reefs (Koop et al. 2001; Hughes et al. 2003). Urban and industrial runoff into coastal environments can contain organic and inorganic (trace metal) pollutants. Increased metal concentrations in coastal waters and sediments can bioaccumulate into marine organisms and metal concentrations increase with increasing trophic levels (i.e. predatory fish have higher concentrations of heavy metals than invertebrates). Heavy metals such as Pb, Cd and Hg are toxic to marine organisms at very low levels. Increasing nutrient concentrations in coastal environments can produce extreme consequences including; ecosystem regime shifts, red tides and fish death (Pandolfi et al. 2003). Thus, it is important to determine whether long term trends in pollution are driving the ecosystem towards a regime shift. Monitoring studies only assess the recent impact of pollution on facets of ecosystems including mangroves, seagrass, kelp, molluscs, fish and corals.

In tropical environments, corals have been used as biomonitors of environmental pollution as they provide a continuous record of the level of impact of pollution over time. Massive corals also have the ability to record the local environment in a pristine condition before anthropogenic development and other forms of monitoring were set in place (e.g. regular monitoring of water quality). Corals not only have the ability to record signals of anthropogenic pollution in their skeletons, but increased concentrations of trace metals can also reflect natural perturbations in climate systems such as El Niño Southern Oscillation events (Linn et al. 1990), trade wind regime shifts (Shen et al. 1992; Shinn et al. 2000) or seasonal upwelling (Shen et al. 1987; Lea et al. 1989; Reuer et al. 2003; Ourbak et al. 2006).

The potential of corals to act as a sentinel of environmental degradation has been the subject of many studies since the 1970s examining eutrophication and pollution contained in coral tissue and skeleton (Veeh & Turekian 1968; Livingston & Thompson 1971; Barnard et al. 1974; St John 1974). Incorporation of trace metals into corals can be the result of coral feeding (Hanna & Muir 1990; Ferrier-Pages et al. 2005), zooxanthellae uptake (Reichelt-Brushett & McOrist 2003), organic matter from coral tissue (St John 1974; Glynn et al. 1989), particulate matter trapped within skeletal cavities (Howard & Brown 1984; Hanna & Muir 1990) or incorporation (via substitution for Ca) into the aragonite crystal lattice (Dodge & Gilbert 1984; Shen et al. 1987; Delaney et al. 1993; Esslemont 1999; Fallon et al. 2002; David 2003; Wyndham et al. 2004). Studies which have examined both the coral tissue and skeleton have observed higher concentrations of trace metals in the tissue, and the trace metal concentrations recorded in the skeleton were consistent with changes in seawater composition (Dodge et al. 1984; Hanna & Muir 1990; McConchie & Harriott 1992; Reichelt-Brushett & McOrist 2003). Hanna and Muir (1990) found little variation between three coral species within contaminated sites and concluded that trace metals are present in coral skeletons due to both geochemical (substitution of metal cations for calcium) and physiological processes. Although early studies observed increased metal concentrations in coral tissue, analyses of coral skeleton allow a long term record of environmental modification to be established.

Climatic changes must also be considered when investigating anthropogenic impacts on a local or regional environment. The growing body of literature on coral bleaching suggests that corals living in degraded environments are more susceptible to bleaching during El Niño events and take longer to recover from physiological stress (Hoegh-Guldberg 1999; Lough 2000; McClanahan et al. 2001) The summer of 1997/1998 experienced a strong El Niño and this caused higher water temperatures in South Australian gulfs (2-5°C hotter) coinciding with lower sea levels. This resulted in the disruption of the recruitment of several macroalgal species (Turner & Cheshire 2002). Corals are known to have temperature sensitive juvenile phases

(Edmunds et al. 2001), however, there is limited understanding of how the ecology of temperate corals will be effected during higher temperatures (Harriott & Banks 2002; Edmunds 2004).

The most common pollution elements and associated tracers analysed include Al, P, V, Cr, Mn, Fe, Cu, Zn, Cd, Sn, Ba, Hg, Pb and a range of rare earth elements (REEs) and anthropogenic radioactive isotopes such as ^{90}Sr (Brown & Holley 1982; Dodge & Gilbert 1984; Dodge et al. 1984; Howard & Brown 1984; Toggweiler & Trumbore 1985; Shen & Boyle 1987; Shen & Boyle 1988; Hanna & Muir 1990; Scott 1990; Brown et al. 1991; Shen et al. 1991; Guzman & Jimenez 1992; Allison 1996; Guzman & Jarvis 1996; Scott & Davies 1997; Bastidas et al. 1999; Bastidas & García 1999; Esslemont 1999; Fallon et al. 2002; Inoue et al. 2004; Ramos et al. 2004; Wyndham 2005). The range of trace elements investigated has increased in recent years due to advancements in analytical capabilities.

New advances in micro-analytical techniques such as laser-ablation ICP-MS allow pollution events on a sub-weekly scale to be analysed (Fallon et al. 2002; Runnalls & Coleman 2003; Wyndham et al. 2004). Although these advances in instrument precision have enabled a larger suite of elements to be analysed, many studies have noted high frequency variation (~ monthly) not related to environmental concentrations. Several suggestions have been put forward to explain the small scale heterogeneity including: metal-binding organic matrix unevenly distributed throughout the skeleton (Allison 1996); biological or kinetic processes impacting skeletal deposition (Cohen et al. 2001; Allison & Finch 2004; Sinclair 2005a; 2005b; Meibom et al. 2006); and changes in the saturation state of the calcifying fluid impacting the ‘precipitation efficiency’ (Cohen et al. 2006; Gaetani & Cohen 2006).

Aims

The primary aim of this chapter is to present analyses of a range of trace elements from eight colonies of *Plesiastrea versipora* in both Gulf St. Vincent and Spencer Gulf to assess the level of anthropogenic pollution recorded in the coral skeletons. The coral analyses are then compared to known industrial and urban development and local environmental conditions to establish the likely sources for trace metal contamination in the coral skeleton. A secondary aim of this chapter is to reconstruct seawater heavy metal concentrations from the distribution coefficients of metals incorporated into coral skeletons. This was attempted to establish the degree of anthropogenic pollution from the pre-European baseline established from corals (in the absence of measured seawater chemistry).

Human impacts in the South Australian Gulfs

Environmental modification has occurred since European settlement in South Australia. The point source of anthropogenic pollution is substantially different between the gulfs with mining and other heavy industry focused in northern Spencer Gulf, whereas the dominant urban areas (including metropolitan Adelaide population > 1,000,000 people) are located on the eastern shore of Gulf St. Vincent. To provide greater clarity to the data presented in this chapter; the data will be divided into three subheadings relating to the type of environmental modification. These are urban impacts, industrial impacts and land use changes or agricultural impacts. Industrial and urban development information has been reviewed below to assist with chronological control of the trace metal concentrations observed in *Plesiastrea versipora*.

Urban Impacts

Sewage and Stormwater

Discharge from rivers in Gulf St. Vincent increases the local coastal turbidity by carrying suspended solids, which can settle out on the seafloor or be resuspended by wave action and winds. Turbid water can originate from both natural and anthropogenic sources. Stormwater runoff contains dissolved and particulate matter from soil erosion, decayed organic matter from catchment regions and pollutants from urban areas. Infrequent storm events with higher than average rainfall can produce large sediment plumes into Gulf St. Vincent, similar to flood plumes observed from tropical rivers (Figure 6.1). Estimates of suspended solids input for the 2000/2001 period into coastal waters include 3000 t from the Torrens River catchment, 2000 t from the Patawolonga catchment and 234 t from the Glenelg waste water treatment plant (Gaylard 2004).

Turbid water is regularly observed along the Adelaide metropolitan coastline for extended periods during the winter months, corresponding with onshore winds and fine grained sediment which often coats coastal reefs during August/September (personal observation). It is still unquantified how much impact urban development has had on coastal turbidity. A regression analysis indicated that there was not a positive correlation between Torrens River discharge, waste water treatment plants and observations of suspended sediments at SeaWIFS stations due to the dominant north-south tidal regime (Petrusevics 2005). Algal blooms can form in summer through a combination of elevated nutrient levels, high solar radiation, local oceanographic features including dodge tides and low winds.

Figure 6.1: Photograph of Torrens River outflow into Gulf St. Vincent during a flood in October 1974. Sediment plume travels northwards (towards head of gulf) due to longshore drift. Photograph from (Lewis 1975).

Stormwater and waste water treated effluent are contributors to heavy metal contamination along the Adelaide coastal zone (Figure 6.2). Discharge of this water to the marine environment has varied through time. Waste water treatment products contributed approximately 45% of the water discharged annually from land based sources (Wilkinson et al. 2003). The first piped discharge from the Glenelg waste water treatment plant to the coastal zone occurred in 1943 with an outfall discharging 350 m offshore. A second outfall was commissioned in 1958 to cope with an increasing population and a digested sewage sludge outfall piped 3.2 km offshore began operating in 1962. Changes in the seagrass species density were observed in the late 1960s along the metropolitan coastline (Wilkinson et al. 2003). Heavy metal concentrations in the waste water discharge have been reduced since the 1970s, and a concerted effort to reduce heavy metal contamination in waste water by 75-95% occurred in the early 1990s for Zn (from 4818 kgyr^{-1} to 1460 kgyr^{-1}) and Pb (from 2130 kgyr^{-1} to 54 kgyr^{-1}) (Wilkinson et al. 2003).

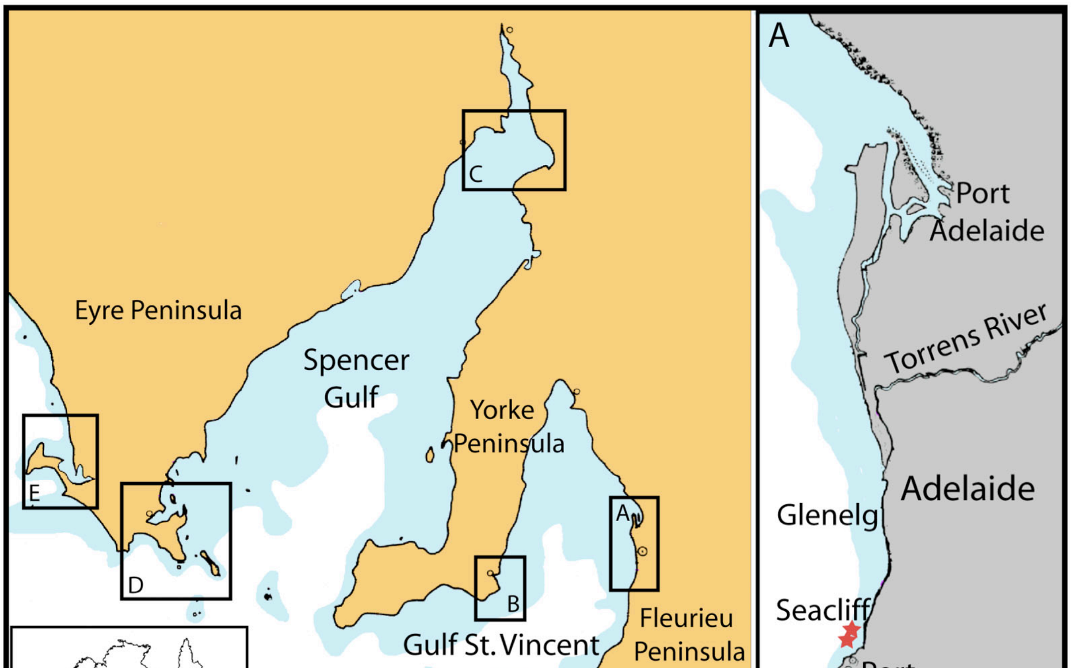

Figure 6.2: Map of the South Australian Gulfs, with inset A, the corals located at Seacliff Reef. Seacliff seawater chemistry may be influenced by the oil refinery at Port Stanvac; treated waste water discharged at Glenelg and stormwater run off from Adelaide.

Oil refinery

Construction of the refinery and port facilities at Port Stanvac was initiated in 1961 and the refinery opened in 1976 and ceased production in late 2003. During optimal production, the Adelaide refinery produced more than 8, 500 000 L day^{-1} of refined products, supplying 90% of South Australian fuel and 10% of Australian petroleum requirements. Little documentation was available on oil spills in the South Australian gulfs. However, figures provided by the Environment Protection Authority (EPA) estimate that between 1973 and 1996 there were at least 108 oil spill incidents involving at least 600,000 L. Records of at least 26 oil spill incidents occurred at Port Stanvac refinery between 1977 and 1997. The impacts of oil contamination on coral colonies are not well understood, however, oil contamination has a detrimental effect on other marine organisms including sea-birds, fish and benthic communities. Coral colonies may be smothered by oil, resulting in death of colonies or reduced growth.

Several large spills have occurred at Port Stanvac including in January 1982 the oil tanker *Esso Gippsland*, leaked a large quantity of industrial fuel oil, and produced a slick five miles offshore. In September 1991 a 22 km slick was found near Troubridge Island in Gulf St Vincent. Three oil spills were reported at Port Stanvac refinery in 1992. In September 1996 10,000 L of light crude oil was spilled from a floating, high tensile ship-to-shore hose. Oil from the spill was reported to have covered reefs and beaches from Port Stanvac to Seaford (http://www.mlssa.asn.au/). In November 1997, an unknown quantity of light crude oil was spilled at Port Stanvac from a Malaysian charter vessel. In June 1999, 25,000 L of crude oil was spilt from the tanker *Chanda*, producing a 1.5km-long oil slick. This was due to a split in the floating hose connecting the vessel to the oil refinery.

Industrial Impacts

Industries contributing to the majority of heavy metals entering the northern region of Spencer Gulf include a lead-zinc smelter at Port Pirie and steelworks at Whyalla (Figure 6.3). The steelworks has been operating since 1937 and produces approximately 1.2 million tonnes of raw steel annually (http://www.onesteel.com).

The smelter at Port Pirie is one of the largest zinc and lead smelters in the world and has been operational since 1889, causing heavy metal pollution in the form of particulate emissions from smoke stacks, dust blown from sites, spillage from ship loading and discharging of liquid effluent. Waste water treatment plants also discharge treated effluent containing heavy metals into the local gulf waters. Estimated annual metal emissions from the Whyalla steelworks for the period 2001/2002 include 3000 kg Zn, 215 kg Pb and 170 kg Cu (Corbin & Wade 2004).

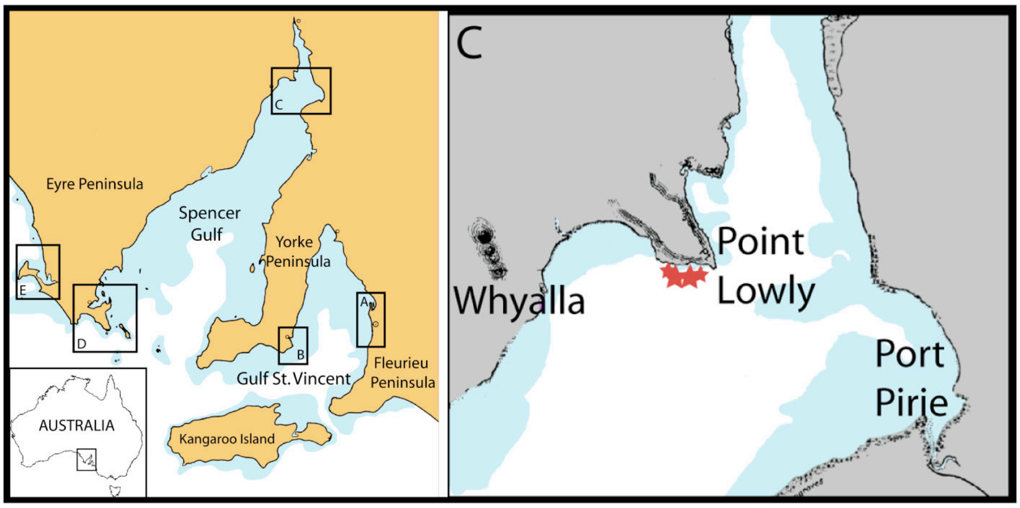

Figure 6.3: Map of the South Australian Gulfs, with inset C, indicating the corals located at Point Lowly, Upper Spencer Gulf. Local seawater chemistry may be influenced by the smelters located at Port Pirie and Whyalla.

Land Use Changes

Regional scale events that are a by-product of anthropogenically modified landscapes may also be present in coral skeletons. Deforestation and agriculture increase the amount of aeolian transport to coastal environments and excess fertilizer may increase phytoplankton blooms. Figure 6.4 displays two examples of regional scale dust storms and phytoplankton blooms captured by satellite images in the last few years.

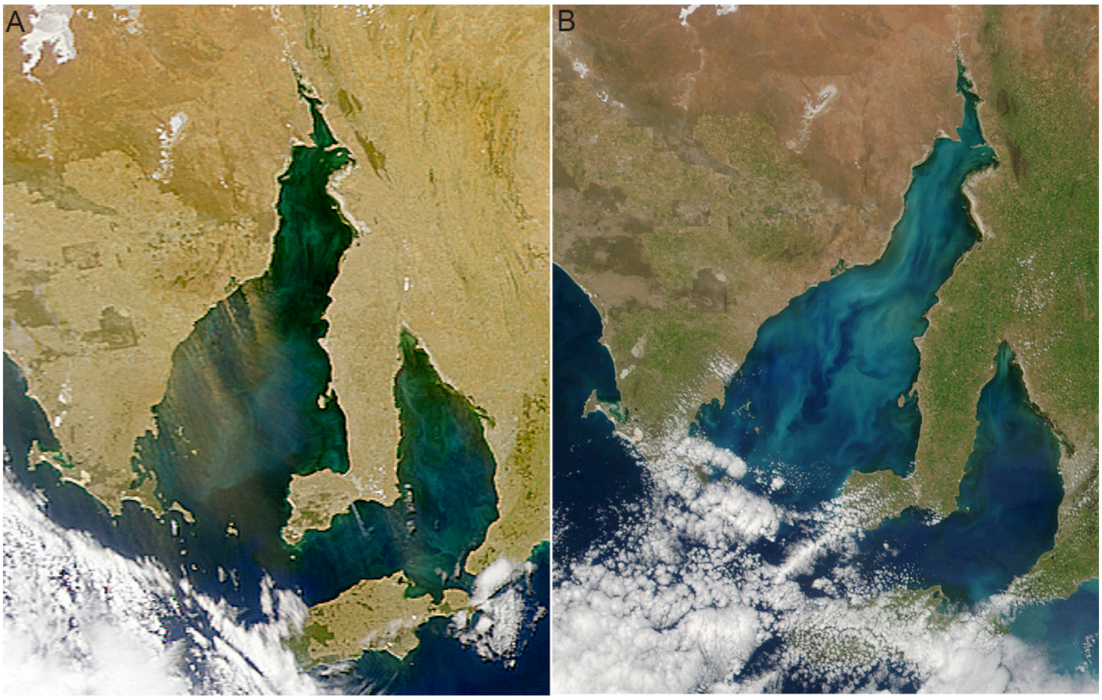

Figure 6.4: Satellite images from LandSat (http://modis.gsfc.nasa.gov/). A: Dust storm on Eyre Peninsula on 17th March 2000 blowing sediments into Spencer Gulf. B: Phytoplankton bloom in both Spencer Gulf and Gulf St Vincent on 20th October 2001.

Sampling and Analytical Methods

Coral coring methodology was described in Chapter 3 and LA-ICP-MS methodology was described in more detail in Chapter 5. Briefly, all data presented in this chapter was collected on the Varian 820 ICP-MS collected between March 2006 and August 2006. In contrast to the stepwise pre-treatments used by Shen and Boyle (1988) this study employed an oxidative step to remove organic material with H_2O_2 and three deionised water baths combined with sonic agitation prior to laser ablation analyses. Rigorous cleaning was conducted with the laser ablation system and instrument conditioning before measuring trace heavy metals. Three preablation scans were conducted at 10 Hz, 50 mJ and 40 μm s^{-1} prior to data collection, with the laser masked to produce a 50 x 500 μm rectangle to ensure that a new surface of the coral was exposed before sample collection.

Two analyses for trace elements were conducted at 10 Hz and 50 mJ and the laser beam is masked to produce a 40 x 400 μm rectangle after the ICP-MS had been operational for several hours. Trace metal analyses were conducted after the ICP-MS had been operational for several hours in a stable instrumental atmosphere, to reduce potential contamination in the system from prior analyses of other material which may have contained higher concentrations of trace metals, such as igneous rocks. The replicate provided a check for analytical drift between analyses. The isotopes monitored were ^{7}Li, ^{11}B, ^{31}P, ^{43}Ca, ^{51}V, ^{55}Mn, ^{57}Fe, ^{59}Cu, ^{66}Zn, ^{89}Y, ^{90}Zr, ^{91}Zr, ^{98}Mo, ^{111}Cd, ^{120}Sn, ^{137}Ba, ^{139}La, ^{140}Ce, ^{141}Pr ^{146}Nd, ^{208}Pb and ^{238}U. All analyses were blank corrected (using the instrumental gas background blank and duplicate analyses of the calibration standards were assessed to correct for instrument drift during analysis. The standard used for minor element calibration included a NIST 614 silicate glass (Horn et al. 1997). Ba, Sr and U were also collected during the minor element analyses to establish chronological control over trace metal spikes.

Results

Pre-European Baseline

Before assessing impacts of environmental modification from anthropogenic sources, an environmental baseline for the local region needs to be established. The concentrations of Mn/Ca, Zn/Ca, Sn/Ca, Cd/Ca and Pb/Ca were assessed from three corals. Two corals located in well-flushed, open gulf positions in Spencer Gulf (Taylors Island coral) and Gulf St. Vincent (Troubridge coral) were used to establish a baseline for heavy metals for South Australian seawater (Figure 6.5).

Table 6.1: Coral chemistry baseline values for three colonies: Troubridge, Taylors Island for the period 1945-2000 and Seacliff A for the period 1820-1875. All trace element/Ca ratios are in μmol/mol.

	V/Ca	*Mn/Ca*	*Cu/Ca*	*Zn/Ca*	*Cd/Ca*	*Sn/Ca*	*Pb/Ca*
Troubridge (1945-2000)	0.156	0.199	0.397	0.454	0.012	0.005	0.026
Taylors Island (1945-2000)	0.200	0.111	1.354	0.593	0.056	0.032	0.066
Seacliff A (1820-1875)	0.109	0.432	2.109	0.848	0.209	0.294	0.030

Concentrations from Seacliff A were also evaluated to ascertain potential differences between open-gulf sites and coastal sites. Trace metal concentrations from Seacliff A were only used for the period 1820-1875, prior to European arrival in South Australia.

