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ANTHROPOGENIC DISTURBANCE
OF
ENVIRONMENTAL SIGNALS
RETAINED IN MASSIVE CORALS

VOLUME I

Thesis submitted by

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for the degree of Doctor of Philosophy

Sir George Fisher Centre for Tropical Marine Studies

James Cook University of North Queensland

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ABSTRACT

Samples of *Porites* coral were removed from seven different reefs (No Name, Hastings, Upolu, Thetford, Batt, Green Island and Brook Islands Reefs), including two from the same reef (Green Island Reef), within Australia's Great Barrier Reef Marine Park. Chemical and morphological data retrieved from these samples were used to investigate historical change in water quality surrounding the growing corals, particularly as this related to the increased use of phosphatic fertiliser on the nearby mainland. The study focused on a narrow section of the continental shelf adjacent to the mouth of the Barron River. In this area coral reefs are close to a mainland significantly altered for anthropogenic purposes. No Name Reef (approximately 300 km north of the study area and reasonably distant from known anthropogenic input) was included as a control. The Brook Islands Reef (approximately 300 km south of the study area) was added for geographic variability. Support data was gained by a two year nutrient monitoring programme of the Barron and Mossman River catchments, and marine waters adjacent to these two river systems. Additional information was acquired by the experimental supplementation of *Acropora formosa* corals with 2.0 μM, 4.0 μM and 8.0 μM PO_4.

Stream phosphate levels responded rapidly to rainfall. During the April 1989 flood period between 710 and 2,850 tonnes of Superphosphate were delivered into the ocean. Estimates vary according to the presumed ratio of soluble to particulate phosphate in the flood plume (e.g. see Cosser 1987 and Brodie & Mitchell 1992). The lower figure is nearly half the total industry estimated fertiliser usage (1810 tonnes) for the Far Northern Statistical Division during 1988. The greater figure is more than a third higher than Australian Bureau of Statistics figures for the same period (Pulsford 1990). The marine monitoring program suggested that nutrient monitoring was an insufficient method of estimating water quality.

The phosphate supplementation experiment showed that elevated levels of phosphate hindered calcium carbonate production with considerable alteration to the internal and external morphology of the coral skeleton.

Chemical analysis of the *Porites* samples suggested that intra-reefal variation in the coral skeleton was minor, but with sufficient inconsistencies in the annual record to suggest that localised, micro-environmental conditions exist and should be recognised when attempting to reconstruct environmental records from the coral skeleton. Statistically, the inner- and inner/mid-shelf sample sets were significantly different from each other and from all other sample sets. No significant statistical difference could be distinguished in the mid- to outer-shelf sample sets, but the relative contribution of each element differed for each of these sample sets.

The difference between the samples from nearer to shore and those from the outer-shelf was also apparent in the reconstructed coral inferred environmental record. Strontium-based sea-surface temperature estimates provided an adequate record of historical sea surface temperatures from the mid- to outer-shelf samples (No Name, Hastings, Upolu and Thetford Reefs), but were unreliable for the closer to shore samples (Batt, Green Island and Brook Island Reefs).

Similar inconsistencies were noted in associations with climatic variables. Data from the outer-shelf No Name Reef sample correlated with climatic data associated with the Southern Oscillation Index (SOI) while data from the Green Island Reef sample correlated with Mean Sea Level Pressure read at Darwin. These inconsistencies were inherent in the coral-inferred record and were not associated with anthropogenic influence.

However, ambiguities in the chemical composition and morphological structure of the Green Island sample were noted post-1950. These inconsistencies were statistically correlated to the use of fertiliser on the nearby mainland. Changes to the internal porosity of the coral skeleton were similar to those noted in the experimental phosphate supplementation programme.

The study concludes that chemical and morphological variations in the skeleton of the massive *Porites* coral are suitable for hindcasting paleoenvironmental conditions laid down in the skeleton at the time of precipitation. The study further concludes that there is significant evidence of anthropogenic influence in the Green Island sample, and that this influence is related to the use of fertilisers on the nearby mainland.