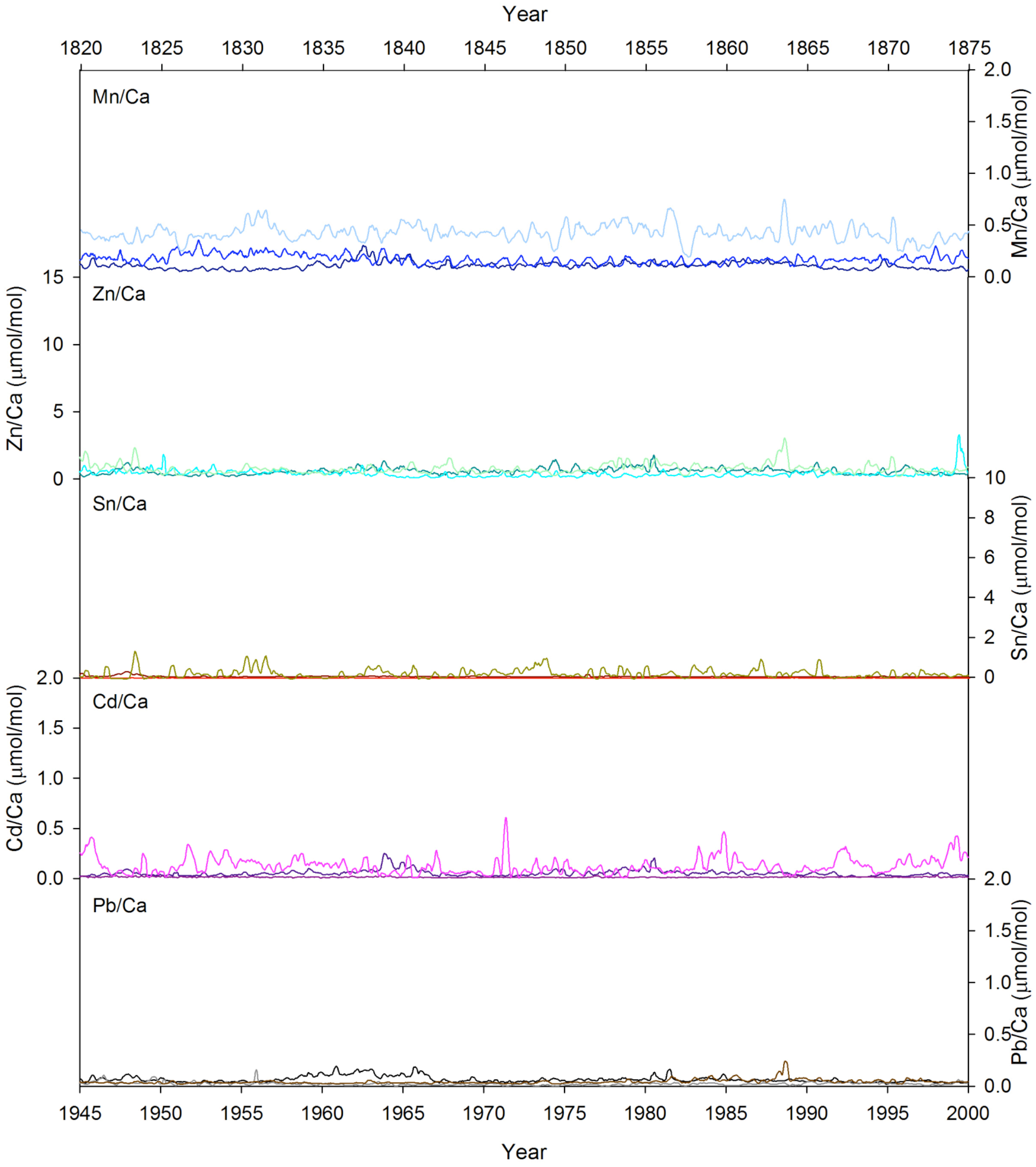

Figure 6.5 Concentrations of Mn/Ca, Zn/Ca, Sn/Ca, Cd/Ca and Pb/Ca for the period of 1945-2000 from Taylors Island coral and Troubridge corals as the baseline chemistry for open gulf seawater concentrations in Spencer Gulf and Gulf St. Vincent, respectively. Concentrations of the same trace metal ratios included from Seacliff A as the pre-European baseline for the period 1820-1875. Seacliff A data are in the lighter colours and display coastal enrichment in all concentrations, especially Mn/Ca and Cd/Ca.

All elements indicated baseline concentrations between 0.05-2 μmol/mol, average concentrations over the 50 year period for the three corals are listed in Table 6.1. Concentration differences were observed between the Troubridge and Taylors Island corals, with higher concentrations of V/Ca, Cu/Ca, Cd/Ca, Sn/Ca and Pb/Ca in the Taylors Island coral. Previous studies on trace metal incorporation have suggested that different coral growth rates may affect the distribution coefficient (K_D) of trace metals incorporated into coralline aragonite (Shen & Boyle 1987; Reuer et al. 2003). The difference in growth rates and coral specific K_D between Troubridge (8 mm yr^{-1}) and Taylors Island (1.5 mm yr^{-1}) may be the cause of the different concentrations measured in the corals rather than actual differences in seawater chemistry between the gulfs.

Trace element concentrations from the coastal coral Seacliff A, suggested significantly higher concentrations in all elements except V/Ca for the pre-European time period. The higher concentrations in the coastal coral may imply coastal enrichment of the 'nutrient-type' elements including Mn/Ca, Cu/Ca, Zn/Ca, Cd/Ca, Sn/Ca and Pb/Ca, especially Sn/Ca which is 58 times higher in Seacliff A than Troubridge. However, Seacliff A also has a slow growth rate (2 mm yr^{-1}) and may have higher distribution coefficients than the Troubridge coral.

Tissue Zone Effects

The most recently calcified portion of the skeleton (containing the tissue zone) indicated increased concentrations of some trace elements including P/Ca and Cd/Ca (Figure 6.6) in all corals compared with older coralline aragonite. Higher concentrations of trace element in the tissue zone has been observed in previous studies (Dodge & Gilbert 1984; Scott 1990; McConchie & Harriott 1992; Esslemont et al. 2000), symptomatic of the organic tissue accumulating more trace metals than the inorganic skeleton. Smoothing of the seasonal cycle in B/Ca, Sr/Ca and U/Ca in the tissue zone was discussed in the previous chapter (Chapter 5). The oxidative pre-treatment cleaning step submerging the coral cores in H_2O_2 has removed artefacts of remnant organic material from the tissue zone. Evidence of the effectiveness of this technique can be observed in the low concentrations in the Troubridge and Taylors Island corals in Figure 6.5.

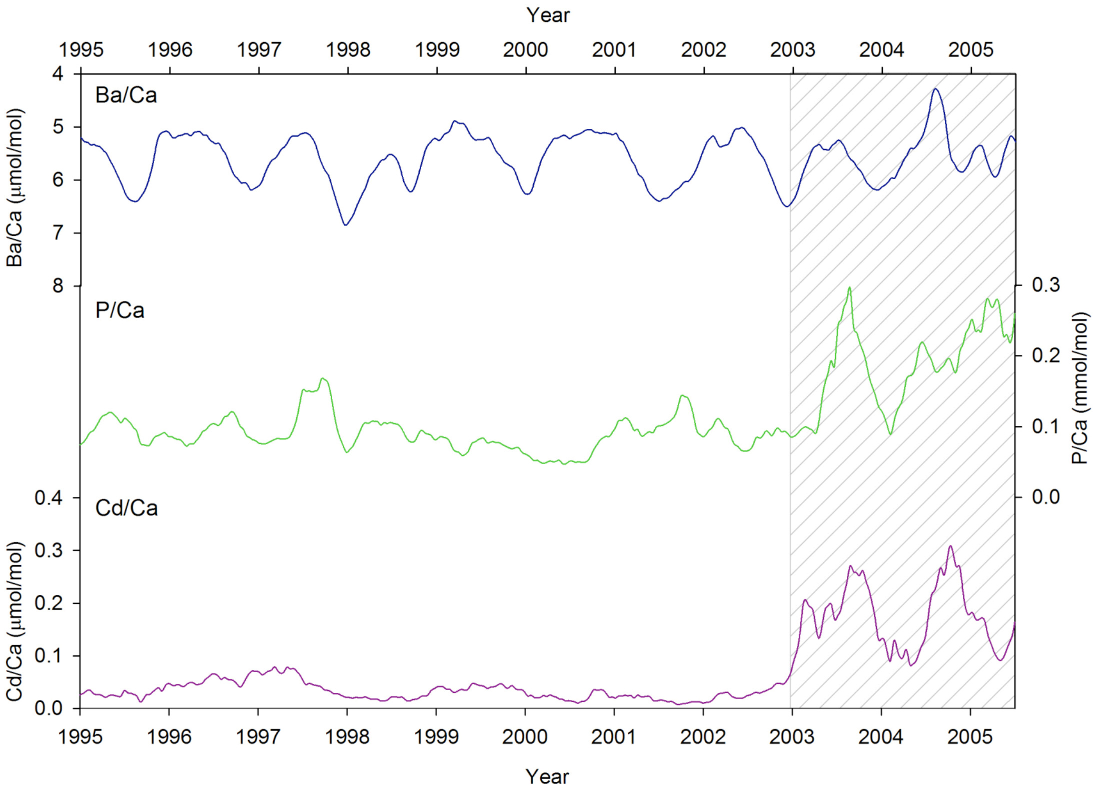

Figure 6.6: Increased concentrations of P/Ca and Cd/Ca from a ten year profile in the upper portion of skeleton containing the tissue zone in the *Plesiastrea versipora* colony Seacliff B. Tissue zone is indicated by grey hatched region.

Trace Metal Reproducibility

All trace metals analysed are presented in Figures 6.7-6.9 for a 20 year period from the Seacliff B coral. Ba/Ca is included in these figures to provide a temporal constraint for other elemental concentrations. A replicate analysis conducted down the same laser track is included for all elements (Figure 6.7-6.9) in black. The small offset between the two analyses is indicative of a difference in the temporal/spatial scale as the laser ablates new coralline aragonite. The high level of reproducibility in the trace metal/calcium ratios suggests that the trace metal concentration variation through time is recorded in the coral skeleton rather than instrumental artefacts.

Li/Ca ranged between 6-14 µmol/mol on a 3-5 year periodic cycle in Seacliff B (Figure 6.7), and this multi-year cycle was observed in all coral colonies. Although Li/Ca has indicated a temperature dependence in some tropical corals (Marriott et al. 2004), no temperature sensitivity was observed in this study.

P/Ca ranged between 0.05-0.6 mmol/mol, and concentrations varied on a seasonal scale. Higher concentrations of P/Ca usually occurred during late summer/autumn and may be coincident with phytoplankton blooms developing when the gulf waters are warmer. Higher concentrations of P/Ca were not observed during winter so it is unlikely that terrestrial runoff (which predominantly occurs during winter rains) is the cause of increased P concentrations. Mn/Ca concentrations (Figure 6.7) ranged between 0.1-1.2 µmol/mol, and varied on a seasonal timescale, with higher concentrations occurring in spring/summer/autumn. No relationship was observed between P/Ca and Mn/Ca (Table 6.2), therefore it is unlikely that P and Mn have the same source of enrichment. Cd/Ca concentrations ranged between 0.01-1.5 µmol/mol with variations in concentration occurring on both an intra and inter annual timescale. Seacliff B incorporated more Cd/Ca in the early 1980s than in the late 1990s, therefore the source of the Cd/Ca enrichment may have reduced over this time period. However, no regular seasonality was displayed or evidence of variability associated with El Niño events (Linn et al. 1990; Delaney et al. 1993). V/Ca concentrations ranged between 0.1-0.3 µmol/mol, with higher concentrations occurring intermittently, and not limited to a particular season. Several of the V/Ca peaks correlate temporally with Cd/Ca peaks although the amplitude of change observed was different.

Cu/Ca concentrations ranged between 0.05-8 µmol/mol (Figure 6.8). Higher concentrations of Cu were recorded by Seacliff B coral in the 1980s, with concentrations decreasing to < 2 µmol/mol from the mid 1990s. Zn/Ca concentrations ranged between 1-10 µmol/mol and indicated annual seasonal variations. Peaks in Zn/Ca did not correlate with concentration spikes in any other trace metals (Table 6.2) and occurred during late summer/autumn. Concentrations of Mo/Ca in the Seacliff B coral skeleton ranged between 0.02-0.3 µmol/mol, and higher concentrations were more frequent in the mid/late 1980s than other times in the record. Mo/Ca concentration spikes temporally correlate with V/Ca and Sn/Ca.

Concentrations of Sn/Ca were higher in the 1980s than in the late 1990s and ranged between 0.02-1.3 µmol/mol. The decrease in concentrations of Cu/Ca, Mo/Ca and Sn/Ca (Figure 6.8) occurs at approximately the same time in the early 1990s, therefore the enrichment source of these trace metals may be similar. Concentrations of Pb/Ca range between 0.005-0.4 µmol/mol, with more variation in concentrations in the early part of the record (1980s). Higher concentrations of Pb/Ca occur during winter/spring and do not appear to coincide with enrichment of other trace metals.

Very little fractionation was observed between the light rare earth elements (LREE) Y/Ca, La/Ca, Ce/Ca, Pr/Ca and Nd/Ca (Figure 6.9). Concentrations of Y/Ca ranged between 20-70 nmol/mol, with higher concentrations generally during the winter/spring months. La/Ca ranged between 3-22 nmol/mol, Ce/Ca ranged between 4-25 nmol/mol, Pr/Ca ranged between 0.5-5 nmol/mol and Nd/Ca ranged between 3-15 nmol/mol during the 20 year record from Seacliff B coral. The highest concentrations during this period occurred in winter 1986 and spring 1991 (Figure 6.9). Variations in the LREE signal also correlated strongly with U/Ca (Table 6.2). Concentrations of Zr/Ca ranged between 5-20 nmol/mol, and enrichment was observed during the winter/spring period, although the regression analysis correlation between Zr and the LREEs was poor (Table 6.2). Two large concentration spikes occurred during the 20 year record of > 50 nmol/mol, although the spikes were reproducible down the same laser track, it is unlikely that this concentration increase represents lattice bound Zr/Ca.

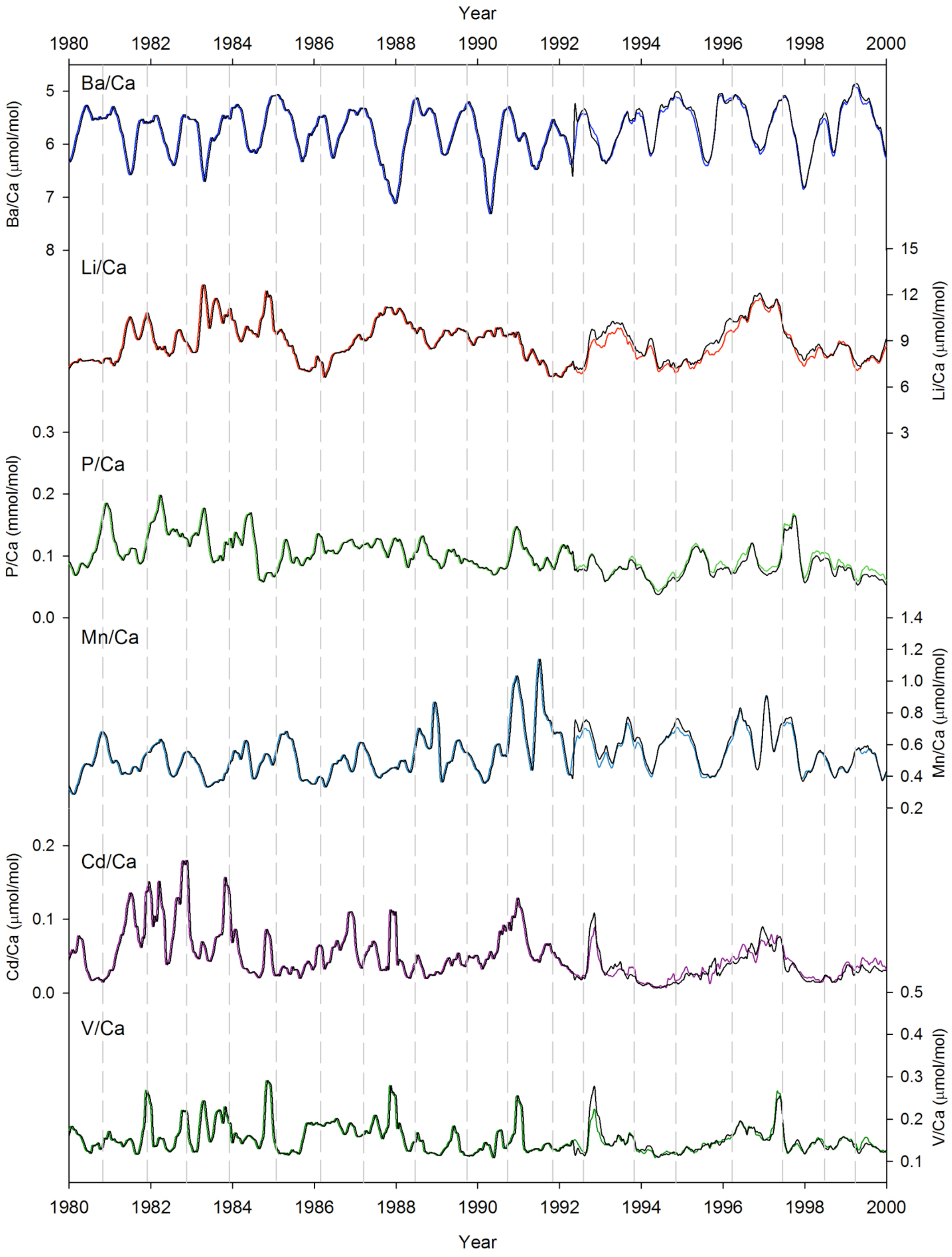

Figure 6.7: Behaviour of minor elements recorded in the Seacliff B colony for a 20 year period. Ba/Ca has been included to display seasonal cycle (note that Ba/Ca axis has been inverted to reflect SST). The units for P/Ca are mmol/mol all other elements are in μmol/mol.

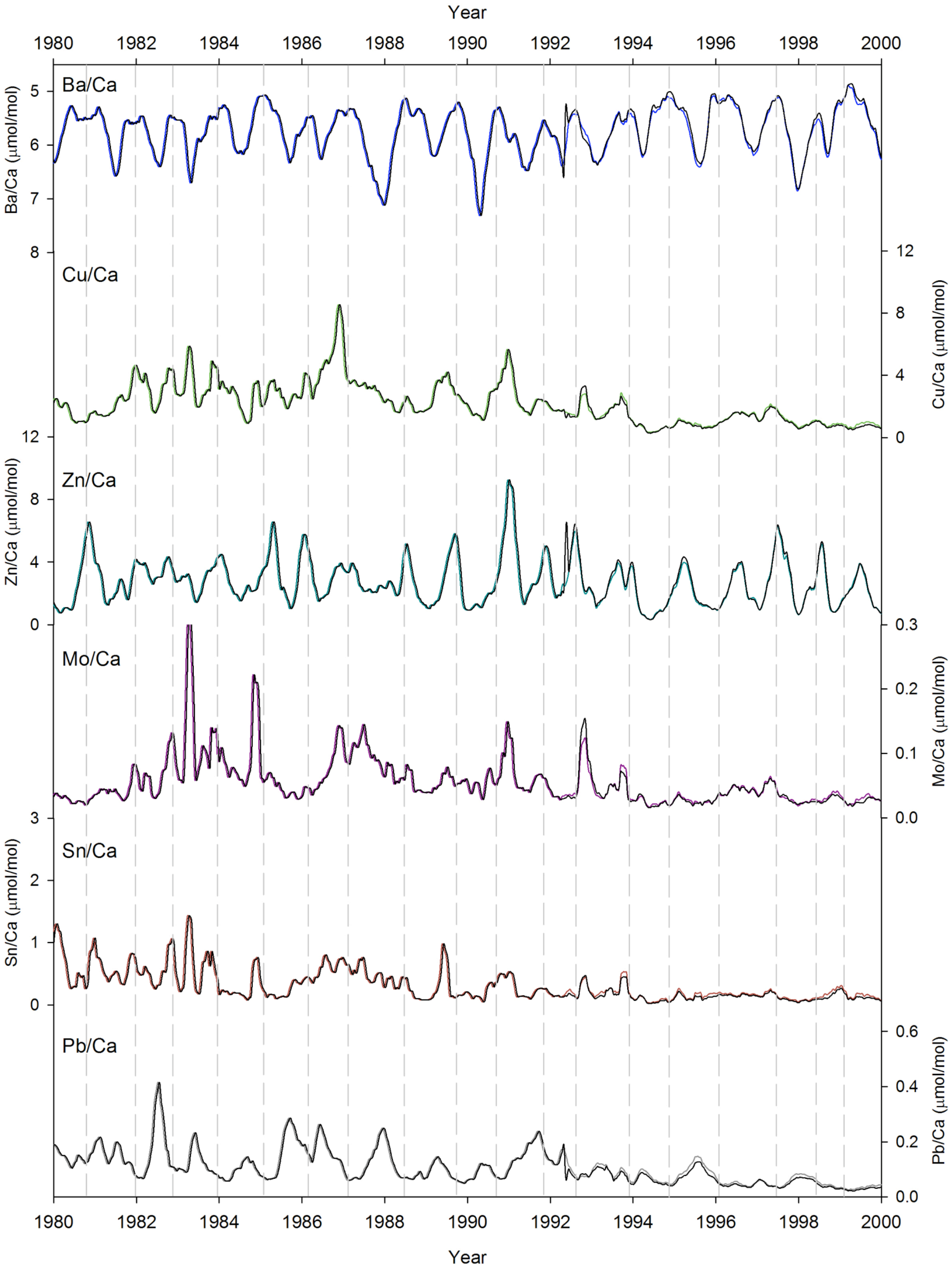

Figure 6.8: Behaviour of minor elements recorded in the Seacliff B colony for a 20 year period. Ba/Ca has been included to display seasonal cycle (note that Ba/Ca axis has been inverted to reflect SST). The units for all elements are in μmol/mol.

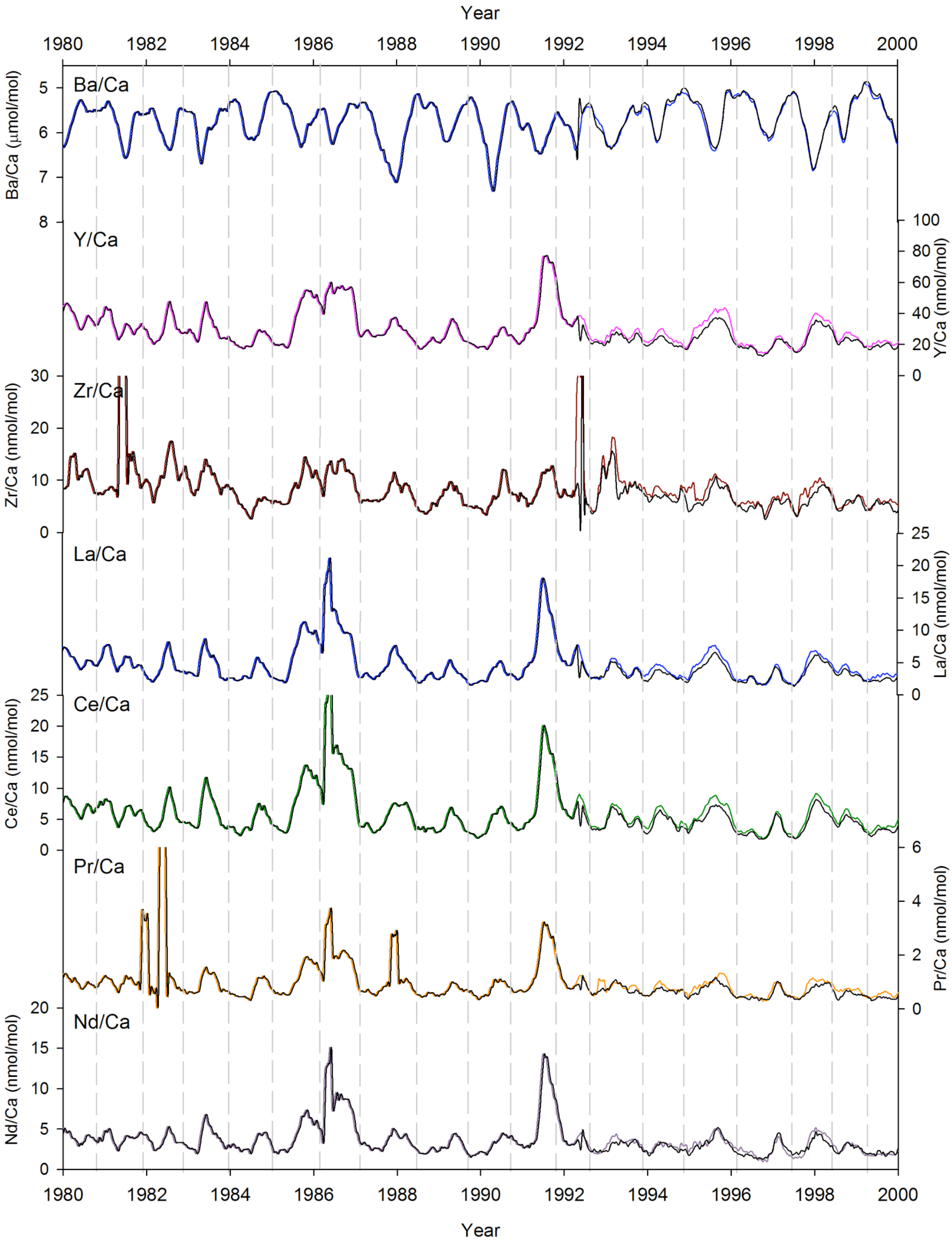

Figure 6.9: Behaviour of yttrium, zirconium and light rare earth elements recorded in the Seacliff B colony for a 20 year period. Ba/Ca has been included to display seasonal cycle (note that Ba/Ca axis has been inverted to reflect SST). The units for Ba/Ca are μmol/mol all other elements are in nmol/mol.

Seacliff B	*Li/Ca*	*B/Ca*	*P/Ca*	*V/Ca*	*Mn/Ca*	*Cu/Ca*	*Zn/Ca*	*Y/Ca*	*Zr/Ca*	*Mo/Ca*	*Cd/Ca*	*Sn/Ca*	*Ba/Ca*	*La/Ca*	*Ce/Ca*	*Pr/Ca*	*Nd/Ca*	*Pb/Ca*
P/Ca	0.07	-0.23																
V/Ca	0.23	-0.33	0.30															
Mn/Ca	-0.07	-0.32	0.36	0.30														
Cu/Ca	0.23	-0.20	0.28	0.22	0.12													
Zn/Ca	0.02	-0.44	0.50	0.39	0.51	0.21												
Y/Ca	-0.29	0.32	0.12	-0.23	-0.12	0.12	-0.20											
Zr/Ca	-0.03	0.09	0.06	-0.12	-0.03	0.22	-0.04	0.27										
Mo/Ca	0.43	-0.25	0.24	0.49	0.06	0.52	0.24	-0.02	0.04									
Cd/Ca	0.18	0.03	0.15	0.08	0.11	0.38	0.11	-0.03	0.13	0.37								
Sn/Ca	0.29	-0.10	0.21	0.18	-0.07	0.58	0.07	0.17	0.17	0.50	0.32							
Ba/Ca	0.10	0.49	0.05	0.03	-0.23	0.07	-0.29	0.38	0.11	0.05	0.02	0.10						
La/Ca	-0.26	0.36	0.11	-0.16	-0.05	0.11	-0.19	0.92	0.29	-0.04	-0.01	0.13	0.47					
Ce/Ca	-0.24	0.35	0.11	-0.15	-0.05	0.12	-0.20	0.91	0.32	-0.03	0.00	0.13	0.43	0.97				
Pr/Ca	-0.14	0.20	0.10	-0.06	-0.02	0.11	-0.12	0.64	0.22	-0.02	0.02	0.11	0.32	0.68	0.67			
Nd/Ca	-0.19	0.28	0.08	-0.18	-0.03	0.13	-0.18	0.87	0.31	-0.02	0.01	0.15	0.38	0.92	0.92	0.65		
Pb/Ca	-0.09	0.06	0.25	0.20	0.04	0.39	0.11	0.41	0.42	0.20	0.12	0.22	0.27	0.43	0.45	0.31	0.40	
U/Ca	-0.46	0.51	0.11	-0.17	-0.25	-0.05	-0.29	0.81	0.19	-0.12	-0.10	0.03	0.49	0.74	0.72	0.48	0.62	0.36

Table 6.2: Trace element correlation table for Seacliff B colony. Correlation coefficients between elements greater than 50% are marked in black, below 50% are in grey. Correlation tables for other *Plesiastrea versipora* colonies in Appendix G.

Eastern Gulf St. Vincent - Urban Impacts

The two Seacliff corals recorded increased concentrations of Cu/Ca, Zn/Ca, Sn/Ca and Mn/Ca (Figure 6.10) throughout the temporal span of the records. Seacliff reef is a metropolitan reef located 3 km offshore from the city of Adelaide and any enrichment in trace metal concentrations is likely to be from urban development. Cu/Ca and Sn/Ca indicate an increase in the 1930s for the Seacliff A coral from background levels (0-0.05 µmol/mol) observed in other corals to peaks of 3 µmol/mol for Sn/Ca and 12 µmol/mol for Cu/Ca. The concentration of Cu and Sn was observed to increase at approximately 1960 in the Seacliff B coral, concentrations of both elements fluctuated for a 30 year period, potentially in a series of pulse events before indicating lower concentrations in the 1990s.

Seacliff A colony displays an initial increase in Zn/Ca concentrations in 1920-1935, followed by a sustained increase from the 1960s. The early 1930s peak in Zn/Ca and Cu/Ca concentrations in Seacliff A are coincident with Pb/Ca peaks (Figure 6.11). Zn/Ca concentrations in the Seacliff B colony also display an increase in the 1960s, with no reduction in concentrations during the 1990s as observed with Cu/Ca and Sn/Ca. Concentrations of Mn/Ca increased in both of the Seacliff corals throughout the skeletal record (1820-2000), but did not display a similar peak in concentrations in the 1970s-1980s, when compared with Cu/Ca, Sn/Ca and Zn/Ca.

Potential sources of copper and tin may include marine paints previously used as an antifoulant to prevent fouling of ships by encrusting organisms. Following a series of toxicity studies of organotin compounds (tributyltin - TBT) in the 1980s; controls were introduced to limit usage. Reduction in the usage of TBT compounds may be why the concentrations of Cu and Sn reduce in the 1990s, however, the initial increase in Cu and Sn observed in the Seacliff A colony is likely to be before TBT was widely used in South Australian waters. The ratio of Cu and Sn in this study differs markedly from a previous study examining corals from Micronesia and concluding that the source of heavy metal increases was from antifoulant coatings with Cu/Ca concentrations 20 times higher than Sn/Ca concentrations (Inoue et al. 2004).

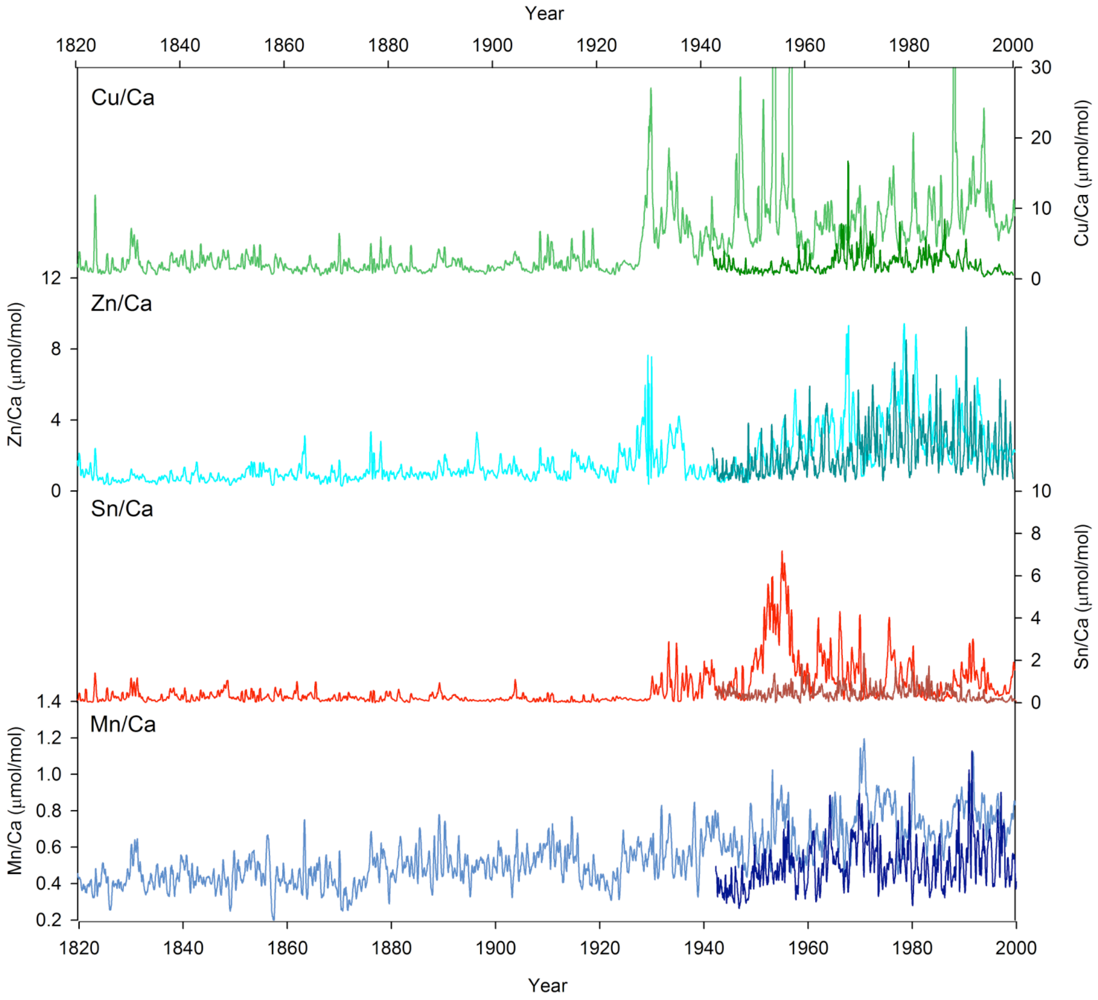

Figure 6.10: Concentrations of Cu, Zn, Sn and Mn (normalised to Ca) for the Seacliff corals. Seacliff A (lighter colours) is the long record extending back to 1820. Seacliff B is a shorter record (dark colours) and is from 1945-2000. Differences in trace metal maximum concentration observed between the two colonies may reflect different K_D due to different growth rates. Concentration increases are observed to be coincident with development of treated sewage outflow into Gulf St. Vincent.

A more likely source of the heavy metal contamination observed in the coastal corals may be from treated sewage released into Gulf St. Vincent at two locations along the metropolitan coastline of Adelaide. Copper, zinc and to a lesser extent tin are utilised in the treatment process for sewage in waste water treatment plants. The first direct discharge of sewage into the gulf occurred in the early 1940s at Glenelg (Wilkinson et al. 2003) located ~ 10 km from Seacliff. The highest concentrations in both Cu/Ca and Sn/Ca were observed in the 1940s and 1950s. The digested sludge outfall at Glenelg was shut down in 1993 (Wilkinson et al. 2003), which improved water quality in the metropolitan coastal region and reduced the waste water impacts on the coastline. The trace metal concentrations in both Seacliff corals reduce in the early 1990s supporting the hypothesis that the source of the elevated trace metals may be the discharge of sewage at piped outfalls in close proximity to the location of the corals.

The behaviour of trace metals differs between the two Seacliff colonies, with concentrations of Cu and Sn three times higher in Seacliff A than Seacliff B. These corals are located less than 10 m apart (discussed in Chapter 3) and were collected from the same depth and similar environmental conditions, however, the growth rates differ significantly and the annual extension rate of Seacliff A is substantially lower (2 mm yr^{-1}) compared with Seacliff B (6 mm yr^{-1}). Previous studies have suggested that coralline metal distribution coefficients may be affected by kinetic fractionation and may vary depending on the coral species and annual extension rate (Shen & Boyle 1987).

Distribution coefficients for trace metals were not able to be established during this study as water analyses were not conducted. However, differences observed in trace metal concentrations between the two Seacliff corals suggest that there is a difference of approximately two-three fold in the K_D between the corals. The Mn/Ca background concentrations varied from 0.2 μmol/mol for Seacliff B and 0.6 μmol/mol for Seacliff A and Cu/Ca background concentrations was 1 μmol/mol for Seacliff B and 2 μmol/mol for Seacliff A.

A potential mechanism for establishing the distribution coefficient of trace metals in *Plesiastrea versipora* is to compare concentrations derived from LA-ICP-MS in this study with concentrations and coral growth rates in published studies to determine a potential K_D. Linn et al (1990) suggested a distribution coefficient for *Pavona clavus* in Galapagos corals of $K_D = \sim 0.3$ for Cu and $K_D = \sim 1$ for Mn. It is unknown if *Plesiastrea versipora* would have a similar distribution coefficient to K_D derived for other coral species. However, if we assume the faster growing coral, Seacliff B has a comparable K_D to previous studies, due to a more similar growth rate, then the Seacliff A K_D may potentially be $D_{Cu} = \sim 0.6\text{-}1$ and $D_{Mn} = \sim 2$.

Lead – Industrial Flux and Vehicle Emissions

Pb/Ca concentrations (Figure 6.11) range between 0.02-0.8 µmol/mol for Seacliff A colony and 0.02-0.6 µmol/mol for Seacliff B. The concentration difference between the two corals during the highest concentrations in the 1970/80s suggests there is a different distribution coefficient for Pb in *Plesiastrea versipora* dependent on growth rate.

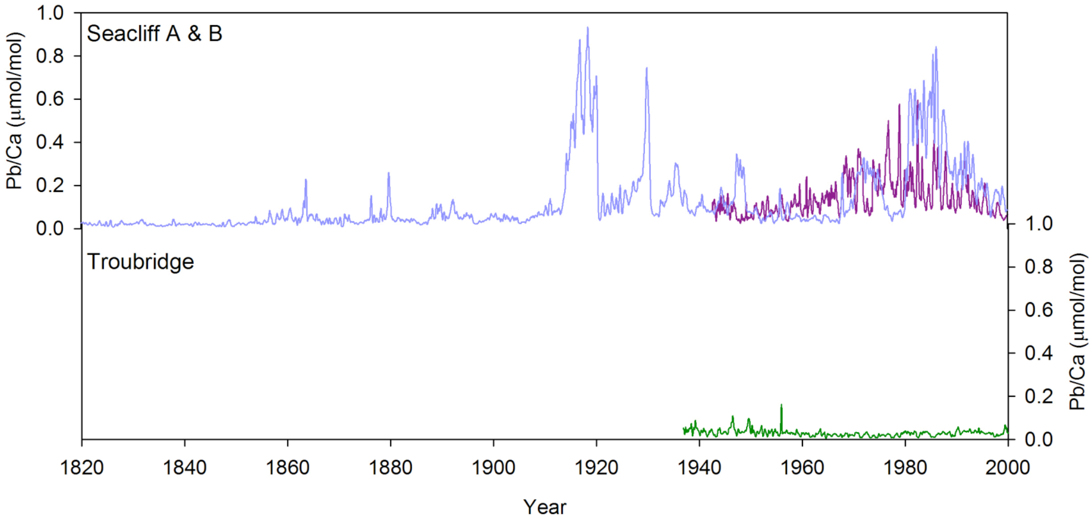

Figure 6.11: Pb/Ca concentrations for three corals from Gulf St. Vincent. Both Seacliff A and B exhibit large increases in Pb concentrations, whereas the Troubridge coral in open gulf waters contains very little Pb.

Pb/Ca concentrations in Seacliff A remain at background concentrations until a series of ‘pulsed’ Pb concentration increases during 1914-1920, 1925-1931, 1932-1938 and 1946-1949. The higher concentrations of Pb in the early part of the twentieth century are too early for the proliferation of vehicles, and may be related to other industrial processes or urban development. The exact source cannot be determined as growth patterns for many large scale industries during the industrial revolution were similar and there are many industries with lead emissions. Lead is used in the sewage treatment process and the higher concentrations in the 1930s and 1940s may be caused by the sewage discharge at Glenelg.

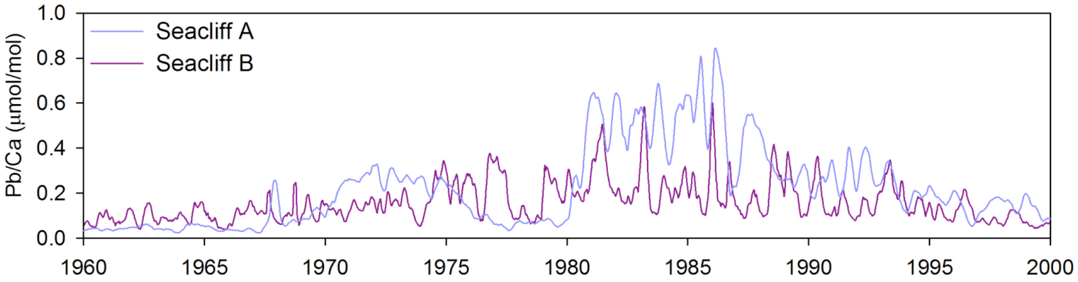

Figure 6.12: Pb/Ca concentrations for the period of vehicle proliferation from 1960-2000 in Seacliff A and Seacliff B.

Both Seacliff corals record a gradual increase in Pb/Ca from the mid 1960s, followed by a decline initiated in the late 1980s (Figure 6.12). There are differences in the maximum concentration and temporal record of the Seacliff corals and this may be related to the different growth rates observed between the two corals. The high Pb concentrations in the latter part of the twentieth century has been observed in other coral studies and has been linked to the development and proliferation of the automobile industry (Shen & Boyle 1987). The peak Pb concentrations in the 1980s are a decade later than the peak Pb consumption in the USA (Shen & Boyle 1987), and this may reflect slower growth and proliferation of vehicles in South Australia compared with the Northern Hemisphere. The reduced concentrations of Pb/Ca observed in the 1990s are consistent with the reduction of lead-based fuels. The phase out of lead-based petrol was initiated in the USA earlier than in Australia, with South Australia using lead-based petrol into the 1990s.

Oil Spills

V/Ca concentrations varied between 0.01-0.5 µmol/mol for all *Plesiastrea versipora* colonies analysed, however, concentrations of V/Ca in Seacliff B displayed a linear increase over the temporal record (Figure 6.13) and this trend was not observed in the Seacliff A colony. Due to elevated concentrations observed in the fast growing coral (Seacliff B) and not in the slow growing coral (Seacliff A), the V and Mo enrichment may be derived from pulse event enrichments. It is likely that the increase in V/Ca over time indicates an anthropogenic source rather than a natural source from continental weathering.

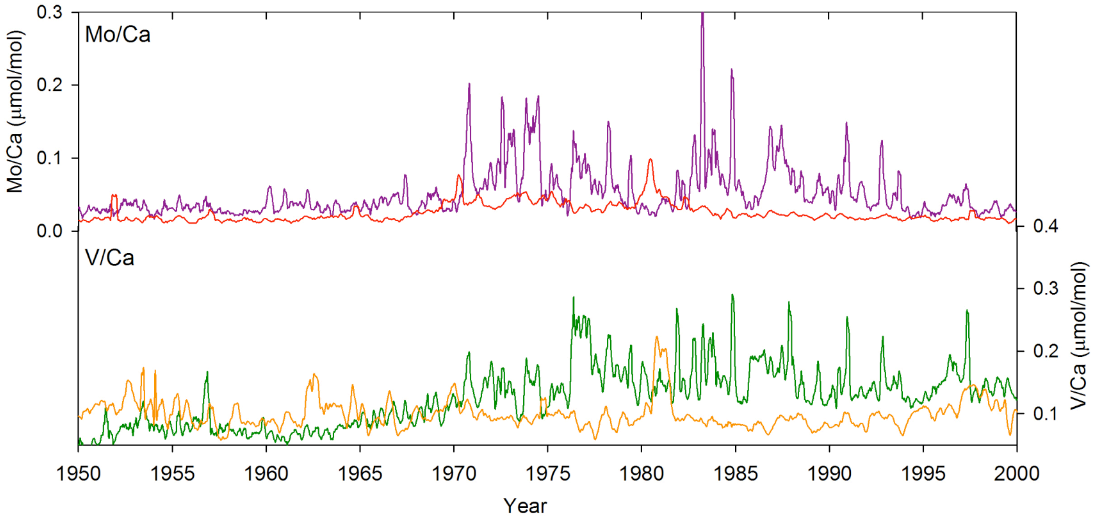

Figure 6.13: Concentrations of Mo/Ca and V/Ca from the two colonies at Seacliff. Seacliff B indicates enrichment in Mo/Ca (purple) and V/Ca (green) from the early 1970s compared with Seacliff A Mo/Ca (red) and V/Ca (orange) concentrations.

One of the principal sources for anthropogenic V in the marine environment includes fossil fuels, especially crude oil. A study on Caribbean corals associated high V concentrations with evidence of oil in coral tissue and skeletons (Guzman & Jarvis 1996). Molybdenum is known to be in elevated concentrations in oil products and together V and Mo may signify evidence of oil contamination recorded in the coral skeletons. Mo/Ca exhibits elevated concentrations in the Seacliff B colony, but this increase was not observed in the Seacliff A coral. Evaluation of the V/Ca and Mo/Ca concentrations in Seacliff B indicated a temporal correlation between the two elements in the elevated concentration spikes (Figure 6.14). However, the amplitude of concentration increase was different between the two elements and V is known to be preferentially excluded from coralline lattice due to the charge imbalance between V^{4+} and Ca^{2+} (Shen & Boyle 1988). The enriched concentrations of V and Mo occurred as pulse-type enrichment and were not limited to a particular season, suggesting the source is likely to be anthropogenic.