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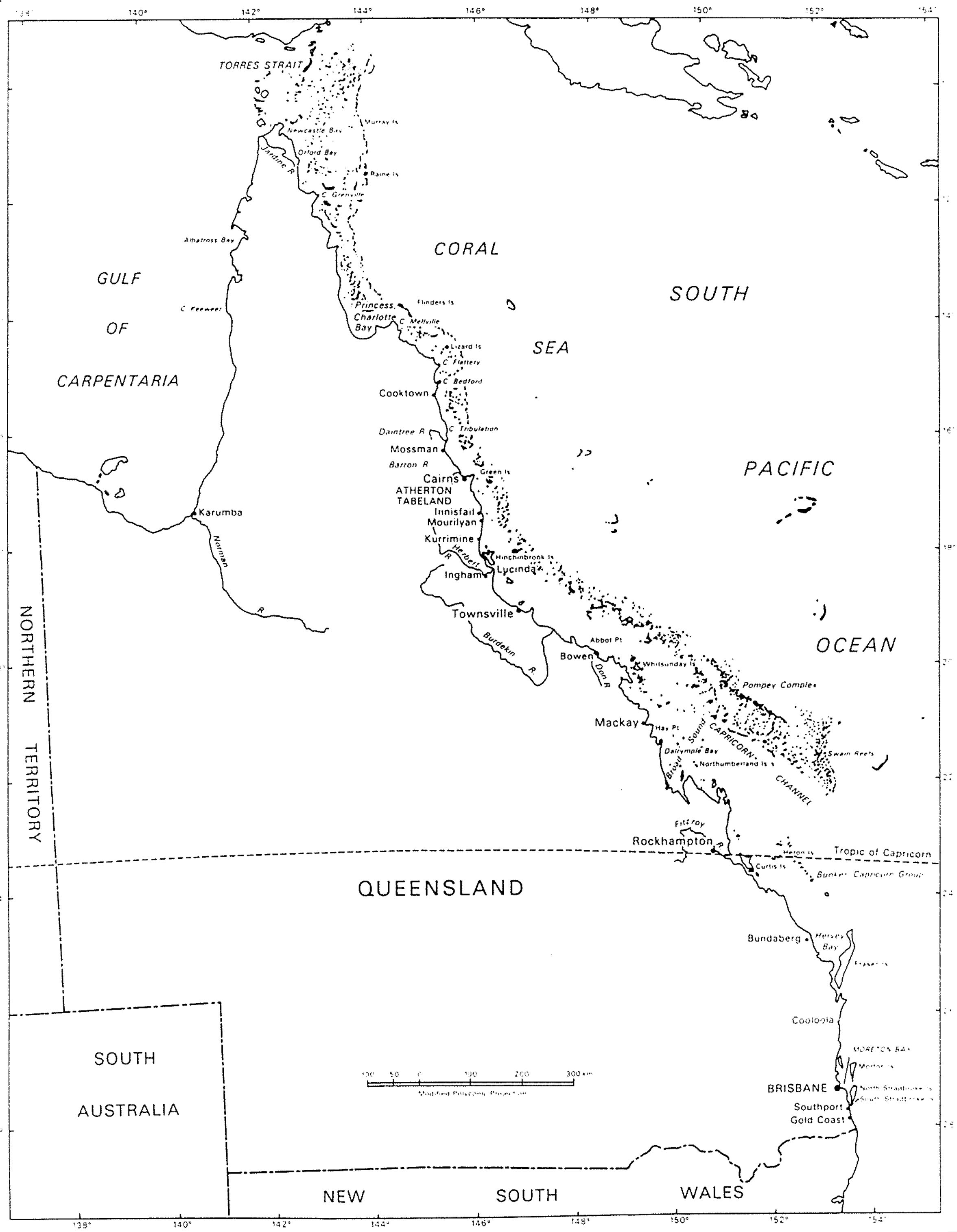

Figure 1: Location of Australia's Great Barrier Reef.

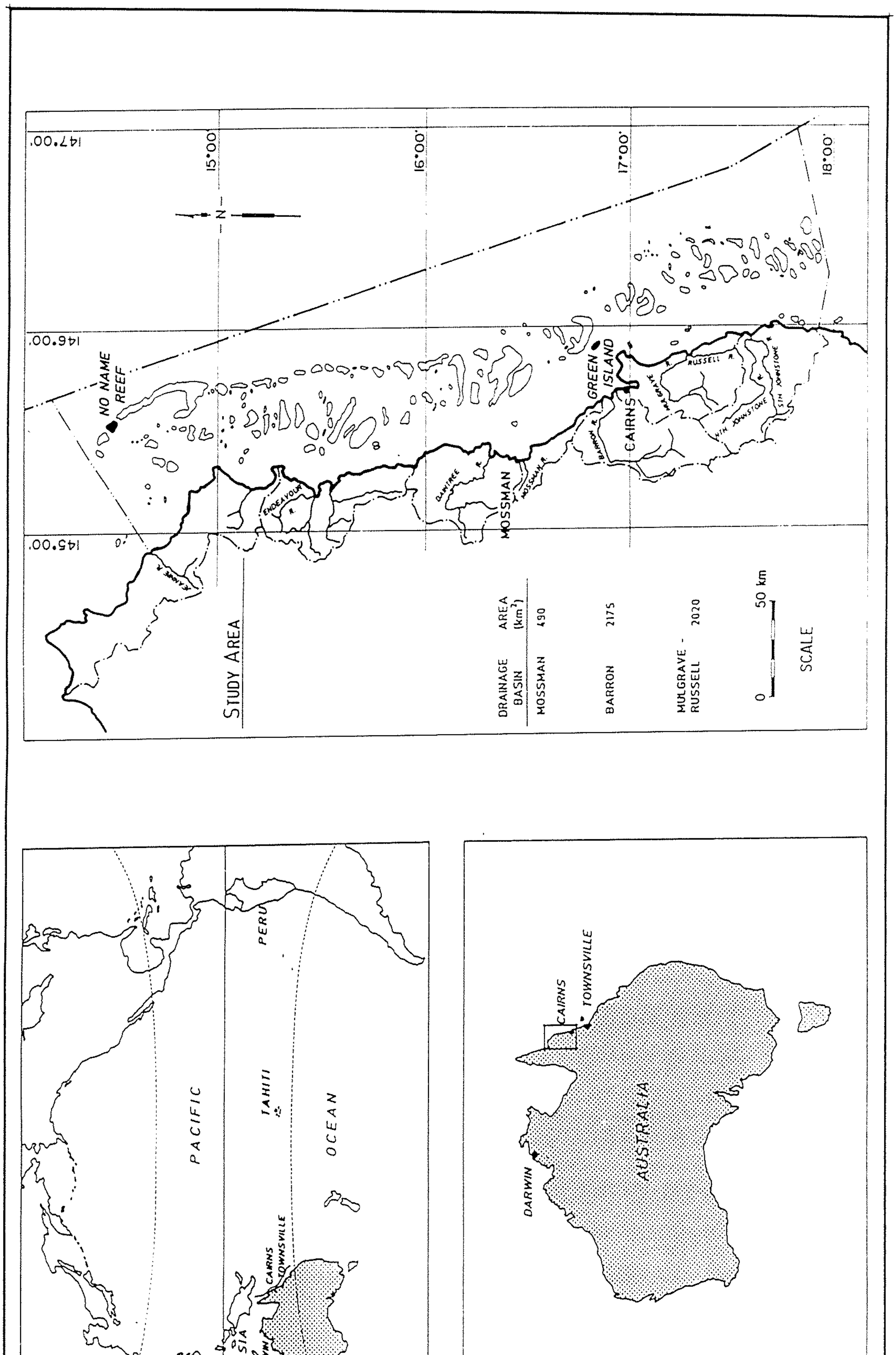

Figure 2: Location of the study area.

CHAPTER 1

ANTHROPOGENIC SIGNALS IN MASSIVE CORALS - AN INTRODUCTION TO THE CONCEPT OF THE THESIS AND SELECTION OF THE STUDY AREA

1.1 INTRODUCTION

Considerable debate exists about the extent of anthropogenic influence on Australia's Great Barrier Reef. A great deal of this debate surrounds the issue of nutrient enhancement (Baldwin *et.al*, 1987; Yellowlees 1990). Ideally, ambient conditions should be known before the onset of any change. Without baseline information, researchers and managers often resort to comparative, experimental, or short-term historical records to understand perceived alterations. Under such circumstances cause and effect situations can be inferred, but without long-term knowledge on the natural variability of the system, inferences must remain tenuous. Interpretations of ecosystem dynamics arising from such methods are ambiguous and invite argument.

Sclerochronology has the potential to provide the necessary information of past environmental conditions. Various trace elements (e.g. strontium, magnesium, sodium, potassium, iron, barium, cadmium and lead), incorporated into biogenic carbonates at the time of deposition, have previously been used as proxy indicators of environmental parameters including oceanic temperature, salinity, nutrient concentration, and rainfall timing and intensity (e.g. Houck *et.al.* 1977; Druffel 1981, 1982; Isdale 1981, 1984; Schneider & Smith 1982; Druffel & Suess 1983; Shen *et.al* 1987; Linn *et.al* 1990).

Use of massive corals with a sclerochronological history pre-dating anthropogenic influence allows interpretation of data laid down in the skeleton prior to major manipulation of adjacent systems. In the Indo-Pacific the massive *Porites* coral produces the most suitable material for sclerochronological studies because -

(a) individual corallites are small (Veron 1986) producing a finely grained, dense skeleton,

(b) alternating density bands enable the skeleton to be dated with a reasonable degree of accuracy (Knutson *et.al* 1974),

(c) *Porites* form some of the largest coral colonies, reaching heights of around eight metres with an average growth rate of around 9 mm per year. Individual colonies may be in excess of 1000 years old (Veron 1986).