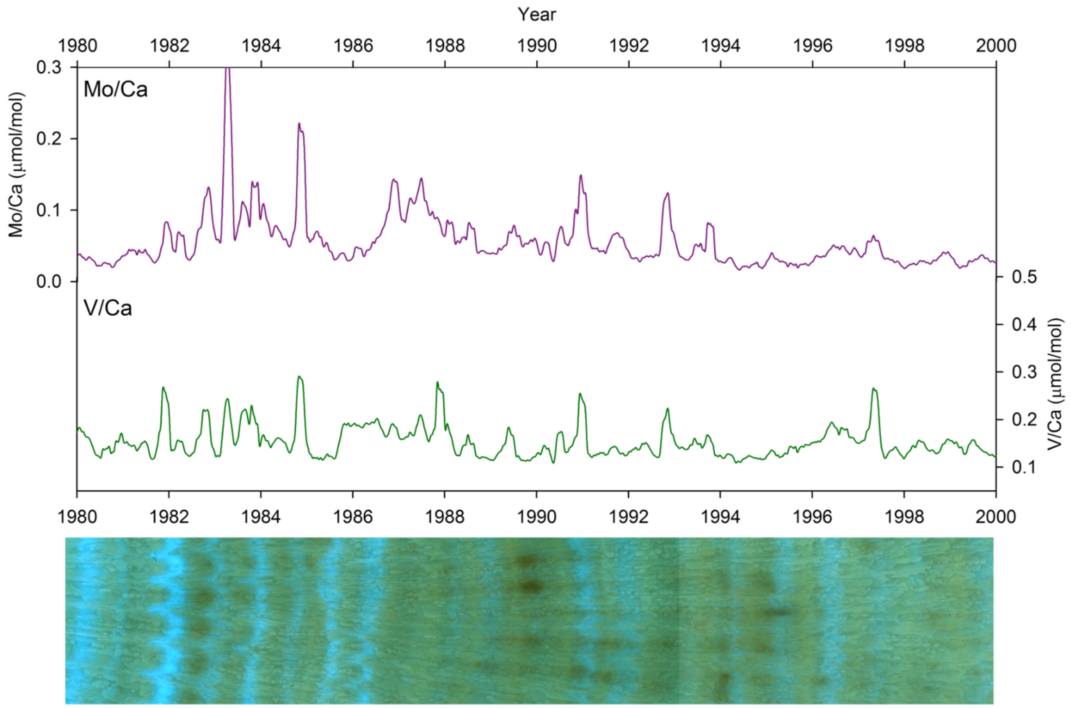

Figure 6.14: Concentrations of V/Ca and Mo/Ca from Seacliff B coral compared with luminescent bands for the period 1980-2000. The strong luminescent band in 1982 was a severe El Niño year, with higher temperatures recorded in South Australia.

Seacliff B is the only coral collected in this study with strong luminescent bands and several of the luminescent bands appear to correlate with the elevated concentrations of V and Mo. There is still debate in the literature about whether coral luminescent bands represent skeleton with a different porosity due to a stress event such as a flood plume or if the luminescence is caused by inclusions of humic acids and other organic material in the coral skeleton (Isdale 1984; Barnes & Taylor 2001; Lough et al. 2002; Barnes & Taylor 2005). Although the Seacliff corals are in close proximity, the growth rate of Seacliff B is three times faster than Seacliff A and this may explain why ‘pulsed events’ are not recorded in the trace metal records from Seacliff A.

Seacliff reef is located less than 5 kilometres from the oil refinery at Port Stanvac. Several oil spills have occurred at Port Stanvac, discussed in the introduction to this chapter, and the elevated concentrations of V and Mo in Seacliff B may be a record of oil contamination near Seacliff. Known oil spills that appear to be coincident with elevated concentrations of V/Ca and Mo/Ca and luminescent lines occurred in 1982, 1991, 1992 and 1996. Luminescent bands do not occur throughout the entire core of the Seacliff B colony, and the luminescent bands become much more frequent in the 1970s. Therefore, it is likely that the luminescent bands in Seacliff B are caused by environmental modification of either increased fresh water into the gulf region from the Torrens or Patawolonga Rivers or through contamination.

Western Gulf St. Vincent – Zn Enrichment

This study observed elevated levels of trace metals in environments where there was no obvious anthropogenic source (Figure 6.15). For example, the *Plesiastrea versipora* colony from Edithburgh exhibits regular seasonal variations of Zn/Ca in late summer/autumn of 3-4 times the background concentration (Figure 6.16). Potential sources of Zn in the gulfs include treated sewage and galvanised products from urban storm water, however, Edithburgh is a small coastal town with a relatively limited impact on the local environment compared with larger urban centres. The enriched Zn/Ca signal occurs in summer, so it is unlikely to be from an anthropogenic source with fluvial transport. If some of the coral colonies utilise more heterotrophic feeding in the warmer months, then one possible hypothesis for the high Zn concentrations may be a phytoplankton signature (Howe & Marshall 2001).

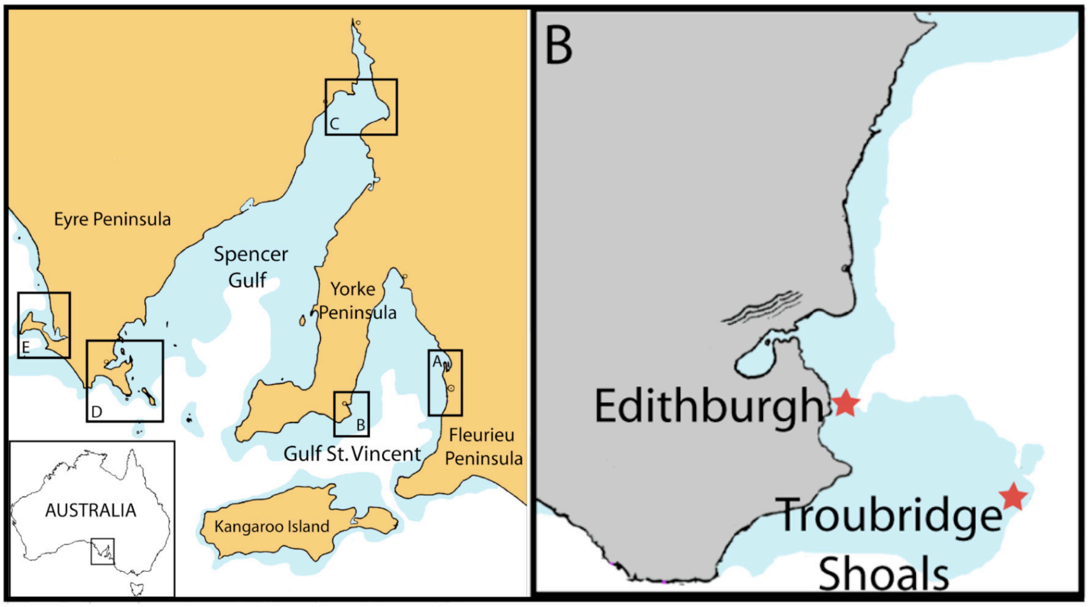

Figure 6.15: Map of the South Australian Gulfs with inset B: indicating coral locations from Edithburgh and Troubridge.

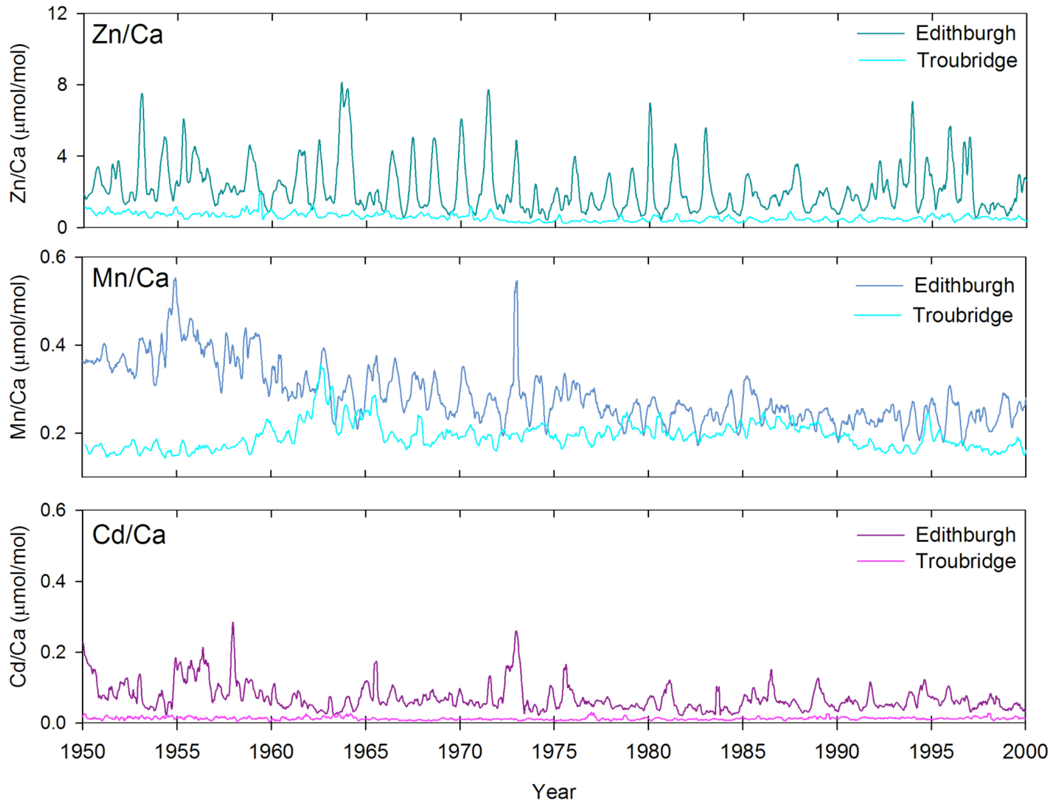

Figure 6.16: Zinc, Manganese and Cadmium concentrations in coral skeletons from Edithburgh (coastal) and Troubridge (open gulf) from relatively pristine sites in Gulf St. Vincent.

Zinc is an important biological element for phytoplankton growth, and a previous study measuring elevated concentrations of Zn in coral tissue suggested it may signify increased phytoplankton consumption (Ferrier-Pages et al. 2005). Phytoplankton blooms predominantly made up of the blue-green algae *Trichodesmium* have been observed in trace element evidence in tropical coral cores (Jones et al. 1986; Wyndham 2005). To test this hypothesis, the elevated Zn/Ca concentrations were compared with Mn/Ca and Co/Ca, as these elements are also known to be in high concentrations in phytoplankton. There was a correlation in the temporal scale of enrichment in both Zn and Mn in the Edithburgh colony (Figure 6.16), however, the amplitude of the concentration peaks were different which reduced the correlation. Concentrations of cobalt was not observed in any corals (i.e. analytical concentrations were the same as the instrument background) suggesting that there is little Co available in the South Australian Gulfs or it is not easily incorporated into coralline lattice.

Upper Spencer Gulf - Industrial Impacts

Two corals from Whyalla were assessed to determine the extent of trace metal contamination from steel smelters in upper Spencer Gulf. Figure 6.17 displays concentrations of seven trace metals (Li/Ca, P/Ca, Mn/Ca, Zn/Ca, Sn/Ca, Cd/Ca and Pb/Ca) analysed from two colonies from Whyalla in Spencer Gulf. Both corals lived for approximately 50 years but were not old enough to predate the smelter (operations began in the 1890s) and provide background concentrations of trace metals in the region. However, metal concentrations in the Whyalla corals can be compared with the pre-European background concentrations derived from the Taylors Island coral (Southern Spencer Gulf). There is a high degree of variability between the two corals and both had low growth rates of less than 2 mm yr^{-1}. The cause of the variations in trace metal concentrations between the two colonies may be related to non-lattice bound material or local variations in trace metal concentrations. The trace metal enrichment is unlikely to be due to sediment trapped in the coral lattice as the elevated concentrations occur for a period of several years.

The most likely explanation for the concentration differences observed between the corals is localised variability in trace metal concentrations due to sediment resuspension. Both corals were collected in ~ 4 m water depth and are subject to high salinities > 40‰ in summer, which may influence the behaviour of trace metals. The corals were located ~ 100 m apart and previous studies on sediment profiles in upper Spencer Gulf have observed heterogeneity on a small spatial scale due to complex local oceanography in the region (Ward & Young 1981).

Concentrations of Zn/Ca, Sn/Ca and Pb/Ca are higher in the Whyalla corals than those observed for Seacliff corals, by an order of magnitude for Pb/Ca. Concentrations of Cd/Ca and Sn/Ca were observed to return to background concentrations for part of the coral record, whereas concentrations of Zn/Ca and Pb/Ca remain enriched. The higher concentrations of Zn and Pb compared with other heavy metals (Sn, Cd) may be due to the lead-zinc smelter at Port Pirie (upper Spencer Gulf) or due to higher distribution coefficients of these elements (Shen & Boyle 1988).

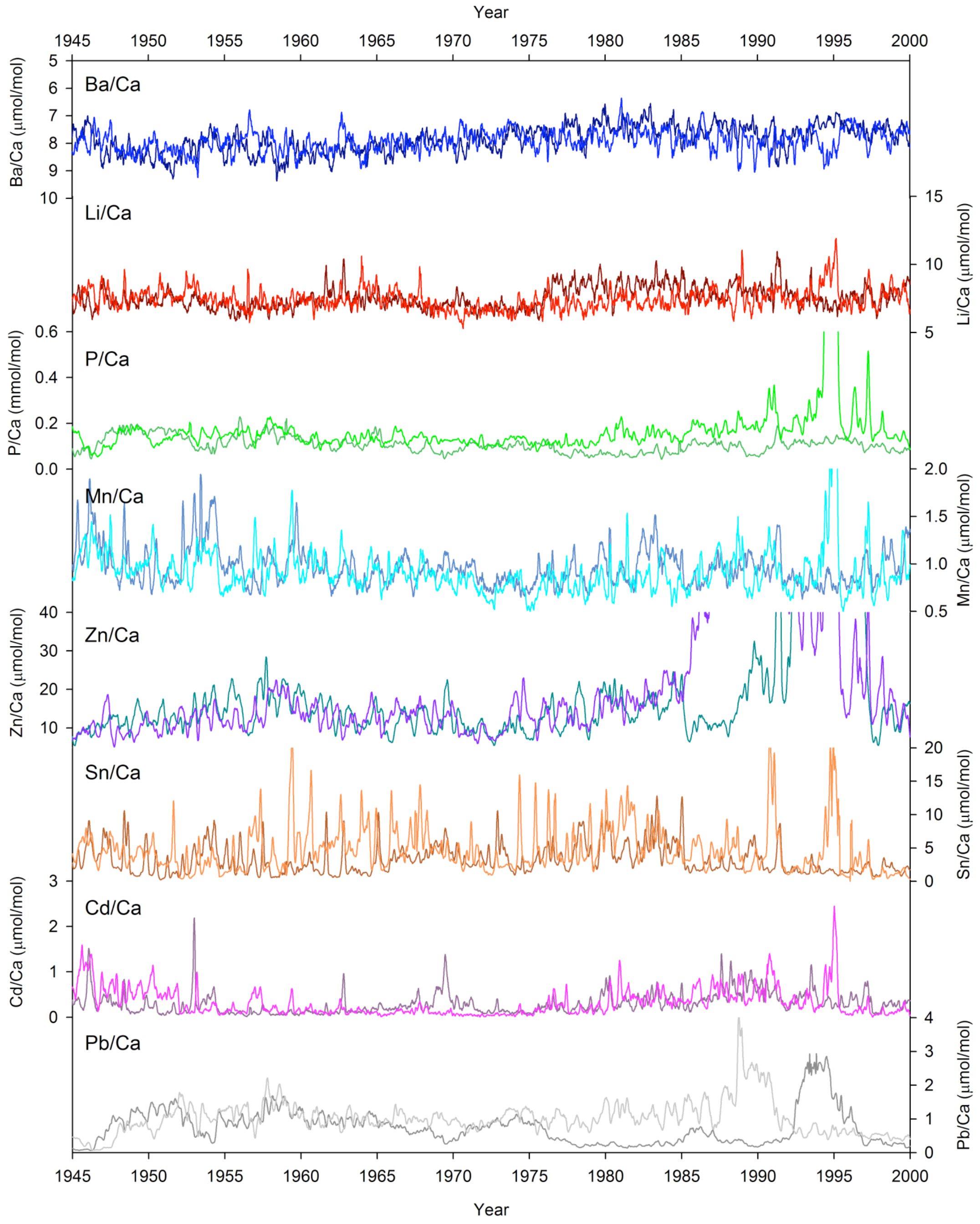

Figure 6.17: Trace metal concentrations (Li/Ca, P/Ca, Mn/Ca, Zn/Ca, Sn/Ca, Cd/Ca and Pb/Ca) from two corals Whyalla A03 and Whyalla B03, collected from Point Lowly near Whyalla (Spencer Gulf). Ba/Ca has been included as a seasonal control and the axis is inverted.

Land Use Changes

Aeolian Dust

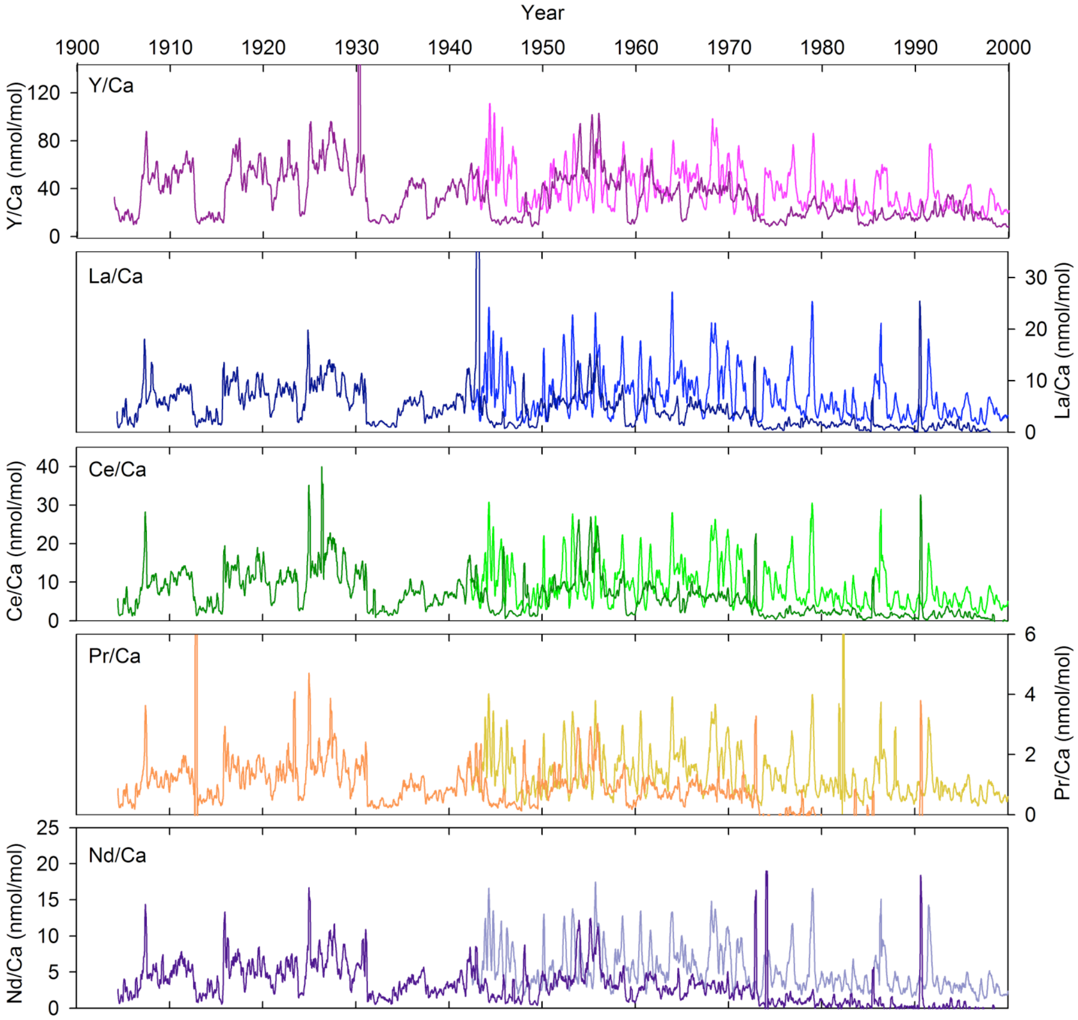

Figure 6.18: Light rare earth elements analyses from two corals Seacliff B and Edithburgh. The shorter record from 1945-2000 in lighter colours is the Seacliff B colony. The two corals display greater coherency in the period 1970-2000.

The rare earth elements (REE) Y, La, Ce Pr and Nd displayed very little fractionation between the elements in all coral cores analysed (Appendix H). The coherent nature of the LREEs is displayed in Figure 6.18, with each element reproducing the same pattern in the elevated concentrations. Similarities were observed in the LREE concentrations in the Seacliff B and Edithburgh corals with less LREE incorporated into the skeleton from the late 1970s to 2000. The time series variations do not appear to be associated with increased runoff from urban areas as corals on both sides of Gulf St. Vincent indicate elevated LREE concentrations and only the eastern coastline has rivers. LREEs have been shown to be incorporated into coral skeletons in proportion to seawater REE concentrations (Sholkovitz & Shen 1995). The distribution coefficients for La and Ce derived by Sholkovitz & Shen (1995) suggest enrichment in the coralline lattice relative to seawater D_{La} = 1.6 and D_{Ce} = 2.9. The differences observed between the frequency of elevated LREE concentrations between the Seacliff B and Edithburgh corals may be due to the corals growth rates. The Edithburgh coral has a growth rate of ~ 3 mm yr^{-1} and may be growing too slowly to capture heterogeneity over short time scales. Extrapolating concentrations of coral REE to seawater may be difficult due to potential differences in species or growth rate specific K_D.