Theoretically, therefore, paleoenvironmental interpretation using massive corals should be restricted only by the age of the colony and knowledge of the relationships between seawater and the chemical and physical properties of the skeleton.

1.2 SELECTION OF THE STUDY AREA

Although the majority of Australia's Great Barrier Reef is sufficiently distant from the mainland to be considered relatively free of terrestrial influence (Figure 1), in the northern sector between latitudes 15°S and 18°S, the shallow continental shelf narrows to approximately 40 km (Figures 1 & 2). Rainfall on the adjacent mainland is high, the hinterland is rugged, and the area between Cairns and Mossman has been significantly altered for agricultural and urban purposes. Hence, the potential exists for the rapid transfer of agricultural and urban additives from the mainland to the vicinity of the reefs.

It has been suggested that Crown-of-Thorn infestations could be related to enhanced levels of nutrients from anthropogenic sources (Endean 1973). Other research has suggested that the Green Island/Low Isles area adjacent to the Cairns/Mossman hinterland (Figures 1 & 2) may be a primary source of Crown-of-Thorn infestations to the Great Barrier Reef (Kenchington 1977). Therefore, study of this area also has application to the whole of the Great Barrier Reef and the most highlighted problems of the last 30 years.

1.3 PREVIOUS WORK BY THE AUTHOR SUGGESTING THE POSSIBILITY OF USING SCLEROCHRONOLOGY TO DETECT ENVIRONMENTAL CHANGE ON CORAL REEFS

Earlier work conducted by the author on Low Isles (Figure 3), suggested that many geomorphological changes that had taken place between 1928-29 (the time of the first Royal Society expedition to the Great Barrier Reef) and 1986 (Rasmussen 1986), could not be attributed to simple reef biological and morphological processes. The expansion of seagrass beds, mangroves and soft coral colonies, the spread of filamentous algae, the increased availability of shingle, and the decline in live coral cover, suggested a reef under stress. Comparisons with a morphologically similar low wooded island also studied by the 1928-29 Expedition (Three Isles, 200 km to the north and distanced from a settled section of the mainland) did not show evidence of similar changes. Research by numerous authors worldwide has attributed similar changes on nearshore coral reefs to terrestrial alteration of adjacent areas (e.g. Smith *et.al* 1981; Cortes and Risk 1985). Geochemical and geomechanical analysis of a coral core removed from a *Porites* colony at Low Isles provided additional circumstantial evidence of anthropogenic perturbations in the water around the growing coral (Rasmussen 1986). Examination of fertiliser data (Australian Bureau of Statistics) showed a strong inverse relationship between the use of phosphatic fertiliser and strontium content of the *Porites* skeleton. The results suggested that the geochemical and geomechanical properties of massive corals had the potential to provide the necessary medium for understanding changes in the marine system, including those of anthropogenic origin possibly related to nutrient enhancement.

1.4 THE POSSIBILITY THAT ENHANCED LEVELS OF PHOSPHATE COULD LEAVE A SIGNAL IN THE CORAL SKELETON SUITABLE FOR USE AS A SURROGATE INDICATOR OF NUTRIENT ENHANCEMENT

Whether phosphorus or nitrogen exerts the major influence on organic production in the sea remains a controversial issue (Smith, 1984; Smith *et.al* 1989). However, there is little or no literature on either systemic or systematic effects of nitrogen bearing species (e.g. NH_4, NO_3) on crystallisation in aqueous calcium carbonate systems[1]. On the other hand, it has been known for over 50 years that PO_4 exerts a systematic effect on crystallisation in such systems (e.g. see Rosenstein 1936; Reitemeier & Buehrer 1950; Simkiss 1964a).

It is not the intention of this study to investigate the chemical pathways followed by various elements in the process of skeletogenesis. This study will concentrate on the

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Following the experimental component of this thesis, Belda *et.al* 1993, examined the effects of combined nutrients on the skeleton of the giant clam *Tridacna gigas*. Their research demonstrated that P, N and P+N all had a deleterious effect on skeletal architecture.

signals retained within the coral skeleton, and attempt to link those signals to environmental changes on the nearby mainland, and in particular with the use of phosphatic fertiliser in adjacent areas. It is acknowledged that agriculture seldom uses only one variety of fertiliser, nor are commonly available fertilisers made up of a single element. Therefore, until the effects of nitrogen enhancement in skeletal material can be separated from those of phosphorus, any signals believed due to elevated levels of phosphorus in the sea can only be considered proxy indicators of total nutrient enhancement.

1.5 RESEARCH PLAN

A research plan was established to promote interpretation of proxy environmental signals from the corals. For the reasons outlined above, the section of the Great Barrier Reef adjacent to the Cairns/Mossman hinterland (Figure 1) was considered the area best suited to the study. The program was designed to include -

(1) ***The examination of samples of Porites corals taken from a number of geographically different areas.*** It was reasoned that if evidence of anthropogenic change could be detected in the coral skeleton, then such change should vary with proximity to the source of the influence, and with the increased incidence of European settlement on the nearby mainland. Therefore, it was necessary to remove samples from a number of *Porites* colonies at a variety of locations within the Cairns Section of the Great Barrier Reef Marine Park. Each core needed to be long enough to include material pre-dating European impact (approximately 130 years).

(2) ***The examination of elevated levels of phosphate on the growth kinetics of reef corals.*** Because there was little information on the effects of elevated levels of phosphate on coral skeletal material, experimental research was necessary. Controlled experiments were planned for aquaria at the James Cook University Orpheus Island Research Station.

(3) ***The examination of the nutrient status of streams, rivers and adjacent marine waters in the study area.*** Following the Low Isles study (Rasmussen 1986) outlined above, considerable argument suggested that phosphate was 'fixed' into the soil profile, and that any phosphorous that may be delivered into the ocean would be quickly utilised by resident marine flora and fauna (Furham 1987; Orrett & Karl 1987; Kuhn 1990; Moody & Chapman 1990; Furnas 1990; Thomson 1991).

It was considered necessary, therefore, to undertake limited studies of the nutrient dynamics of both the terrestrial and marine segments of the study area. Lack of information on the generation and transport of nutrients through the fluvial system into the marine environment, under North Queensland climatic conditions, also necessitated this part of the study. Information gained from the monitoring program is used, not to fully document the nutrient flux, but to demonstrate -

(a) the potential of agricultural areas to generate high levels of nutrients to nearby rivers,

(b) the importance of rainfall events in raising the nutrient status of river systems draining these agricultural lands, and

(c) the relationship between rainfall events, river discharge, agricultural practices and nutrient enhancement in adjacent marine waters.

The synthesis of these areas of study, as discussed in Chapter 8, suggests that the corals examined do retain a record of environmental change. A long-term variability apparently associated with the main driving force of North Queensland weather, the El Niño Southern Oscillation, is over-ridden in recent times by a dominant anthropogenic influence.