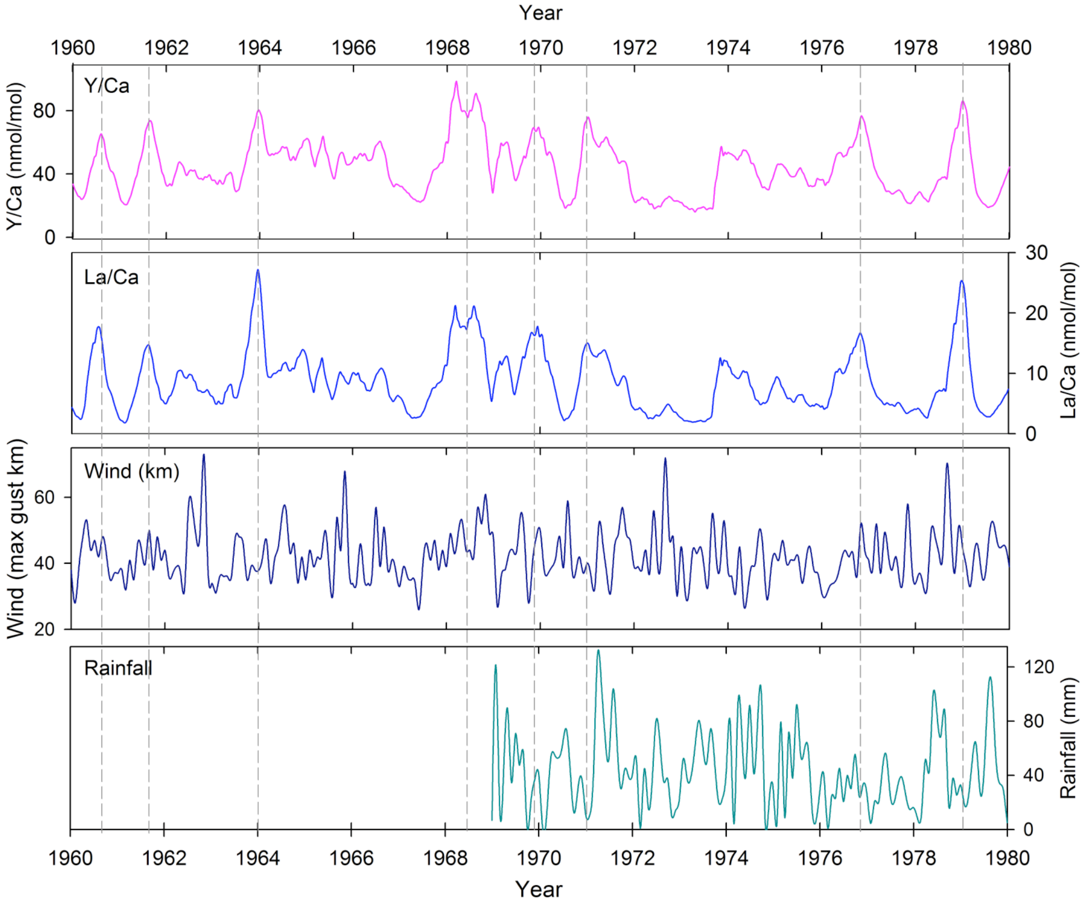

Figure 6.19: Light rare earth elements analyses for a 20 year period from Seacliff B. LREE concentrations were compared with wind and rainfall records from Adelaide Airport. Environmental data provided by the Bureau of Meteorology.

The range of measured concentrations of REE from *Plesiastrea versipora* were similar to concentrations observed in previous coral studies (Sholkovitz & Shen 1995; Fallon et al. 2002; Wyndham et al. 2004). The source of LREE entering Gulf St. Vincent is likely to be weathering from local country rock and may be transported through aeolian or fluvial mechanisms. To assess the mechanism for elevated LREEs the Seacliff B coral record was compared with rainfall and wind speed data from the Bureau of Meteorology in Adelaide (Figure 6.19). The coherency between the REE concentrations and rainfall was very low, suggesting that riverine transport was not the source of REE enrichment. Although wind speed did not correlate well with peaks in REE, it is considered to be a more likely transport mechanism due to the elevated LREE concentrations on both sides of Gulf St. Vincent. Combining wind direction data may help establish whether wind is the dominant mechanism of REE transport into the gulfs.

Discussion

Metal concentrations were significantly different between different colonies in different parts of both gulfs, indicating a spatially and temporally variable pattern of metal sources within both gulfs. Possible pollution sources in the region include point sources of pollution such as storm water, waste water treated sewage, industrial effluent, by-products from vehicles, ports and dockyards, oil and metal refineries; and non-point source pollution including agricultural wastes (fertilizers, herbicides and pesticides) and soil erosion. As two of the corals (Seacliff A and B) are from a metropolitan reef off the coast of Adelaide it may not be possible to identify the contaminants from a particular source as storm water, vehicle emissions, industrial chemicals, antifouling and anticorrosive paints and treated sewage all contain heavy metals. However, these corals provide a long-term record (pre-European arrival) of anthropogenic impacts on water quality in the South Australian gulfs. This study provides the first long-term records of anthropogenic impacts in South Australia.

The two Seacliff corals reinforce the hypothesis that distribution coefficients are growth rate dependent. However, due to the variability in maximum concentrations recorded by each coral, it was not possible to extrapolate coral trace metal concentrations to seawater concentrations.

The role of environmental factors impacting metal incorporation into corals still needs to be established, apart from the well established effects of local metal concentration in seawater (Shen & Sanford 1990). When analysing trace metals which have temporally highly variable concentrations (e.g. increased metal concentrations associated with pollution events such as river flood plumes) it is difficult to accurately assess how changes in salinity and sea surface temperature effect skeletal incorporation. The role of SST is well recognised for the incorporation of Sr and other elements such as B, Mg, U and Ba but it is not known how corals incorporate other transition metals into their skeleton with different temperatures. For example, this study has found a strong temperature influence on the substitution of Ba for Ca, which was also observed by Lea et al. (1989) in a site with regular oceanic upwelling and supported by inorganic precipitation experiments by Gaetani and Cohen (2006). Barium has also been related to terrestrial sources, McCulloch and co-authors (2003) used Ba/Ca concentrations to document the anthropogenic impact in northern Queensland through deforestation and livestock grazing. The changes in Ba concentration observed during flood plume events in McCulloch et al (2003) were three times greater than the variable concentration attributed to temperature discussed in Chapter 5. A strong Ba/Ca signal has also been observed in Kenyan flood plumes (Fleitmann et al. 2007). However, large Ba/Ca spikes do not always relate to flood events (Sinclair 2005b) and flood events may occur without an associated Ba/Ca peak (Sinclair & McCulloch 2004).

It is difficult to compare the ranges of trace metal between different studies due to different techniques utilised with the cleaning methodology and analysis (including technical instrumental advancements over the last decade). However, the trace metal concentrations observed in *Plesiastrea versipora* are comparable to other contaminated sites around the world. Most of the trace metal levels measured in *Plesiastrea* coral skeletons by LA-ICP-MS were lower than ranges observed in corals from Thailand (Brown & Holley 1982; Brown & Howard 1985; Allison 1996), the Red Sea (Hanna & Muir 1990), Hong Kong (Scott 1990), Costa Rica and Panama (Guzman & Jimenez 1992), and Japan (Ramos et al. 2004) but higher than northern

Australian sites (Zn, Pb (St John 1974; Esslemont 1999; Esslemont et al. 2000). The corals indicating trace metal concentrations higher than those observed in this study are from severely impacted coastal sites with much higher population and industrial densities (Central America, Hong Kong and Thailand).

Understanding the transport mechanisms distributing anthropogenic pollutants to the coastal environment is crucial to establish the source of contamination, and provide effective environmental management. Previous studies on tropical corals have determined that the suspended sediment load in rivers is the most important transport mechanism (Guzman & Jimenez 1992; Fallon et al. 2002; Ramos et al. 2004). The South Australian gulfs experience a Mediterranean style climate with low rainfall. Although sediment plumes can occur in Gulf St. Vincent (Figure 6.1), they occur sporadically and therefore aeolian transport of trace metals may play a more significant role than it does in tropical environments with high annual rainfall.

Urban Pollution

Treated Sewage

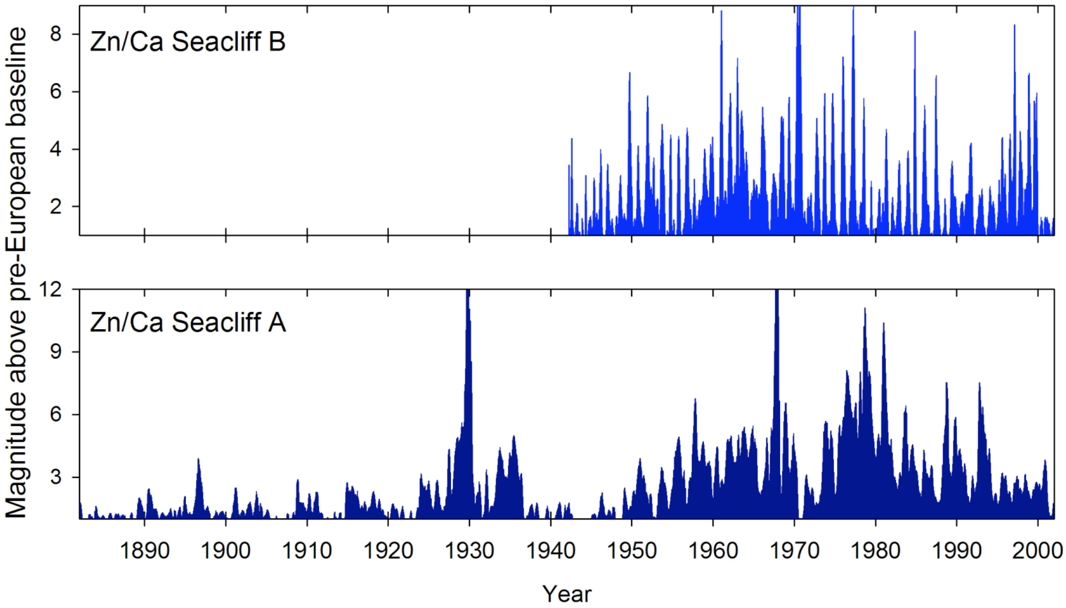

Figure 6.20: Comparison of enrichment of Zn/Ca in Seacliff B and Seacliff A, normalised to a pre-European baseline concentration for Zn.

The enrichment of Zn/Ca, Cu/Ca, Sn/Ca and Mn/Ca observed in the Seacliff corals appears to coincide with development of the waste water treatment processing plant at Glenelg. Concentrations of Sn/Ca and Cu/Ca increase in the 1940s when treated sewage was first discharged into Gulf St. Vincent and again in the 1960s with the first outfall built at Glenelg (Figure 6.20, 6.21). Therefore, it is suggested that elevated levels of these trace metals may reflect the population growth and urban development of the regional city (Adelaide).

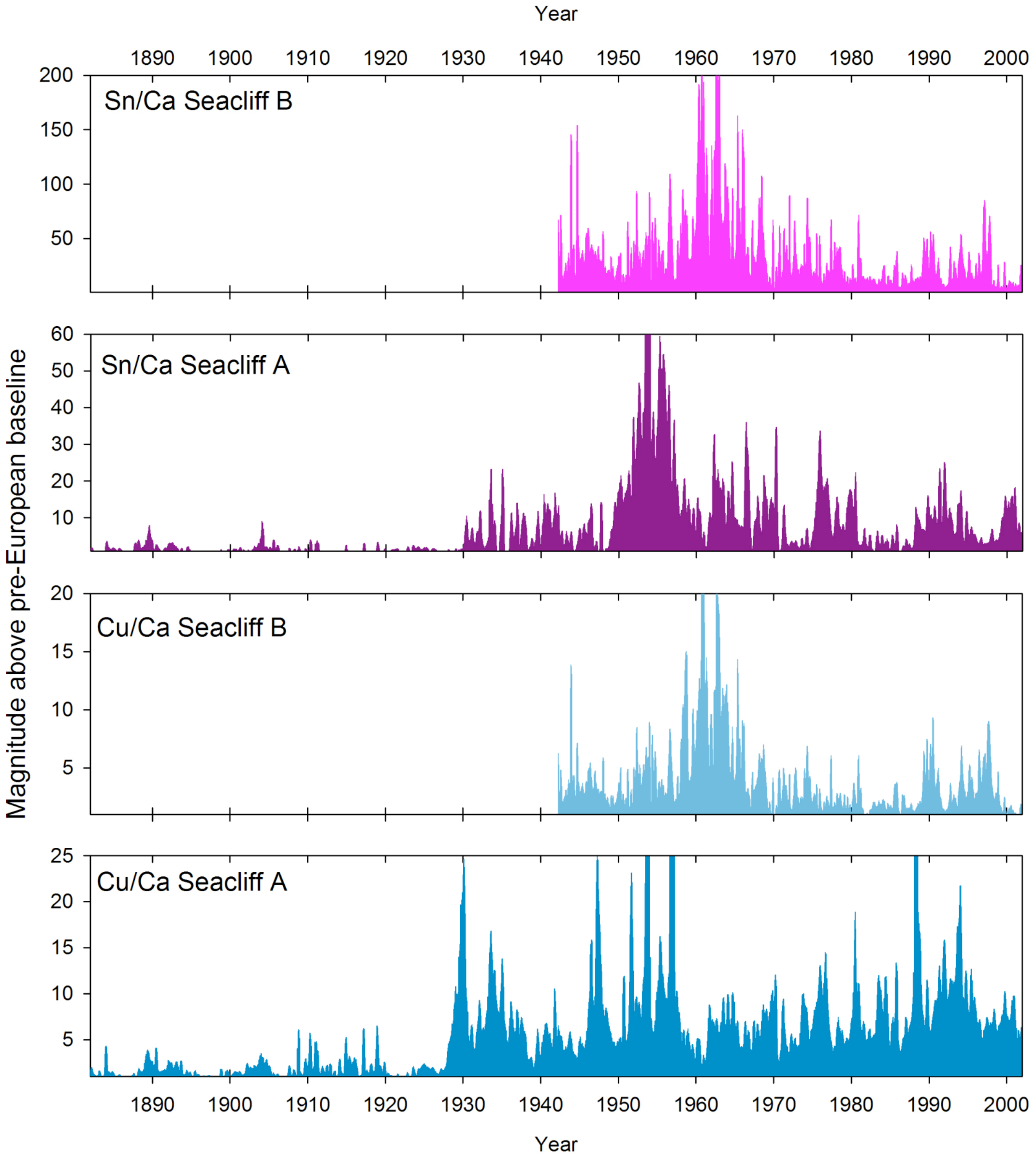

Figure 6.21: Comparison of the magnitude of enrichment for Cu and Sn in Seacliff B and Seacliff A, normalised to a pre-European baseline concentration.

An offset is present between the timing of the peak enrichment of Sn and Cu in Seacliff B and Seacliff A (Figure 6.21). This suggests that the chronology of Seacliff A may be out of temporal alignment by approximately 5 years. Seawater concentrations of Zn/Ca, Cu/Ca, Sn/Ca and Mn/Ca could not be extrapolated from the coral skeleton concentrations, due to the variability in trace metal distribution coefficients between the corals with different growth rates. However, the magnitude of enrichment above the pre-European baseline could be established for Seacliff B (Figure 6.20) and Seacliff A (Figure 6.21) corals. The magnitude of change was determined by normalising the trace metal/Ca concentrations with the pre-Europeans baseline derived from the early part of the Seacliff A record (1820-170). Tin was observed to have the greatest enrichment of over 150 times above baseline levels.

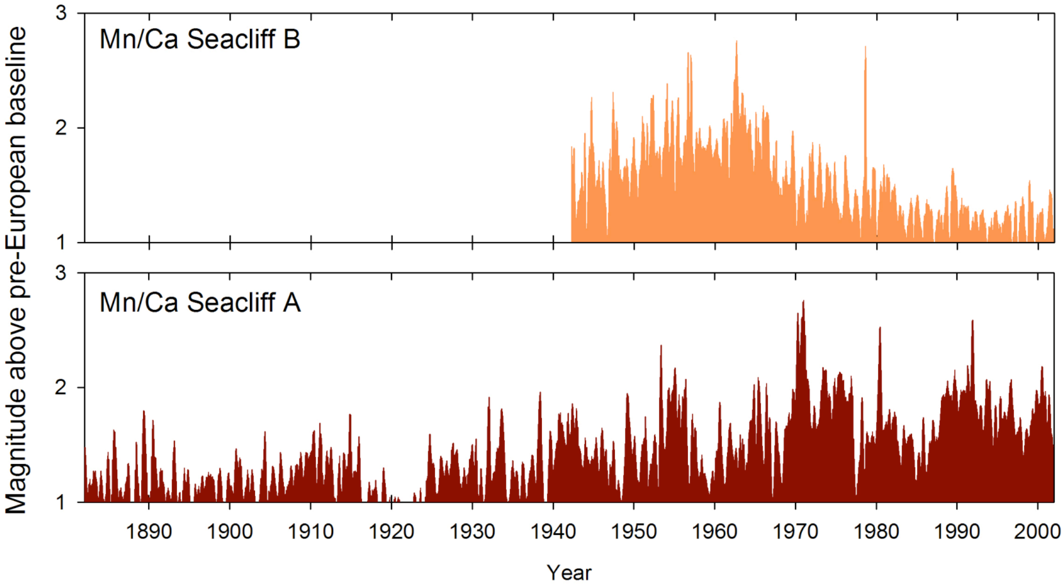

Figure 6.22: Comparison of the magnitude of enrichment for Mn in Seacliff B and Seacliff A, normalised to a pre-European baseline concentration.

Suggested processes controlling seasonal variations in Mn concentrations include an increase in photoreductive dissolution of suspended sediment Mn-rich particulates which increases in spring with increasing solar radiation (Fallon 2000; Alibert et al. 2003) or a diagenetic release of Mn due to reductive conditions resulting from decaying organic matter of Mn at the seawater-sediment interface (Alibert et al. 2003). Mn appears to be discriminated against in the coralline lattice and distribution coefficients have been determined to be D_{Mn} ~ 0.1-0.5 (Shen et al. 1991). The variation in Mn K_D implies that extrapolation back to seawater concentration would not be very accurate. However, the behaviour of Mn is different to the other trace metals in the Seacliff corals. Concentrations of Mn remain higher than preindustrial backgrounds, whereas other trace metals return to background concentrations after 'pulse events' of elevated concentrations (Figure 6.22).

Lead

The background Pb/Ca levels recorded in the two Seacliff corals are 0.02-0.03 µmol/mol, these values are higher than concentrations of Pb/Ca observed in other coral studies of 10 nmol/mol (Dodge & Gilbert 1984; Shen & Boyle 1987; Linn et al. 1990; Reuer et al. 2003). The highest concentrations observed in this study (800 nmol/mol) are an order of magnitude higher than concentrations observed in other studies (70 nmol/mol), (Shen & Boyle 1987). The anthropogenic enrichment of Pb in South Australian coastal waters is over 30 fold baseline concentrations compared to the 6-8 fold enrichment observed by Shen & Boyle (1988). The coral colonies used in this study are more proximal to the source of anthropogenic lead, compared to the corals from Bermuda recording anthropogenic contamination from the USA in the Shen & Boyle (1987) study.

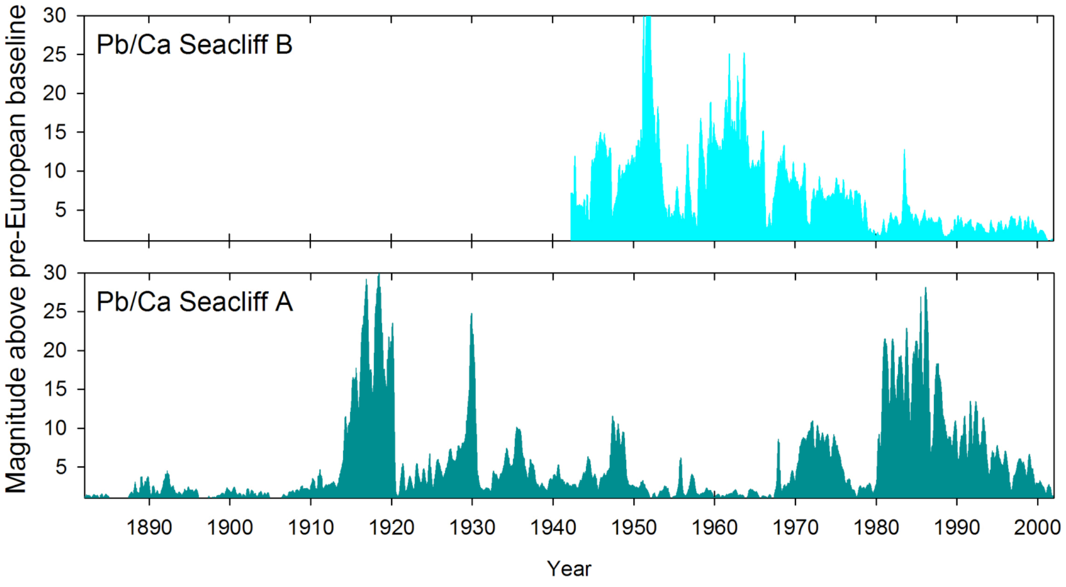

Figure 6.23: Comparison of the magnitude of enrichment for Pb in Seacliff B and Seacliff A, normalised to a pre-European baseline concentration.

The higher concentrations of Pb recorded in this study may be due to several reasons including; (1) closer proximity to Pb source, (2) higher concentrations in the local environment, (3) contamination from tissue was present, (4) not-only lattice bound Pb was measured or, (5) different distribution coefficients in *Plesiastrea versipora* compared with tropical coral species.

Several studies from the Northern Hemisphere have examined Pb increases in corals and sclerosponges with industrialisation and observed concentration increases in the mid-1800s due to industrialisation (Dodge & Gilbert 1984; Shen & Boyle 1987; Wu & Boyle 1997; Lazareth et al. 2000). Corals in Atlantic sites such as Bermuda and St Croix record the global augmentation of environmental lead levels by industrialisation (Dodge & Gilbert 1984; Shen & Boyle 1987; Shen & Boyle 1988). Cadmium concentrations analysed in corals from Bermuda have also recorded industrialisation with higher concentrations due to aeolian transport from North America (Shen et al. 1987). However, no correlation between Pb/Ca and Cd/Ca concentrations were observed in the South Australian corals. These studies contributed high Pb concentrations to industrial atmospheric fallout. Although industrialisation occurred later in Australia than in the USA and Europe, there appears to be little evidence of aeolian transport as the corals from the western coastline of Gulf St. Vincent and in open gulf waters do not exhibit an increase in Pb concentrations. In the South Australian environment, the lead enrichment is dominated by local pollution.

During evaluation of background trace metal concentrations, it was observed that the coastal coral Seacliff A had higher concentrations than the open gulf corals, suggesting a local source of trace metals from river outflow or coastal sediments. The higher background concentration of Pb observed in *Plesiastrea versipora* compared with other coral studies suggests there is more lead present in the gulfs than in open ocean environments where other coral studies were located (Linn et al. 1990). The cleaning techniques used in this study included an oxidative step with H_2O_2, sonification and ablating a ‘fresh’ aragonite surface before analyses were conducted, reductive steps with acid leaching or heating to remove oxides were not included in this study. Therefore, it is possible that some of the measured Pb may be from small particles trapped in the lattice rather than true lattice bound Pb. The difference in Pb/Ca concentrations between this study and measurements conducted at MIT (Shen & Boyle 1988; Reuer et al. 2003) are likely to be a combination of the different cleaning methodology, combined with local oceanography and the variable growth rates of corals used in this study.

Oil

Little is known about the incorporation of hydrocarbons and other organic molecules into coral skeletons, and whether complex molecules are fractionated against lighter more soluble elements, which may be preferentially taken up into the coral skeleton. A recent study examining hydrocarbons in coral cores from Saudi Arabia to assess the exposure of corals to the 1991 oil spill only found evidence of oil exposure in one coral core and no correspondence with other stress indicators such as reduced growth (Poulsen et al. 2006).

Previous studies have detected coral growth responses to oil spills and differences in trace metal chemistry (Burns & Knap 1989; Guzman & Holst 1993; Guzman et al. 1994; Guzman & Jarvis 1996; Readman et al. 1996). Guzman and Jarvis (1996) used vanadium (an abundant element in crude oil) as a long term tracer of oil pollution in corals from Panama. The distribution coefficient for V has been determined for corals from Bermuda $D_V = 0.027$ (Shen & Boyle 1988).

To accurately determine whether the luminescent bands observed in Seacliff B may be due to oil contamination, further research would need to be conducted. Organic geochemical analyses targeting the luminescent bands may be able to determine any trace of hydrocarbons (Burns & Knap 1989). Skeletal tomography examining structural variations between luminescent bands and normal *Plesiastrea versipora* skeleton would also establish the role of organic inclusions versus different crystal structure causing the luminescence (Carricart-Ganivet & Barnes 2007).

Industrial Pollution

Heavy metal contamination of marine sediments and aquatic organisms has been the subject of several studies (Ward & Young 1981; Ferguson 1983; Ward & Young 1983; Harbison 1984; Noye 1984; Harbison 1986; Maher 1986; Ward 1989; Edwards et al. 2001). Metals such as Fe, Cu and Zn have biological functions and are essential elements for many organisms. However, other metals such as Cd and Pb have no known biological function and are toxic at very low concentrations (WHO 1992). Studies conducted on the ecosystems of northern Spencer Gulf have indicated that contamination in this region has adversely affected biodiversity (Ward & Young 1983). The seagrass ecosystems in this region have a high storage capacity for heavy metal contamination with 73 t Cd, 51 t Pb and 571 t Zn estimated from seagrass leaves in a survey conducted over a 2 km^2 area (Ward & Young 1981). Several organisms found in this region were analysed for heavy metal tissue content (including crustaceans, bivalves, prawns, crabs and fish), with results indicating elevated concentrations of toxic metals. Furthermore, most species exceeded health guidelines for human consumption. However, no distinct relationship was observed between metal concentration and distance from the Whyalla steelworks in contaminated sediments and shellfish (Harbison 1984). Seasonal patterns in currents and variability in turbidity in this region of the gulf may mask gradients in concentration (Harbison & Wiltshire 1998).

Land-use Change

REE abundance of seawater is largely controlled by scavenging processes where LREE are preferentially adsorbed onto surface particles and REEs are incorporated into coral skeletons in proportions similar to seawater concentrations (Wyndham et al. 2004). Large aeolian input has been suggested as the major contributing factor to the death of Holocene reefs in the Gulf of Carpentaria (DeDeckker et al. 1991; Marshall 2006) and the demise of modern reefs in the Caribbean and Africa (Shinn et al. 2000; Garrison et al. 2003; McClanahan et al. 2004).

Summary

The results from this chapter add to the growing literature on coral pollution studies. This study analysed a broad suite of elements and observed some elemental relationships that have not been revealed in previous studies. Coral baseline chemistry was established for both Spencer Gulf and Gulf St. Vincent using corals from open gulf locations. Changes in trace element concentrations observed from *Plesiastrea versipora* indicate local environments that have been heavily modified by anthropogenic influences. The corals from the metropolitan reef (Seacliff) off the coast of Adelaide record the progress of urban development over the last 70 years. The sources of point source pollution measured in *P. versipora* were correlated to historical information including discharge of treated sewage, oil contamination, vehicle proliferation and heavy metal smelters.

European settlement occurred in the region over 150 years ago and the South Australia gulfs contain a large metropolitan city and heavy industry. The corals analysed in this chapter exhibit a broad range of environmental degradation from anthropogenic influences including:

1. Coastal water degradation from waste water treatment plants
2. Historical increases in urban coral lead chronologies reflecting industrial development
3. Records of oil spills from an oil refinery
4. Heavy metal contamination from ore and steel smelters
5. Land use changes recorded by changes in LREE concentrations in coral skeletons.

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Chapter 7:

Records of the Suess Effect in *Plesiastrea versipora*

Chapter 7: Records of the Suess Effect in South Australian corals

Introduction

Human activities such as the burning of fossil fuels and land-use changes have emitted anthropogenic CO_2 that is strongly depleted in ^{13}C due to the preferential uptake of ^{12}C during photosynthetic carbon fixation by plants. The resulting depletion of the atmospheric $^{13}C/^{12}C$ by anthropogenic CO_2 emissions is known as the ^{13}C Suess effect (Revelle & Suess 1957; Suess 1980). The oceanic ^{13}C Suess effect i.e. the decrease of $\delta^{13}C$ in dissolved inorganic carbon (DIC) has recently attracted interest because it provides a means for estimating the ocean's uptake rate of fossil fuel CO_2 (Broecker & Peng 1982). In addition, the oceanic Suess effect is potentially a constraint on the magnitude of gross carbon exchange fluxes between the atmosphere and the terrestrial biosphere (Keir et al. 1998). Direct observation of anthropogenic changes in DIC and $\delta^{13}C$ of DIC are hampered by significant site-specific variations, as well as seasonal and inter-annual variability (Quay et al. 1992). Equilibration times for DIC and $\delta^{13}C$ between the surface ocean and atmosphere differ by an order of magnitude and variability in surface water residence time and circulation with respect to gas exchange results in spatial variability of the oceanic $\delta^{13}C$/DIC perturbation ratio (Körtzinger et al. 2003). Understanding the ocean's role in the uptake and storage of anthropogenic CO_2 provides important constraints for our understanding of the modern carbon cycle and our predictions of future climate change.

However, determination of oceanic $\delta^{13}C$ changes has been difficult due to the scarcity of oceanic $\delta^{13}C$ data from the past (Quay et al. 1992). Recent ocean geochemical studies during the GEOSECS surveys in the 1970s (Ostlund & Stuvier 1980) and the WOCE surveys of the 1990s (Key et al. 1996) have sought to determine the magnitude of oceanic uptake of atmospheric CO_2. Many of these studies have centred around the change in $\delta^{13}C$ of the surface oceans (Keeling et al. 1979; Quay et al. 1992; Bacastow 1996; Gruber et al. 1996; Heimann & Maier-

Reimer 1996). The atmospheric $\delta^{13}C$ composition has become depleted by ~1.5‰ since the industrial revolution due to the burning of ^{13}C-depleted fossil fuels (Keeling et al. 1995). The global mean $\delta^{13}C$ change in the surface ocean is estimated at -0.16 ±0.02 ‰ per decade between the 1970s-1990s (Quay et al. 2003). However, the $\delta^{13}C$ depletion in the upper part of the water column varies depending on the ocean basin; the eastern Atlantic displays a depletion of ~0.62‰ (Beveridge & Shackleton 1994), and the Arctic Ocean of ~ 0.9‰ (Bauch et al. 2000), whereas the Subantarctic Zone south of Australia indicates a depletion during the last 20 years of ~0.32‰ (McNeil et al. 2001), highlighting the importance of this region as a sink for atmospheric CO_2. One of the most direct means of determining the oceanic $\delta^{13}C$ Suess effect is from time series of individual station data, i.e. Bermuda station data (32°N) indicates considerable (~0.2‰) seasonal variability and interannual variability in temperature that biased the high rate of change of $\delta^{13}C$ DIC of -0.25 (±0.02‰) per decade for the last 20 years (Gruber et al. 1999). Another way to estimate the oceanic ^{13}C Suess effect is to compare $\delta^{13}C$ of DIC data from open ocean measurements sufficiently far apart in time to resolve relatively small long-term $\delta^{13}C$ changes from seasonal and interannual variability. This approach has afforded rough estimates of the $\delta^{13}C$ Suess effect in the Pacific (Gruber et al. 1999; Sonnerup et al. 2000; Quay et al. 2003) and the Indian (Gruber et al. 1999) Oceans; however data may be aliased by seasonal, spatial, and interannual variability in $\delta^{13}C$ and is sensitive to potential long-term changes in circulation and biological remineralization rates.

Time series of $\delta^{13}C$ generated from biogenic organisms (corals and sclerosponges) have provided an archive of $\delta^{13}C$ in DIC when corrected for mass dependent fractionation (Nozaki et al. 1978; Druffel & Benavides 1986; Böhm et al. 1996; Fallon et al. 2003). Analyses of the $\delta^{13}C$ of aragonite incorporated into Jamaican sclerosponges (18°N, 78°W) in the Caribbean imply that local surface water $\delta^{13}C$ DIC values decreased by 0.5 ‰ during 1910-1970 (Druffel & Benavides 1986) and that the $\delta^{13}C$ decrease rate during 1970-1990 was approximately -0.18 ‰ per decade (Böhm et al. 1996). Interpreting long-term trends in the $\delta^{13}C$ signal from massive scleractinian corals is confounded by several physiological and environmental signals including depth (Swart et al. 1996), light intensity (Reynaud-Vaganay et al. 2001), photosynthesis, mass spawning (Gagan et al. 1996), heterotrophic feeding (Grottoli & Wellington 1999), and cloud cover (McConnaughey 1989).

In this study, we present $\delta^{13}C$ measurements for three coral cores from the cold-water faviid *Plesiastrea versipora* collected from Gulf St Vincent (35ºS), South Australia. We compare the $\delta^{13}C$ archive generated from these temperate corals with previously published records from massive *Porites* corals to examine the ocean-atmosphere mixing regime and fidelity of this archive.

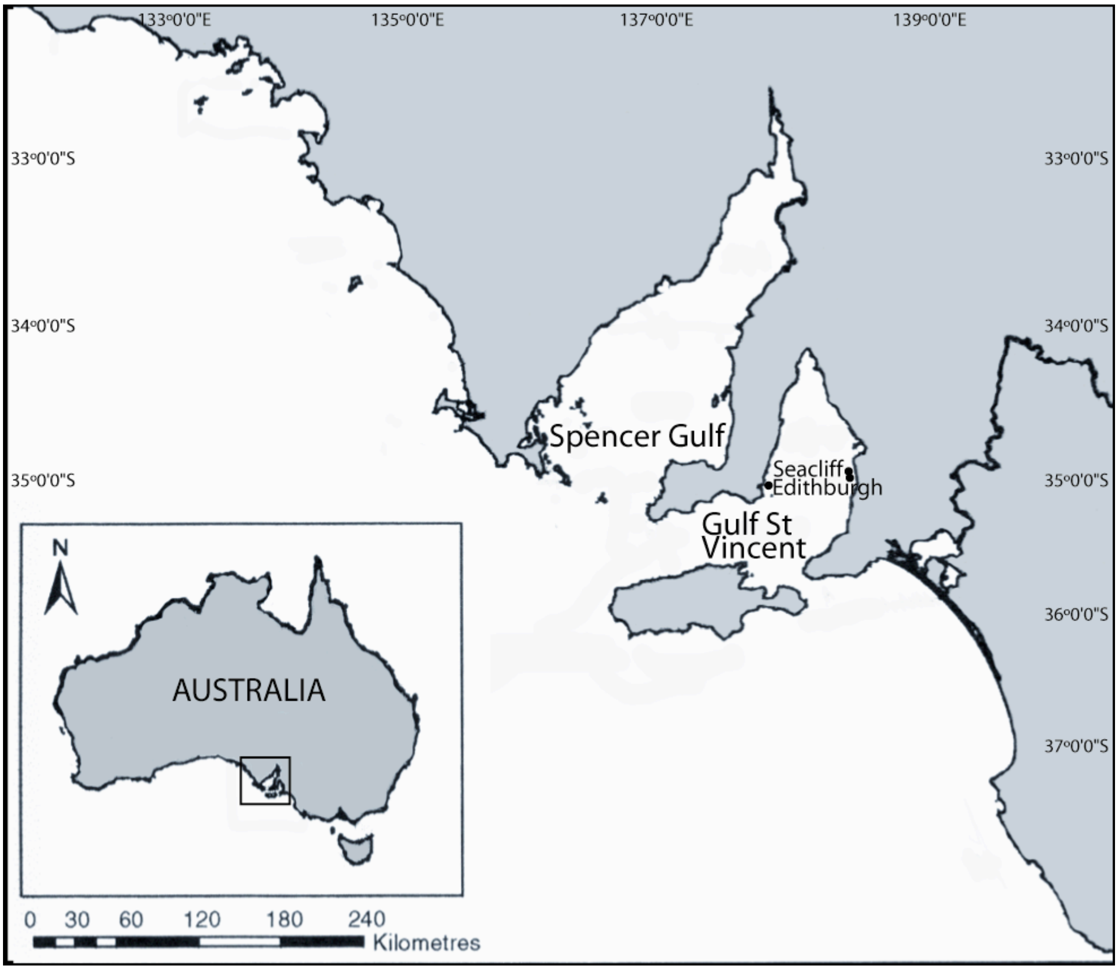

Figure 7.1: Location of coral cores collected and analysed for $\delta^{13}C$ in Gulf St Vincent, South Australia.

Methods

Cores were drilled from live colonies of the faviid coral *Plesiastrea versipora* during November 2003 and May 2005 in Gulf St Vincent, South Australia (Figure 7.1). The pneumatic coring techniques required some modification from the *Porites* coring technique (Sinclair et al. 1998; Fallon et al. 1999) used in tropical environments due to the increased density of *P. versipora*. Once the core sample was extracted from the coral colony the core hole was capped with a cement plug to prevent borers and other organisms from attacking the coral internally. Two cores were collected from Seacliff reef in 14 m of water and one core collected from a subtidal rocky reef at Edithburgh in 4 m water at low tide.

Coral cores collected along the axis of maximum vertical extension were cut into 7 mm slabs for X-ray analysis. Coral sections were X-rayed at a commercial X-ray medical facility, using an exposure of 55 kV and 5 mA for 15 sec with a Kodak CR500. The chronology of the coral cores were assessed using X-rays and U/Th dating techniques. Carbonate samples were milled at a sampling resolution of monthly to five yearly increments (200 μm – 6 mm) along the growth axis of coral cores. Milling techniques are similar to those described in Gagan et al. (1994) and Hendy et al. (2002). Analyses presented in this chapter include annual samples from Seacliff B, biennial samples from Edithburgh and five-yearly samples from Seacliff A and following the sampling procedure described in the stable isotope methodology in Chapter 5. Powdered samples were analysed for $\delta^{18}O$ and $\delta^{13}C$ in an automated individual carbonate-reaction Kiel (III) device coupled with a Finnigan Mat-251 mass spectrometer at the Research School of Earth Sciences, the Australian National University. Powdered coral samples weighing 180-220 μg were reacted with two drops of 103% phosphoric acid at 90° C. The resulting H_2O-CO_2 gas was purified by freezing and removing the water then vaporising the CO_2 in a double trap system using liquid nitrogen, and then passed through to the inlet system of the mass spectrometer for measurement. All isotopic data are reported as per mil (‰) deviations relative to the Vienna Peedee Belemnite standard (VPDB), based on measurements of the National Bureau of Standards NBS-19 ($\delta^{18}O$ =-2.20‰; $\delta^{13}C$ =+1.95‰). Analytical precision for replicate measurements ($n = 40$) of $\delta^{13}C$ in NBS-19 was ± 0.02‰ (2σ).

Results and Discussion

The dominant feature of the three coral $\delta^{13}C$ records (shown in Figure 7.2) is the curved trend towards lower $\delta^{13}C$ beginning in the late 19th century with the slopes steepening towards the present day. The Suess effect has been recorded in the

Atlantic subtropical surface ocean as ~0.8‰ (Gruber et al. 1999). However, records of the Suess effect in biogenic organisms have the depletion ranging between 0.5‰ from 1820-1972 (Druffel & Benavides 1986) 0.9‰ from 1800-1990 for the Caribbean and 0.7‰ for the same time period for the Coral Sea (Böhm et al. 1996), and 0.9‰ from 1953-1999 (Fallon et al. 2003).

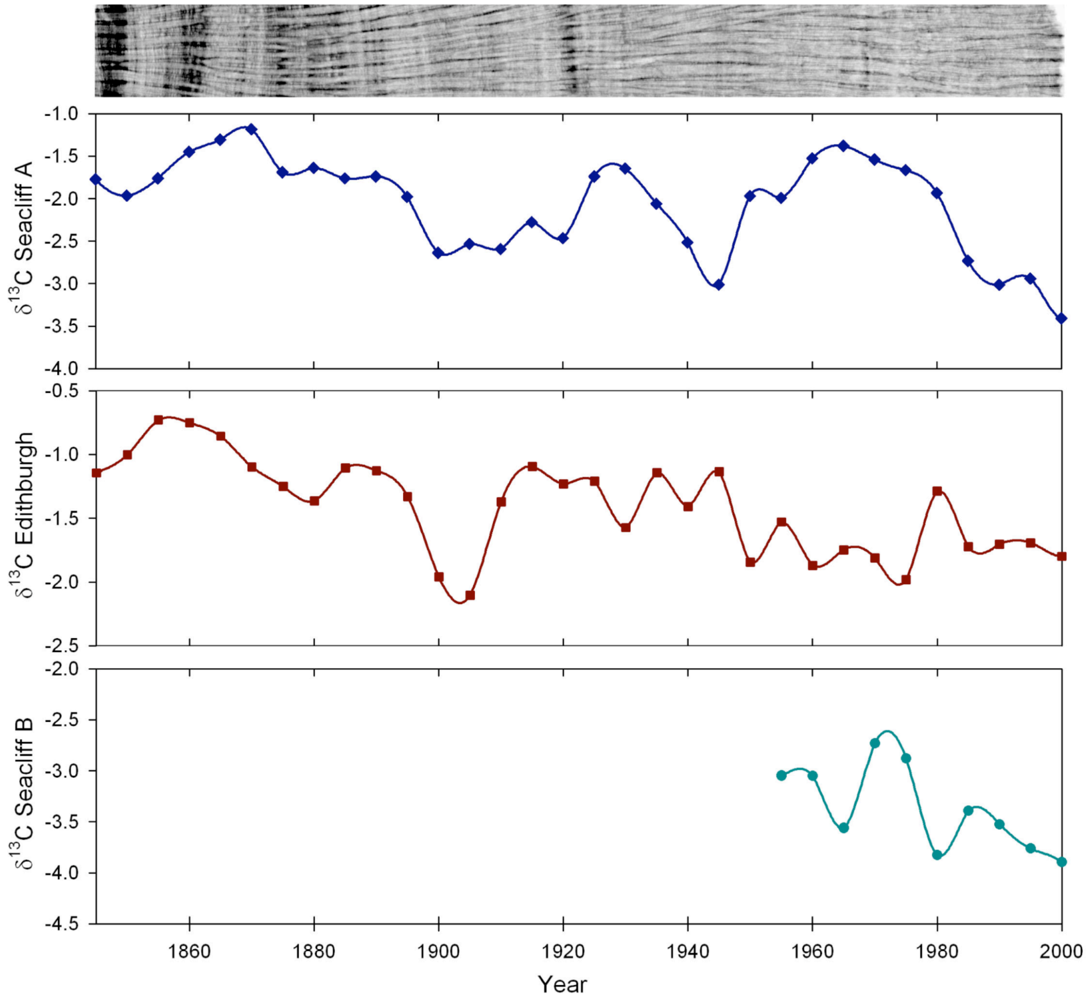

Figure 7.2: Raw δ^{13}C data for the three South Australian coral cores. (A) X-ray of the Edithburgh core showing 155 years growth. (B) SeA05 core δ^{13}C record. (C) Ed03 δ^{13}C record, this data is more depleted in ^{13}C as the coral was growing at much shallower depths. (D) SeB δ^{13}C record for the last 50 years.

The depletion shown in this study (Figure 7.2) of 0.82‰ and 0.74‰ for two coral records from 1850-2005 is comparable to the previous studies. The shorter coral record from 1953 -2005 δ^{13}C decreased by 0.9‰, which although faster than the two records from more slow growing corals is comparable to a sclerosponge (Fallon et al. 2003). Although the scale of δ^{13}C is comparable to sclerosponges (approximately 2.5 ‰) there is a large offset due to isotopic fractionation incorporating ^{13}C into the coralline aragonite.

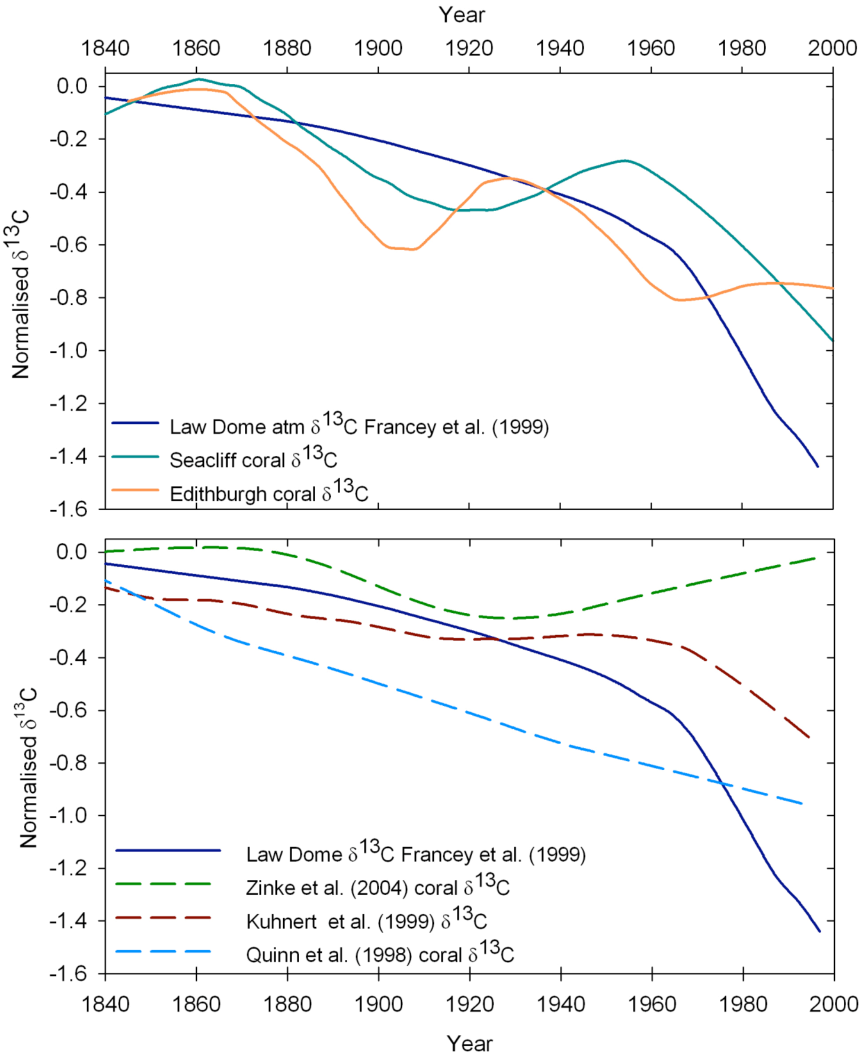

Figure 7.3: (A) Two long (150 year) coral δ^{13}Crecords from this study compared with atmospheric δ^{13}C records from an Antarctic ice core (Law Dome) and Cape Grim weather station (Tasmania) (Francey et al. 1999). (B) Comparison of three published δ^{13}C records (data from NOAA's National Climatic Data Center: http://www.ncdc.noaa.gov/paleo/ftp-coral.html) compared with the Francey et al. (1999) record.

Preindustrial atmospheric CO_2 levels from Antarctic ice cores (Law Dome) were in the range of 275-284 ppm, with the lower end of the range during the Little Ice Age 1550-1800 (Etheridge et al. 1996). However, it may be inappropriate to refer to a single preindustrial atmospheric CO_2 level due to natural variations in biosphere contribution or cooling in global climate. The atmospheric CO_2 record stabilized at ~ 310-312 ppm for just over a decade (~ 1940-1955) before increasing the rate of change to the 2005 CO_2 level of 375 ppm (MacFarling Meure et al. 2006). The total change in atmospheric $\delta^{13}C$ from preindustrial to modern time is 1.2 ‰ (estimated from Antarctic firn, Etheridge et al. 1996). The change in the $\delta^{13}C$ of the surface ocean is approximately half that of the atmospheric $\delta^{13}C$ change (Quay et al. 1992). The mid 20th century $\delta^{13}CO_2$ record suggests an additional oceanic sink rather than lower fossil fuel emissions or a biospheric sink (Etheridge et al. 1996).