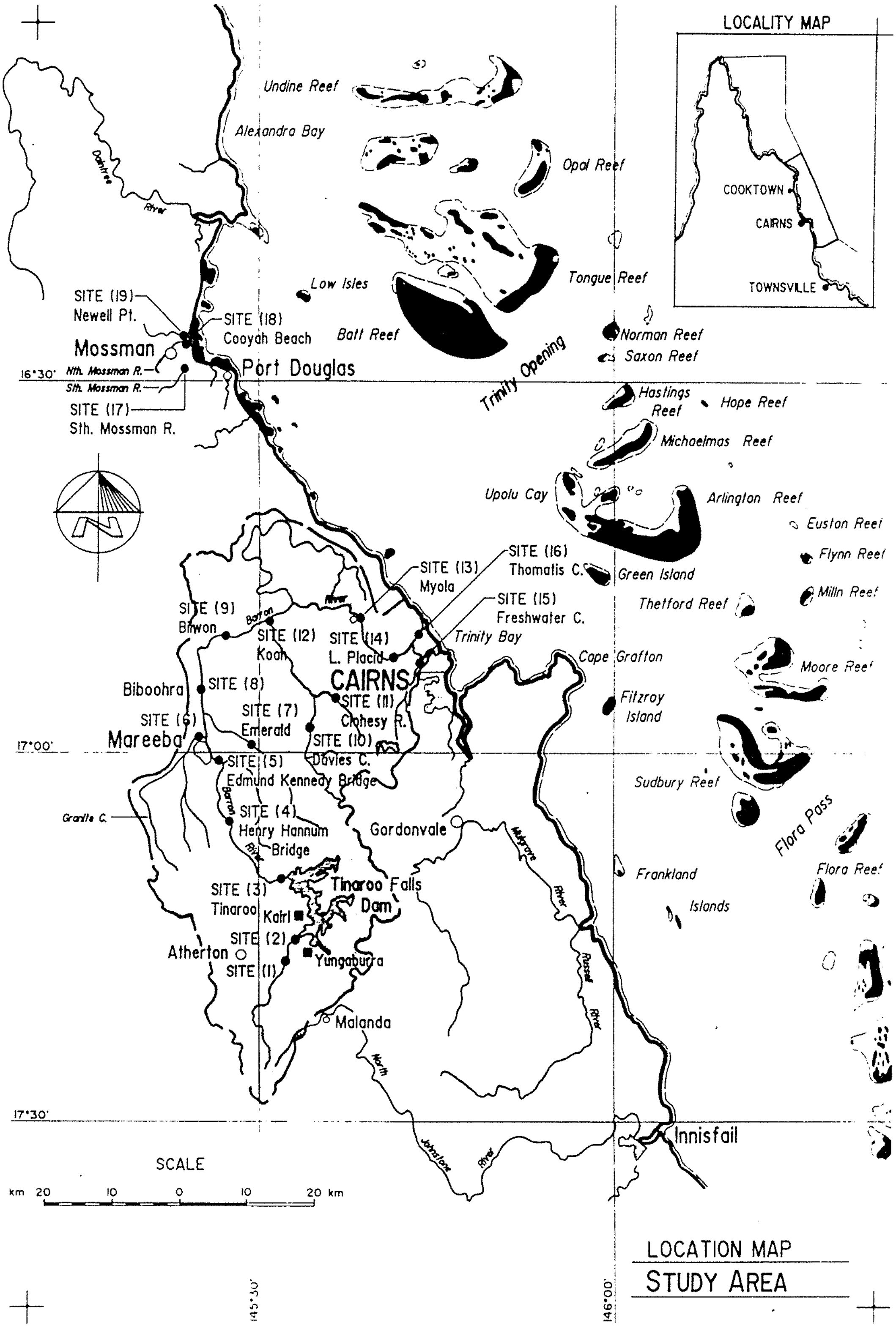

Figure 3: Location of study sites.

CHAPTER 2

THE ENVIRONMENT OF THE STUDY AREA

2.1. THE CAIRNS-MOSSMAN AREA AND ITS HINTERLAND - THE POTENTIAL FOR IMPACT IN ADJACENT MARINE ENVIRONMENTS.

Geologic, biologic, climatic, oceanic and tectonic forces (Hopley 1982) have produced a particularly diverse community of reefs and islands near an equally diverse tropical rainforest environment in the Cairns region. Climatic conditions and the perceived fertility of rainforest soils have encouraged the expansion of primary industries. Before European settlement most of the coastal areas of Northeast Queensland and the Atherton Tablelands were forested. The luxuriant growth of the rainforests was thought to indicate highly fertile soils capable of returning high agricultural yields. Between 1918 and 1932 agrarian development increased by 100% in the Cairns/Mossman district. The construction of an irrigation network associated with the completion of Tinaroo Dam in 1958 allowed major expansion of agriculture to spread into drier areas of the Atherton Tablelands.

The effect of land clearance on the fluvial system has been well documented (e.g. see Ward 1975). However, in the Cairns/Mossman region, the climate can be erratic and extreme. The "wet season" in North Queensland broadly covers the period November to April, but intensity, duration, and onset vary dramatically. For example, in 1973/74 Atherton recorded 2391 mm of rain from 121 raindays, with nearly half falling over a 28 day period in March (1107 mm). By contrast, the total 1977/78 seasonal rainfall (716 mm) was less than that of March 1974. Seasonal variations are further displayed in Table 2.1.

Annual rainfall occasionally exceeds 5000 mm along the coastal strip between Cairns and Mossman. Individual rainfall events during the 'dry' season can produce daily totals of more than 100 mm (Australian Bureau of Meteorology). During spring and early summer, intense thunderstorms of short duration are often responsible for falls of 40 mm in less than 20 minutes (Douglas 1973). Under such circumstances, the effects of man superimposed on to the climatic regime outlined above combines to create a rapid and efficient method of transportation. In an area where geological characteristics produce a profile conducive to erosion, the effect will be exacerbated.

Table 2.1: Seasonal rainfall extremes in the study area.

SEASONAL AVERAGE (ATHERTON)			*WET SEASON*		*DRY SEASON*	
SEASON (NOV-OCT)	*TOTAL YEARLY RAINFALL (mm)*	*NUMBER OF RAIN DAYS FOR YEAR*	*ONSET OF WET SEASON*	*HIGHEST RAINFALL MONTH (mm)*	*RAINFALL (mm)*	*RAINDAYS FOR THAT MONTH*
1973/74	*2776*	*152*	*NOVEMBER (238 mm)*	*MARCH (1107)*	*77 (AUGUST)*	*2*
1977/78	*716*	*171*	*NOVEMBER (15 mm)*	*JANUARY (196)*	*31 (AUGUST)*	*15*

Source: (Australian Bureau of Meteorology)

2.2 THE TERRESTRIAL ENVIRONMENT OF THE STUDY AREA

2.2.1. GEOGRAPHICAL CHARACTERISTICS

The Barron River and its tributaries link the Atherton Tablelands to the Great Barrier Reef Lagoon (Figures 1,2 & 3). Draining a catchment of 2100 km^2 from its headwaters near Mt. Hypipamee (elevation 1100 m) over a distance of approximately 160 km, the Barron River enters the ocean approximately 12 km north of Cairns.

The coastal strip between Cairns and Mossman includes the catchments of the Lower Barron River and its anabranch Thomatis Creek, Freshwater Creek, South Mossman River, North Mossman River and Newell Creek (Figure 3). Freshwater Creek drains sugarcane farms before joining the Barron River just prior to discharge into Trinity Bay. The Thomatis Creek anabranch of the Barron River drains sugarcane farms, and enters Trinity Bay north of the main mouth of the Barron River. South Mossman River, North Mossman River and Newell Creek are short runoff streams draining sugarcane lands. The major contribution of the short runoff streams to the hydrology of the area occurs during periods of short duration under the intense precipitation of the wet tropical environment. The mouths of all rivers support extensive estuarine mangrove habitats.

2.2.2. GEOLOGICAL AND PEDOLOGICAL CHARACTERISTICS

The geology of the area is shown in Figure 4. In the upper reaches of the Barron River catchment parent material is mainly Atherton Basalt, with small inliers of Barron River Metamorphics around Yungaburra, and Elizabeth Creek Granite on the southwestern boundary. The major group of sedimentary rocks in the northwest area of the Atherton Tablelands is the Hodgkinson Formation. This formation comprises thick monotonous sequences of massive to thin bedded sandstone, greywacke and mudstone, with intercalated chert, conglomerate, breccia, and rare limestone lenses (Douglas 1973). In the northern section of the Tablelands the river flood plain has established large areas of alluvium from parent material in the upper catchment.

On the Atherton Tablelands the soils are primarily structured sesquioxides with fine granular or crumb structure (Gillman and Sumpter 1985). Chemical properties of the soils are determined by the parent rock. Depending on soil parent material, the clay mineralogical composition is dominated by kaolinite, with various amounts of iron and aluminium hydroxides and oxyhydroxides, chloritized vermiculite, and illite (Gillman and Sumpter 1985). The clay content of the soils formed from the basalt of the Atherton Tablelands is at least three times greater than those of the other soil types (Toreu *et al* 1988). The basaltic clays of the area are dominated by oxides of iron and aluminium, greatly increasing the ability of the soils to sorb phosphates (Toreu *et al* 1988). Soils formed on the granites have a lower clay content of a longer range order than those present in the basaltic soils, indicating a lower specific surface and a reduced capacity to sorb phosphate (Toreu *et al* 1988). The P-sorption characteristics of soils formed on metamorphic rock or alluvial parent material are intermediate between those of basaltic and granitic origin, dependent upon clay content and composition (Toreu *et al* 1988). In the north and east of the Barron catchment, large areas of soils have formed from Barron River Metamorphics. Douglas (1973) suggested the high silicate content of these sediments produced easily erodible, nutrient poor soils following removal of the natural vegetation.

Soils along the coastal strip are a combination of -

(a) highly weathered material formed on basaltic, granitic and metamorphic rocks (Toreu *et al* 1988),

(b) alluvium and colluvium derived from one or more of the parent materials (Toreu *et al* 1988), with

(c) a significant input from coastal marine deposits (Jones 1985).