The three coral records have large decadal-scale oscillations in the time series, not related to the oceanic Suess effect, but probably due to a complex interaction between $\delta^{13}C$ fractionation in corals and photosynthesis-light/insolation variability. These decadal scale oscillations are not present in atmospheric records from Cape Grim station data or Antarctic ice core records (Francey et al. 1999).

The *Plesiastrea* $\delta^{13}C$ records in this study record the oceanic Suess effect with high fidelity but with strong modulation compared with other coral studies which underestimate the depletion in $\delta^{13}C$ for the last 150 years (Figure 7.3) (Quinn et al. 1998; Kuhnert et al. 1999; Zinke et al. 2004). These published studies were used as comparisons due to their regional proximity (West Coast of Australia, Madagascar and New Caledonia) of the records generated in this study and the length of the coral records. Previously published *Porites* $\delta^{13}C$ values may reflect the complex interaction of different environmental variables influencing $\delta^{13}C$ fractionation in tropical corals, and localised oscillations in oceanic DIC. One previous study on the slow-growing coral *Diploria* from Bermuda concluded the Suess effect was the cause of the depletion in $\delta^{13}C$ of 0.5‰ from 1900-1974 (Nozaki et al. 1978).

The corals (*Plesiastrea versipora*) assessed in this study appear to record surface ocean $\delta^{13}C$ depletion with higher fidelity than tropical corals, which may be caused by two different effects. Firstly, the coral position in the water column affects the $\delta^{13}C$ fractionation into the coral skeleton. As temperate corals grow much more slowly (~2-6 mm yr^{-1}) than their tropical counterparts (up to 30 mm yr^{-1}), and are generally found at greater depths, their position in the water column does not change as they grow. However, *Porites* colonies may change the growing depth and therefore light intensity reaching the colony by up to 5 m during the growth of a single colony. The second factor influencing $\delta^{13}C$ fractionation relates to the dependence on autotrophic versus heterotrophic feeding. Tropical corals are dependent on photosynthesis through their symbiotic zooxanthellae which causes enrichment of $\delta^{13}C$ in the DIC of the calcification reservoir (Swart 1983; McConnaughey 1989). Due to increased turbidity and reduced water clarity in temperate systems, cold-water corals have polyps extended during daylight hours to provide heterotrophic nutrition. *Plesiastrea versipora* has a larger calyx than *Porites* and potentially more live tissue, and therefore may require more heterotrophic feeding in general. Therefore, these corals may have less dependence on their symbiotic algae for nutrition and associated carbon isotope fractionation.

South Australian Gulf Carbon Cycling

The long record generated from Seacliff A indicates a high level of periodicity, with an amplitude of approximately 1 ‰ (Figure 7.4). In the 300-year record, there are approximately eight cycles. Spectral analysis verifies that the cyclicity has a period of approximately 40-50 years (Figure 7.5). A previous study on tropical corals in the Great Barrier Reef observed a cyclicity with a period of approximately 50 years in $\delta^{13}C$ and $\delta^{11}B$, which was related to the Pacific Decadal Oscillation (Pelejero et al. 2005).

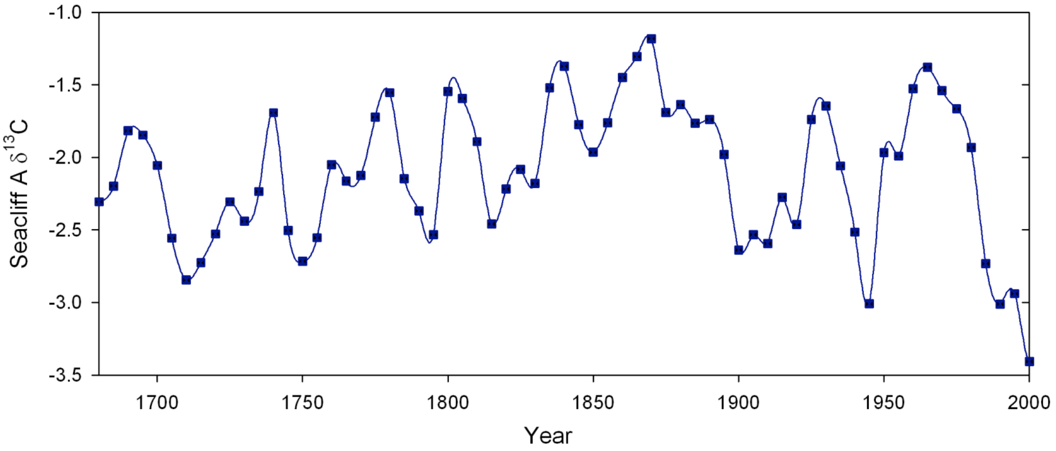

Figure 7.4: $\delta^{13}C$ record from Seacliff A. Data was collected in 5 year bulk samples.

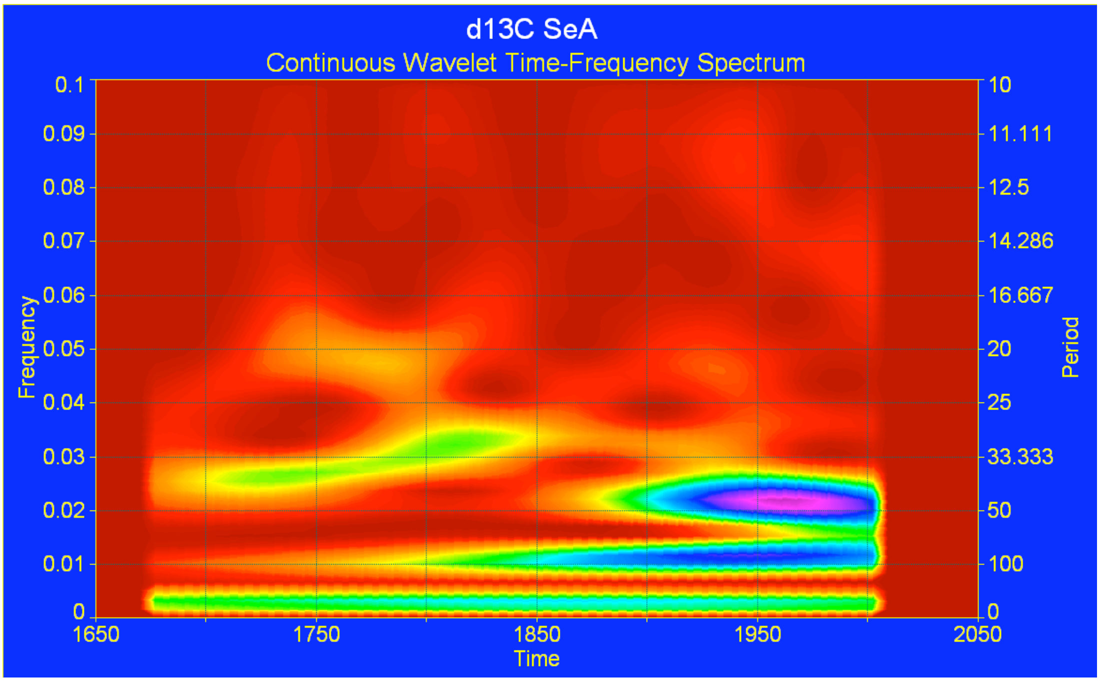

Figure 7.5: Continuous wavelet frequency analysis of the $\delta^{13}C$ record from Seacliff A, potentially reflecting changes in DIC cycling on a 40-50 year frequency. Wavelet spectrum was created using a Gaussian derivative filter in the AutoSignal® software.

The changes in dissolved inorganic carbon in the South Australian Gulfs are likely to be related to changes in upwelled shelf slope water entering the gulfs, or changes in the intensity of upwelling in the eastern Great Australian Bight on a decadal scale. It is speculated that the 50-year periodicity in $\delta^{13}C$ observed in this study may be related to the Pacific Decadal Oscillation, or decadal-scale changes in the Southern Annular Mode. Modelling the $\delta^{13}C$ data collected in this study with $\Delta^{14}C$ analyses would establish changes in carbon cycling in the South Australian Gulfs through time. Corals located in the eastern Great Australian Bight may enable differentiation between upwelling intensity or entrance of nutrient-rich deep water into the gulfs. Unfortunately, no large corals suitable for long-term proxy reconstructions were located in this area during the surveying for this project, and should be a focus for any future work.

Summary

Plesiastrea versipora colonies in the South Australian Gulfs record the Suess effect. $\delta^{13}C$ records from these corals document the surface ocean $\delta^{13}C$ depletion more clearly than records from tropical records, which frequently underestimate the anthropogenic $\delta^{13}C$ depletion. Two coral cores recorded a depletion in $\delta^{13}C$ of ~0.8‰ from 1850-2005, which is almost equal to estimates of the oceanic Suess effect. The $\delta^{13}C$ records presented from these temperate corals are less complicated than carbon isotope records from faster-growing tropical corals. This is inferred to be due to a more consistent position in the water column compared with tropical corals which may increase their light intensity by over 100% during the course of fifty years growth, and less impact from vital affects. The cold-water corals experienced large-scale multidecadal oscillations which may be related to DIC cycling caused by changes in upwelling or insolation effects. Temperate corals may be used as a high-resolution archive of anthropogenic impacts on the marine environment where other biogenic calcifying organisms such as tropical corals and sclerosponges do not occur.

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Chapter 8:
Synthesis and Future Directions

Chapter 8: Conclusions and Future Directions

Summary and Conclusions

The field work component of this study located twelve colonies of *Plesiastrea versipora* in the South Australian Gulfs and core samples were collected from eight colonies. Whole colonies were collected from a reef complex in northern Spencer Gulf (Whyalla) as the colonies were too small to easily core. All colonies contained zooxanthellae and coral colour ranged between beige, green and purple. Most of the *P. versipora* colonies had extended polyps during the day and therefore may rely on both autotrophic and heterotrophic nutrition. The only exception was the corals in Dutton Bay which had retracted polyps during daylight hours, and these corals were from the shallowest site of 2 m. All reefs surveyed contained both encrusting and massive forms of *Plesiastrea versipora.* This study has not shed any light on the mechanism controlling coral habit formation after settlement of juvenile corals. Since both growth forms co-occurred on a small spatial scale, the mechanism controlling growth habit in *P. versipora* is more likely to be genetically-controlled rather than controlled by environmental conditions.

Large skeletal density variations were observed between the different coral colonies, including colonies sampled from the same reef (Seacliff). The growth histories of five colonies of *Plesiastrea versipora* from Gulf St Vincent and Spencer Gulf were examined using X-ray band counting and ^{238}U/^{230}Th dating techniques. Density bands of varying widths (0.5 mm – 7 mm) and definition were present in each coral, and often there was greater density variation between different architectural elements (e.g. septal region versus corallite wall) than between proposed summer and winter calcification. The U/Th dating was used to verify that the density bands were annual high-low density band couplets in all corals examined. Average annual extension rates of colonies varied between 1.2 and 8 mm yr^{-1}. These extension rates are among the slowest growth rates reported for hermatypic corals and are more comparable to growth rates of deep-sea corals. Estimated ages derived from the density bands ranged from 90 to 320 years, whereas ages derived from the U/Th dating were between 105 and 381 years. Differences in age estimation from the two techniques ranged from 2-19% suggesting that the age of *P. versipora* cannot be determined accurately from density bands alone. However, both dating techniques contain inaccuracies biasing the derived age. It is difficult to accurately assign a calendar year to bands that are less than 1 mm wide, and have more density variation within a corallite than between summer and winter seasons. Two of the older samples analysed for U/Th ages have contamination from non-radiogenic ^{232}Th (in the order of ~ 3 ppb) which introducing an error ten-fold higher than the blank-corrected analytical error. While the detrital ^{232}Th error remained at approximately 10% of the U/Th derived age for the older colonies, the radiometric dating was considered to give a more accurate age approximation than the band counting.

There were few luminescent bands observed in *Plesiastrea versipora*. Only one colony, Seacliff B had significant luminescent banding and the bands became more frequent in the 1960s, suggesting an environmental change occurred, recorded by the coral skeleton. The lack of luminescent banding in the other coastal corals (Seacliff A, Edithburgh and Whyalla) suggests that luminescent banding is not an accurate chronological marker in the South Australian corals.

The potential of *Plesiastrea versipora* to capture the full seasonal cycle of SST variation (10-24°C) in the South Australian gulfs was assessed by comparing skeletal chemistry with in situ SST data. Both trace elements and stable isotopes were measured in this study to allow simultaneous evaluation of *Plesiastrea versipora*'s value as a paleoclimate archive and the reproducibility of the independent tracers in temperate latitudes. Analyses of the trace element paleotemperature proxies produced some surprising results. Proxy/SST calibrations generated from the fast growing corals (> 6 mm yr^{-1}) of Sr/Ca, U/Ca and δ^{18}O were comparable to published SST calibrations for other species. Very little temperature dependence was observed for B/Ca and Mg/Ca, and concentrations of these elements were amplified by secondary precipitates and other sources of contamination, and did not reflect temperature dependent fractionation in *P. versipora*.

The trace element which captured the full amplitude of the seasonal cycle with highest fidelity was Ba/Ca. Although Lea et al. (1989) suggested a temperature dependence in the incorporation of Ba/Ca in corals from the Galapagos, this was due to temperature variation between coastal water and upwelled water rather than a reflection of variation in seasonal SST. The majority of studies examining Ba/Ca concentrations in coral have observed greater influence from river flood plumes carrying high levels of suspended sediment to the coastal zone (Sinclair 1999; McCulloch et al. 2003; Fleitmann et al. 2007) or upwelling of nutrient rich water (Lea et al. 1989; Fallon et al. 1999; Reuer et al. 2003; Montaggioni et al. 2006; Ourbak et al. 2006). The seawater concentrations of Ba in the South Australian gulfs are unlikely to be influenced by either terrestrial or deep water sources. There is very little fresh water discharge to the gulfs due to the low rainfall and the gulfs are thermally stratified and exchange little with shelf water when summer upwelling occurs off the coast of the Western Eyre Peninsula. Concentrations of Ba/Ca are constant in both the coastal corals which may be influenced by land runoff, and the open gulf corals which are unlikely to be influenced by fresh water. Another faviid species from the Mediterranean (*Cladocora caespitosa*) also displayed temperature dependence in the incorporation of Ba/Ca (Montagna et al. 2007), with a comparable slope to the calibration generated in this study for the fast growing corals (Seacliff and Troubridge). Furthermore, experimental studies on Ba/Ca concentration uptake in inorganic aragonite found a high temperature dependence on the fractionation (Dietzel et al. 2004; Gaetani & Cohen 2006).

Corals with a very slow extension rate (less than 2 mm per year) did not capture the full amplitude of the seasonal cycle in either the trace elements or $\delta^{18}O$ analyses and may only be useful for decadal-centennial scale climate reconstructions, if at all. Sr/Ca and U/Ca concentrations were observed to behave with a ‘bimodal’ distribution in the coral skeleton which was reproducible down the same laser track, but offset between adjacent tracks. The bimodal distribution in Sr and U was only observed in the corals with an extension rate of less than 2 mm yr^{-1}. This behaviour has implications for coral studies on other species with low extension rates, because it suggests that the coral polyp is mediating the fractionation of Sr and U (i.e. biological fractionation) rather than the thermodynamic relationship exhibited by inorganic aragonite and fast growing coral species such as *Porites*. The high coherency exhibited between Sr and U suggests that they may be incorporated through the same ionic pathway (using the McConnaughey Ca^{2+} -ATPase calcification pump model) and therefore subject to the same biological or ‘vital’ effects. Additionally, because Sr and U may be incorporated into the carbonate lattice via different mechanisms (direct substitution of Ca^{2+} by Sr^{2+}, compared with substitution of $UO_2(CO_3)^{2-}$ for the CO_3^{2-}) suggests that the bimodal distribution is a primary feature, as it is unlikely that both components of the aragonite lattice may be replaced in equal proportion.

The trace metal analyses conducted on *Plesiastrea versipora* revealed substantial contamination in several sites in Spencer Gulf and Gulf St. Vincent. Trace metal contamination was associated with changes in urban and industrial development and land use changes. The coastal corals from Seacliff reef recorded increased concentrations of lead, most likely due to the proliferation of automobiles in the 1960s. Increased concentrations of other heavy metals including Cu, Sn, Zn and Mn may be related to the discharge of treated sewage at a coastal site less than 10 km away. Vanadium and Mo (high concentrations in petroleum products, particularly oil) have enriched concentrations in pulse events which are recorded by the fast growing Seacliff coral (Seacliff B), with higher concentrations correlating with luminescent bands in this colony and were coincident with known oil spills in the region. The corals from Whyalla indicated higher concentrations in the heavy metals Zn, Sn and Pb and the source of the contamination is likely to be nearby smelters.

The maximum concentrations of several metals including Cu, Mn, Zn, Sn and Pb were different for the two coastal corals, implying different distribution coefficients for different coral colonies because the seawater chemistry is unlikely to change on such a small spatial scale. This suggests that distribution coefficients for trace metals in *Plesiastrea versipora* is dependent on growth rate. Therefore, seawater concentrations of trace metals can not be estimated from the coral trace metal concentrations. Although Shen & Boyle (1988) proposed that distribution coefficients show little variation between different coral species and growth rates, the results of this study suggest that distribution coefficients do vary within a species, and are dependent on growth rate or another colony specific mechanism. Caution should be used when applying published distribution coefficients to different species and growth rates.

Long-lived, slow-growing faviids such as *Plesiastrea versipora* can potentially provide geochemical proxy archives two-three times longer than *Porites* corals of the same colony size. Biological and physiological characteristics of the coral *Plesiastrea versipora* making it a useful indicator species of environmental change include:

1. High tolerance to a range of temperature and salinity fluctuations
2. Relatively low growth rate producing colonies spanning several centuries
3. Efficient suspension feeding combined with zooxanthellate nutrition
4. Broad geographical expanse

Ecological Perspective

Populations of *Plesiastrea versipora* in the South Australian gulfs have been severely impacted by trawling conducted for prawn fisheries and it is unknown what ramifications this has had on the local ecosystems. The trace element records generated during this study imply that some regions in both Spencer Gulf and Gulf St. Vincent have been contaminated by anthropogenic sources for most of the last century.

The fast growing coral at Seacliff reef appears to be recording seawater chemistry changes or point source pollution events from sources located both to the north (waste water treatment plant and urban runoff) and to the south (oil refinery at Port Stanvac) of the reef. The unique oceanography in the South Australian gulfs with very little mixing with shelf waters in summer when the gulfs are thermally stratified may enable the Seacliff corals to record environmental impacts from the surrounding region with greater fidelity. Further studies on local seawater chemistry should be conducted to determine the length of time contaminants stay in the coastal environment.

Little is known about the effects of water quality on the recruitment of organisms on to temperate reefs and the associated impacts on community structure. Research conducted on tropical reefs suggests that corals and other encrusting invertebrates are replaced by algal species (Hughes & Tanner 2000; Hughes et al. 2003). Impacts associated with declining water quality along metropolitan coastlines have been demonstrated in macro-algae (Shepherd & Womersley 1970; Turner & Cheshire

2002) and seagrass (Neverauskas 1987) communities which indicate an increase in opportunistic and turfing species. The coral colonies located on urban reefs in South Australia record a significant anthropogenic impact over the last 70 years with concentrations of heavy metals over 30 times pre-industrialisation levels. At this stage, we do not have a clear understanding of the impact of higher metal concentrations on coral growth and recruitment. Continued research into temperate reef health especially in coastal regions undergoing increasing urbanisation should be established to detect changes in structure, function and recruitment of corals.

Future Directions

The results of this thesis advocate that fast growing colonies of *Plesiastrea versipora* are useful archives of paleotemperature, and all colonies examined contained detailed records of changes in seawater chemistry from anthropogenic pollution. Several questions have arisen during the course of this thesis that were not able to be addressed due to time constraints.

One of the most obvious avenues of further research is to determine why the trace element and stable isotope records are so different between neighbouring corals with different growth rates. A better understanding of the mechanisms of coral calcification and the role of thermodynamic (inorganic) fractionation versus biologically mediated fractionation will substantially improve the accuracy and extend potential applications of coral proxy generated records. The trace element relationships observed during this study suggest that Ba may be incorporated into the coralline lattice through a different ionic pathway to Sr and U. Furthermore, the variation in trace metal concentrations suggest that a different level of control is exerted over different ionic pathways and this may be due to biological mediation or chemical speciation due to environmental conditions in the calcification fluid, such as pH changes.

Further collections of *Plesiastrea versipora* colonies may establish which extension rate is the dominant growth form, from the corals surveyed in this study it appears that temperate corals usually calcify less than 3 mm yr^{-1}. The extension rate of

Plesiastrea versipora colonies from temperate latitudes in the northern hemisphere remains unknown. Combining biological growth experiments (tank experiments) with geochemical analyses would improve our understanding of summer/winter calcification and the role of genetics or zooxanthellae on mean annual extension rate. Tank experiments could also include radiogenic spikes or supersaturated conditions (in Mg, Sr, Ba, U) to advance our knowledge of cation substitution in the aragonite lattice.

Isotope-dilution ICP-MS analyses conducted on the milled samples would be a more accurate comparison between the trace elements and δ^{18}O paleotemperature records. An initial examination of the influence of ENSO on δ^{18}O records in *Plesiastrea versipora* was inconclusive. Frequency analysis of the long records of trace element and stable isotope paleotemperature proxy data would be very useful to establish the role of climate dynamics from different ocean basins, including ENSO, Indian Ocean Dipole, Pacific Decadal Oscillation and the Southern Annular Mode.

Combining in situ seawater chemistry analyses with coral geochemical analyses would enhance our understanding of water chemistry and trace metal cycling in the South Australian gulfs. Specifically whether trace elements with a ‘nutrient style’ behaviour such as Ba have constant concentrations in the gulfs between seasons. Knowledge of seawater chemistry would also enable the distribution coefficients of trace metals to be established for corals with different growth rates.

The δ^{13}C analyses from *Plesiastrea versipora*, recorded the Suess effect and indicated a cyclicity in dissolved inorganic carbon (DIC), possibly due to mixing with upwelled shelf/slope water entering the gulfs. To establish the variability of DIC through time, analyses of Δ^{14}C combined with the δ^{13}C may enable accurate modelling of carbon cycling in temperate latitudes. It is well established that the surface oceans are becoming more acidic due to absorption of anthropogenic CO_2 from the atmosphere (Kleypas et al. 1999; Orr et al. 2005; Pelejero et al. 2005). However, the impact of ocean acidification on marine ecosystems, particularly calcifying organisms remains unclear (Langdon & Atkinson 2005), temperate latitudes are considered to be more sensitive to changes in oceanic pCO_2 (Kleypas et al. 1999). A pilot study of δ^{11}B negative TIMS analyses conducted during this thesis indicated a 0.2 pH change from 1945-2003 in the Seacliff B coral. Continuous high resolution $\delta^{11}B$ analyses from the Seacliff A coral would complement the $\delta^{13}C$ signal and ascertain if large scale fluctuations in pH occur in temperate latitudes, as has been observed in tropical coral records (Pelejero et al. 2005).

Trace metal analyses of *Plesiastrea versipora* colonies in other regions of Australia would provide a more complete picture of anthropogenic change since European settlement and industrialisation. For example, colonies of *P. versipora* are known to occur in Port Phillip Bay (G. Parry *pers comm.*) and are likely to record urban and industrial development in Victoria.

Fossil corals present a unique archive of information on climate variability in the Quaternary and *Plesiastrea versipora* is commonly preserved in Quaternary beach dunes along the eastern coast of Australia (I. Goodwin *pers comm*.). Several studies have used fossil tropical corals to provide information on past SST changes, hydrological balance (Gagan et al. 1998; Abram et al. 2007), global ice volume (Guilderson et al. 1994) and ocean mixing (Edwards et al. 1993). Geochemical analyses on well preserved fossil colonies of *Plesiastrea versipora* may improve our understanding of Quaternary climate dynamics at temperate latitudes.

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Appendices

Appendix A: Published coral proxy calibrations

Appendix B: Field log for coral collection

Appendix C: South Australian coral X-rays and luminescence images (on DVD)

Appendix D: LA-ICP-MS data files (data on DVD)

Appendix E: Stable isotope data files (on DVD)

Appendix F: Trace element correlation tables

Appendix G: RSES final seminar (on DVD)

Appendix A

Table 1: Published $\delta^{18}O$ calibration equations

Species	Location	Intercept	Slope	Reference
Porites sp	Ryukyu Islands, Japan	-1.21	0.134	(Mitsuguchi et al. 1996)
Porites sp	Ryukyu Islands, Japan	-0.611	0.165	(Suzuki et al. 1999)
Porites sp	South China Sea	-1.02	0.174	(Yu et al. 2005)
Porites sp	Pacific, various	0.45	0.20	(Juillet-Leclerc & Schmidt 2001)
Porites sp	Fiji	-0.03	0.17	(Le Bec et al. 2000)
Porites sp	Eilat, Red Sea	0.54	0.16	(Felis et al. 2003)
Porites lobata	Galapagos	0.59	0.21	(McConnaughey 1989)
Porites lutea	Tahiti	-0.42	0.15	(Boiseau et al. 1998)
Porites lobata	Costa Rica	1.36	0.22	(Carriquiry et al. 1994)
Porites lobata	Galapagos	0.89	0.22	(Wellington et al. 1996)
Porites sp	Guam, NW Pacific	-0.86	0.150	(Asami et al. 2004)
Porites sp	Guam, NW Pacific	-1.09	0.140	(Asami et al. 2004)
Porites sp	Panama	-0.026	0.196	(Wellington & Dunbar 1995)
Porites sp	Orpheus Is, GBR	0.002	0.174	(Gagan et al. 1998)
Porites sp	Orpheus Is, GBR	0.447	0.189	(Gagan et al. 1998)
Porites sp	Pandora Reef, GBR	0.183	0.180	(Gagan & Chivas 1995)
Porites sp	New Caledonia	1.23	0.133	(Stephans et al. 2004)
Porites sp	New Caledonia	-0.91	0.151	(Quinn et al. 1998)
Porites sp	New Caledonia	0.004	0.189	(Quinn et al. 1996)
Porites sp	Oeno Atoll, SE Pacific	-0.304	0.132	(Ayling et al. 2006)

Table 2: Published Sr/Ca vs SST calibrations for inorganic aragonite, *Porites* and other coral species.

Species	**Location**	**Intercept**	**Slope**	**Reference**
Inorganic aragonite		10.99	0.045	(Kinsman & Holland 1969)
Inorganic aragonite		11.27	0.043	(Dietzel et al. 2004)
Pocillopora damicornis	Hawaii	11.01	0.071	(Smith et al. 1979)
Montipora verrucosa	Hawaii	11.64	0.089	(Smith et al. 1979)
Porites sp.	GBR	10.94	0.07	(Smith et al. 1979)
Pocillopora eydouxi	Hawaii	11	0.076	(de Villiers et al. 1994)
Pavona clavus	Galapagos	10.646	0.0675	(de Villiers et al. 1994)
Diploria labyrinthiformis	Bermuda	10.03	0.045	(Cardinal et al. 2001)
Montastrea annularis	Florida	9.994	0.0377	(Swart et al. 2002)
Diploastrea heliopora	Indonesia	10.57	0.06	(Correge et al. 2004)
Goniopora sp.	South China Sea	9.6	0.0305	(Yu et al. 2004)
Porites sp.	Eilat, Red Sea	10.78	0.0597	(Felis et al. 2004)
Porites lutea	Ryukyu, Japan	10.5	0.0608	(Mitsuguchi et al. 1996)
Cladocora caespitosa	Adriatic Sea	10.33	0.066	(Montagna et al. 2006)
Porites lobata	Shirigai Bay, Japan	10.76	0.063	(Fallon et al. 1999)
Porites lobata	Hawaii	10.96	0.079	(de Villiers et al. 1994)
Porites lobata	Taiwan	10.27	0.0505	(Shen et al. 1996)
Porites lobata	Taiwan	10.32	0.0528	(Shen et al. 1996)
Porites lutea	South China Sea	9.84	0.0424	(Yu et al. 2005)
Porites lutea	South China Sea	10.6	0.0504	(Wei et al. 2000)
Porites lutea	Fiji	10.65	0.053	(Linsley et al. 2004)
Porites	Rabaul, PNG	10.64	0.061	(Quinn et al. 2006)
Porites lutea	Java, Indonesia	10.78	0.066	(Gagan et al. 1998)
Porites lutea	Alor, Indonesia	10.51	0.062	(Correge et al. 2004)
Porites sp.	Christmas Is (Indian)	10.38	0.0593	(Marshall & McCulloch 2001)
Porites lutea	Galapagos	10.55	0.0514	(Schrag 1999)
Porites lobata	Hawaii	10.965	0.067	(Allison & Finch 2004)
Porites lobata	Hawaii	10.86	0.08	(Allison & Finch 2004)
Porites sp	Davies Reef GBR	10.48	0.0615	(Alibert & McCulloch 1997)
Porites lutea	Myrmidon Reef, GBR	10.40	0.0575	(Marshall & McCulloch 2002)
Porites lutea	Orpheus Is, GBR	10.73	0.0639	(Gagan et al. 1998)
Porites sp	Flinders Reef, GBR	10.11	0.451	(Calvo et al. 2007)
Porites sp	Havannah Is, GBR	10.11	0.0412	(Fallon et al. 2003)
Porites sp	Pandora Reef, GBR	10.62	0.0652	(Fallon et al. 2003)
Porites sp	Orpheus Island, GBR	10.23	0.052	(Fallon et al. 2003)
Porites sp	Davies Reef, GBR	10.39	0.0602	(Fallon et al. 2003)

Porites sp	Davies Reef, GBR	10.73	0.0707	(Fallon et al. 2003)
Porites sp	Myrmidon Reef, GBR	10.42	0.0565	(Fallon et al. 2003)
Porites sp	Wheeler Reef, GBR	10.35	0.0595	(Fallon et al. 2003)
Porites lutea	Dampier, Western Aust.	10.68	0.0616	(Gagan et al. 1998)
Porites lobata	New Caledonia	10.48	0.0625	(Beck et al. 1992)
Porites lutea	New Caledonia	10.073	0.052	(Quinn & Sampson 2002)
Porites lutea	New Caledonia	10.12	0.057	(Quinn & Sampson 2002)
Porites lutea	New Caledonia	10.38	0.061	(Quinn & Sampson 2002)
Porites lutea	New Caledonia	10.73	0.0657	(Correge et al. 2000)
Porites lobata	New Caledonia	8.94	0.0532	(Min et al. 1995)
Porites lutea	New Caledonia	10.51	0.062	(Correge et al. 2004)
Porites lutea	New Caledonia	10.38	0.0614	(Crowley et al. 1999)
Porites lutea	Rarotonga	11.57	0.0823	(Linsley et al. 2000)
Porites lobata	Madagascar	10.011	0.037	(Zinke et al. 2004)
Porites sp	Oeno Atoll, SE Pacific	10.086	0.0495	(Ayling et al. 2006)
Porites mayeri	GBR	10.8	0.07	(Sinclair et al. 1998)
Porites sp.	Kiritimati	10.7	0.0614	(Evans et al. 1999)
Porites sp.	Huon Peninsula, PNG	10.7	0.062	(McCulloch et al. 1999)

Table 3: Published B/Ca calibration equations

Species	Location	Intercept	Slope	Reference
Porites sp	Havannah Is, GBR	0.5238	0.004436	(Fallon et al. 2003)
Porites sp	Pandora Reef, GBR	0.9093	0.01707	(Fallon et al. 2003)
Porites sp	Orpheus Island, GBR	0.819	0.01457	(Fallon et al. 2003)
Porites sp	Davies Reef 2, GBR	0.9247	0.01805	(Fallon et al. 2003)
Porites sp	Davies Reef 8, GBR	0.1098	0.02609	(Fallon et al. 2003)
Porites sp	Myrmidon Reef 2, GBR	0.8952	0.0165	(Fallon et al. 2003)
Porites sp	Wheeler Reef, GBR	0.788	0.01288	(Fallon et al. 2003)
Porites lobata	Japan	0.766	0.00933	(Fallon et al. 1999)
Cladocora caespitosa	Adriatic Sea	1.239	0.024	(Montagna 2004)

Table 4: Published Mg/Ca calibration equations

Species	Location	Intercept	Slope	Reference
Cladocora caespitosa	Adriatic Sea	1.68	-0.12	(Montagna et al. 2006)
Porites lobata	Shirigai Bay, Japan	1.38	-0.0879	(Fallon et al. 1999)
Porites sp	Ryukyu, Japan	1.15	-0.129	(Mitsuguchi et al. 1996)
Porites sp	Havannah Is, GBR	0.104	-0.116	(Fallon et al. 2003)
Porites sp	Pandora Reef, GBR	-0.603	-0.1155	(Fallon et al. 2003)
Porites sp	Orpheus Island, GBR	1.044	-0.1123	(Fallon et al. 2003)
Porites sp	Davies Reef , GBR	1.338	-0.08934	(Fallon et al. 2003)
Porites sp	Davies Reef 8, GBR	0.7037	-0.1321	(Fallon et al. 2003)
Porites sp	Myrmidon Reef 2, GBR	3.73	-0.00661	(Fallon et al. 2003)
Porites sp	Wheeler Reef, GBR	0.759	-0.1161	(Fallon et al. 2003)

Table 5: Published U/Ca calibration equations

Species	Location	Intercept	Slope	Reference
Porites sp		2.386	0.053	(Min et al. 1995)
Cladocora caespitosa	Adriatic Sea	1.47	0.024	(Montagna 2004)
Porites lobata	Japan	2.215	0.04539	(Fallon et al. 1999)
Porites sp	Havannah Is, GBR	2.165	0.0294	(Fallon et al. 2003)
Porites sp	Pandora Reef, GBR	2.36	0.0431	(Fallon et al. 2003)
Porites sp	Orpheus Island, GBR	2.001	0.0351	(Fallon et al. 2003)
Porites sp	Davies Reef , GBR	1.806	0.0286	(Fallon et al. 2003)
Porites sp	Davies Reef , GBR	2.02	0.0398	(Fallon et al. 2003)
Porites sp	Myrmidon Reef, GBR	1.46	0.01469	(Fallon et al. 2003)
Porites sp	Wheeler Reef, GBR	2.03	0.0364	(Fallon et al. 2003)

Table 6: Published maximum values of heavy metals from pollution studies in Thailand, Red Sea, Japan, Central American and Northern Australia most elemental concentrations in ppm except for values marked with ^ = ppb # = µmol/mol; * = nmol/mol. Values obtained during this study are in the last row in bold.

V	Fe	Mn	Cu	Zn	Y	Cd	Pb	Reference
				2.4			0.27	(St John 1974)
	45-94		0.8-1.6	1.4-3.7				(Brown & Holley 1982)
				1.8-12	1.5-3			(Howard & Brown 1984)
0.05		0.008-0.02		0.02-0.07		0.0008-0.008	0.01-0.1	(Shen & Boyle 1988)
5.9-7.6	11-38	5.6-6.8	0.78-0.84	3.4-9.3		0.04-0.06	44-51	(Hanna & Muir 1990)
0.1-0.8			8		0.05-0.15	2 ^	0.2-0.8	(Scott 1990)
			15-75 *					(Linn et al. 1990)
40	70-113	7	2-4	9-10		7.6	32	(Guzman & Jimenez 1992)
		1.4-4.7				0.06-0.14	0.18-0.58	(McConchie & Harriott 1992)
0.03-1.6	1.3-300		3.3-89	0.8-42			0.03-4.7	(Bastidas et al. 1999)
0.4 #		1.2 #	25 #	30 #	150 *	2 #	3 #	This study

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Appendix B

Location	*Gulf*	*Depth*	*Size of colony*	*Date collected*	*Remarks*
Seacliff: Coral 1	Gulf St Vincent	12 m	~ 150 cm	23/06/03	Very dense coral – only 17 cm core obtained in 2003
Seacliff: Coral 2	Gulf St Vincent	12 m	~ 120 cm	24/06/03	Coral partially dead. Easy to core. Temperature logger placed at site 07/05/03
Edithburgh	Gulf St Vincent	4 m	~ 28 cm	27/11/03	Coral to the north of jetty
Troubridge	Gulf St Vincent	5 m	~ 170 cm	27/11/03	Temperature logger placed at site 27/11/03
Dutton Bay	Coffin Bay	2 m	~ 20 cm	01/08/03	Temperature logger placed at site 05/08/03
	Coffin Bay	2 m	~ 25 cm	01/08/03	Corals located under jetty
Taylors Island	Spencer Gulf	22 m	~ 25 cm	29/07/03	
	Spencer Gulf	21 m	~ 31 cm	13/11/03	Heavily bored throughout core, coral rolled and axis changed mid way through core
Moonta Bay	Spencer Gulf	4	~ 140 cm	17/12/03	Teeth on core barrel broke so only 5 cm core collected. Colony mostly dead. Temperature logger placed at site.
Whyalla	Spencer Gulf		< 15 cm	19/11/03	Only small, massive colonies found 4 collected
Cowell	Spencer Gulf	??	~ 40 cm	1980/1981	Coral dumped under jetty from a prawn trawler – not sure of death date
Pt Broughton	Spencer Gulf	??	~ 40 cm	April 1981	Neil’s garden ornament

Appendix F

Seacliff A	*Li/Ca*	*P/Ca*	*V/Ca*	*Mn/Ca*	*Cu/Ca*	*Zn/Ca*	*Y/Ca*	*Zr/Ca*	*Mo/Ca*	*Cd/Ca*	*Sn/Ca*	*Ba/Ca*	*La/Ca*	*Ce/Ca*	*Pr/Ca*	*Nd/Ca*
P/Ca	-0.12															
V/Ca	0.24	0.11														
Mn/Ca	-0.13	0.40	0.03													
Cu/Ca	-0.03	0.17	0.20	0.36												
Zn/Ca	-0.15	0.37	0.05	0.47	0.28											
Y/Ca	-0.32	0.55	-0.08	0.15	0.11	0.02										
Zr/Ca	0.04	0.03	-0.01	0.00	0.00	0.00	0.01									
Mo/Ca	0.34	0.14	0.33	-0.14	-0.09	-0.10	-0.10	-0.01								
Cd/Ca	0.19	-0.08	0.25	0.05	0.25	0.05	-0.19	-0.02	0.13							
Sn/Ca	0.08	-0.05	0.49	0.22	0.47	0.12	-0.08	0.00	-0.07	0.33						
Ba/Ca	-0.12	0.69	0.07	0.36	0.18	0.17	0.64	0.04	0.03	-0.11	-0.04					
La/Ca	-0.29	0.48	-0.07	0.12	0.09	0.01	0.97	0.01	-0.09	-0.17	-0.08	0.59				
Ce/Ca	-0.30	0.47	-0.06	0.12	0.11	0.01	0.97	0.01	-0.10	-0.16	-0.08	0.58	0.98			
Pr/Ca	-0.26	0.44	-0.06	0.13	0.09	0.02	0.92	0.01	-0.10	-0.16	-0.07	0.55	0.94	0.94		
Nd/Ca	-0.25	0.43	-0.06	0.13	0.10	0.01	0.93	0.00	-0.10	-0.14	-0.05	0.53	0.95	0.95	0.91	
Pb/Ca	-0.17	0.50	-0.01	0.26	0.20	0.34	0.63	0.00	-0.12	-0.10	-0.03	0.52	0.59	0.58	0.56	0.55

Edithburgh	*Li/Ca*	*P/Ca*	*V/Ca*	*Mn/Ca*	*Cu/Ca*	*Zn/Ca*	*Y/Ca*	*Zr/Ca*	*Mo/Ca*	*Cd/Ca*	*Sn/Ca*	*Ba/Ca*	*La/Ca*	*Ce/Ca*	*Pr/Ca*	*Nd/Ca*
B/Ca	-0.11															
P/Ca	0.14															
V/Ca	0.21	0.25														
Mn/Ca	0.03	0.03	0.08													
Cu/Ca	0.43	0.29	0.40	0.02												
Zn/Ca	0.01	0.34	0.22	0.02	0.22											
Y/Ca	-0.10	0.14	0.30	0.73	0.21	0.17										
Zr/Ca	0.00	0.00	0.08	0.00	0.03	-0.01	0.00									
Mo/Ca	0.45	-0.03	0.19	0.01	0.36	0.10	-0.10	0.00								
Cd/Ca	0.41	0.29	0.26	0.01	0.52	0.19	0.03	0.02	0.38							
Sn/Ca	0.41	0.20	0.32	0.02	0.77	0.16	0.17	0.00	0.32	0.37						
Ba/Ca	0.29	0.25	0.27	0.02	0.41	0.00	0.34	-0.02	0.10	0.24	0.42					
La/Ca	0.04	0.15	0.54	0.01	0.25	0.08	0.29	0.08	0.02	0.20	0.13	0.24				
Ce/Ca	0.04	0.19	0.66	0.02	0.28	0.11	0.35	0.10	0.02	0.21	0.14	0.26	0.78			
Pr/Ca	0.04	0.13	0.58	0.01	0.26	0.09	0.32	0.09	0.03	0.21	0.14	0.25	0.67	0.82		
Nd/Ca	0.05	0.17	0.63	0.02	0.28	0.11	0.32	0.10	0.03	0.22	0.14	0.24	0.76	0.93	0.81	
Pb/Ca	-0.01	0.26	0.38	0.03	0.41	0.22	0.54	0.02	-0.08	0.34	0.27	0.48	0.44	0.48	0.46	0.46

Troubridge	*Li/Ca*	*P/Ca*	*V/Ca*	*Mn/Ca*	*Cu/Ca*	*Zn/Ca*	*Y/Ca*	*Zr/Ca*	*Mo/Ca*	*Cd/Ca*	*Sn/Ca*	*Ba/Ca*	*La/Ca*	*Ce/Ca*	*Pr/Ca*	*Nd/Ca*
P/Ca	0.29															
V/Ca	0.29	0.37														
Mn/Ca	0.38	0.31	0.15													
Cu/Ca	0.34	0.37	0.41	0.24												
Zn/Ca	0.32	0.40	0.27	0.49	0.39											
Y/Ca	-0.41	0.10	0.12	-0.16	0.06	-0.03										
Zr/Ca	0.04	0.09	0.02	0.03	0.13	0.09	0.05									
Mo/Ca	0.34	0.31	0.54	0.21	0.67	0.34	0.01	0.00								
Cd/Ca	0.12	0.09	0.17	0.14	0.14	0.17	0.02	-0.01	0.13							
Sn/Ca	0.30	0.21	0.23	0.29	0.23	0.34	-0.02	0.19	0.16	0.16						
Ba/Ca	0.04	0.04	0.10	-0.10	0.02	-0.01	0.23	0.02	0.02	0.15	0.15					
La/Ca	-0.23	0.08	0.11	-0.06	0.07	0.02	0.63	0.11	0.01	0.04	0.29	0.22				
Ce/Ca	-0.17	0.10	0.12	0.02	0.10	0.08	0.60	0.11	0.03	0.08	0.10	0.20	0.46			
Pr/Ca	-0.08	0.08	0.13	0.01	0.11	0.09	0.41	0.11	0.04	0.06	0.09	0.12	0.40	0.35		
Nd/Ca	-0.11	0.09	0.12	-0.01	0.10	0.08	0.43	0.13	0.04	0.05	0.09	0.10	0.36	0.34	0.33	
Pb/Ca	-0.13	0.23	0.20	0.13	0.24	0.32	0.59	0.05	0.07	0.13	0.22	0.28	0.47	0.47	0.33	0.30

Taylors Island	*Li/Ca*	*P/Ca*	*V/Ca*	*Mn/Ca*	*Cu/Ca*	*Zn/Ca*	*Y/Ca*	*Zr/Ca*	*Mo/Ca*	*Cd/Ca*	*Sn/Ca*	*Ba/Ca*	*La/Ca*	*Ce/Ca*	*Pr/Ca*	*Nd/Ca*
B/Ca	0.44															
P/Ca	0.35															
V/Ca	0.00	0.24														
Mn/Ca	0.49	0.48	0.03													
Cu/Ca	0.09	0.41	0.08	0.19												
Zn/Ca	0.30	0.64	0.17	0.52	0.41											
Y/Ca	-0.46	0.22	0.25	-0.29	0.05	0.10										
Zr/Ca	0.00	0.12	0.07	0.08	0.00	0.10	0.10									
Mo/Ca	0.30	0.57	0.24	0.31	0.20	0.56	0.13	0.08								
Cd/Ca	0.36	0.37	0.09	0.50	0.03	0.45	-0.03	0.20	0.58							
Sn/Ca	0.45	0.53	0.07	0.46	0.44	0.42	-0.12	0.11	0.28	0.34						
Ba/Ca	0.18	0.54	0.18	0.21	0.23	0.41	0.29	0.07	0.24	0.21	0.29					
La/Ca	-0.34	0.23	0.23	-0.21	0.06	0.16	0.87	0.06	0.16	0.01	-0.08	0.29				
Ce/Ca	-0.37	0.25	0.24	-0.20	0.09	0.16	0.88	0.09	0.15	0.01	-0.06	0.29	0.88			
Pr/Ca	-0.21	0.20	0.17	-0.11	0.03	0.13	0.61	0.05	0.13	0.03	-0.02	0.22	0.64	0.63		
Nd/Ca	-0.22	0.18	0.18	-0.14	0.05	0.11	0.63	0.06	0.15	0.03	-0.03	0.23	0.65	0.65	0.54	
Pb/Ca	0.39	0.41	0.18	0.48	0.03	0.42	0.03	0.20	0.48	0.77	0.44	0.32	0.08	0.07	0.09	0.09