2.2.3. THE EFFECTS OF CLIMATE AND HYDROLOGY ON SEDIMENT YIELD

The area has been the location for several studies on water movement and sediment yield (e.g. see Douglas 1966 and the summarisation by Pringle 1986). It is now also known that North Queensland's weather patterns are strongly influenced by the intensity and duration of the El Niño Southern Oscillation (ENSO) (e.g. see McBride & Nicholls 1983; Allan 1988, 1991). ENSO is a family of oceanographic and meteorological events closely linked to the oscillation between the South Pacific subtropical high (measured at Tahiti) and the Indonesian equatorial low (measured at Darwin, Australia). Variations between the two pressure cells provide an indication of the intensity of the ENSO event (Quinn *et al* 1978). An ENSO year is associated with a weakening of the equatorial easterly winds and the strengthening of the westerlies above Queensland (Australia), forcing a mass of warm water across the Pacific (e.g. Quinn *et al* 1978; Rasmusson & Carpenter, 1982; Rasmusson & Wallace 1983). As a consequence, sea levels rise along the west coast of South America. The slope of the oceanic mixed layer across the Pacific is reversed, depressing the thermocline on the equatorial eastern side of the ocean. Equatorial upwellings of cold nutrient rich water induced by the combination of trade winds and the coriolis force are restrained. Sea surface temperatures become warmer in the eastern Pacific and slightly cooler in the western Pacific (Rasmusson & Carpenter 1982). During periods of strong ENSO activity (the active phase of the ENSO cycle) heavy rains occur in southern Ecuador and northwest Peru and droughts are experienced in Australia. During periods of anti-ENSO activity (the passive phase of the ENSO cycle), the reverse applies. Sea surface temperatures warm in the western Pacific, cyclonic activity increases along the north Australian coast, heavy rains occur in Australia (McBride & Nicholls 1983), with droughts in Ecuador and Peru.

Climatic conditions in North Queensland are generalised as tropical. However, distance from the sea, elevation, and location of coastal highlands and ranges, mean sharp contrasts in rainfall and temperature can occur within very short distances

(Report by the Commonwealth Department of National Development and the Queensland Department of Industrial Development 1971). Therefore, while summer temperatures of above 38°C are common, in the higher areas of the Atherton Tablelands frosts can occur during the short winter period. Consequently the Atherton Tablelands experience a sub humid to humid climate with marked wet/dry seasons (Department of Primary Industries note, Anon), with more than 85% of the rain falling in the December to March period.

The coastal strip of the North Queensland wet tropics receives very high rainfall, occasionally over 5000 mm per annum. Rainfall is strongly seasonal (predominantly summer), of long duration (four to six months), and often intense. Precipitation rates of 3300 mm were recorded during a two week period in 1979 (Australian Bureau of Meteorology). Thus, soils in the area are at, or above, field capacity during most of the wet season (Douglas 1973; Figure 7). However, although rainfall is strongly seasonal, heavy downpours can occur throughout the year. Individual rainfall events during the 'dry' season can produce daily totals of more than 100 mm (Gilmour *et al* 1982). Hydrologic processes consistent with such environments are constantly operating to -

(a) transport moisture and nutrients from the saturated zone to the water table, and

(b) respond rapidly to rainfall events resulting in saturated overland flow and accompanying soil movement.

Prove (1987) has shown that under the conditions operating along the wet tropical coastal strip of North Queensland, high intensity rainfall causes overland flow (or runoff) to occur. Douglas (1973) also showed that in the Barron River catchment, the high runoff per unit area makes large quantities of dissolved matter available for evacuation. Most of the material removed from these very wet catchments is carried in suspension or as bed load (Douglas 1973). The estimated ratio of dissolved to suspended load is approximately 0.5 with over 50% of the sediment load removed on fewer than seven days of the year (Douglas 1973). Under cultivated conditions evacuated material could be expected to be considerably higher.

Douglas (1973) considered that climate was the most important controlling factor for runoff processes in the Barron River catchment. Under normal conditions hydrological processes are controlled by the synergistic interaction of rainfall variability, seasonality, intensity, duration and timing. Douglas (1973) concluded that when the effects of man are superimposed on to a strongly seasonal climate with sudden, intense precipitation of long duration, and with periods of intense wet interspersed with periods of extreme dry, the combined effects produce a rapid and efficient method of transportation from the terrestrial to the marine environment.

The importance of these combined effects on the transportation of sedimented particles is shown in Douglas's (1973) water balance diagrams (Figure 7). Before the onset of the wet season, air temperatures are high and cloud cover low. Evaporation exceeds precipitation and soil moisture loss is extreme. Fields are prepared and crops sown specifically to take advantage of the first storm rains. Therefore, most of the fields are free of vegetative cover when the first rains occur. Trash retention and minimum tillage have not been normal land management practice in the Cairns/Mossman district and adjacent hinterlands. Relatively little flat land is available for farming. The first storm rains (November/December) of the wet season (November to May) are often sudden and intense. Precipitation during this period contributes significantly to overland flow and/or sheet flow before infiltration into the soil profile. Soils during this period are particularly vulnerable to erosion.

Erosion is a major problem on the Atherton Tablelands, with the most severe erosion in the cultivated areas around Atherton (Kneipp & Bolt, 1971). Comparisons between a rainforest area at the headwaters of the Barron River and an area further downstream draining agricultural lands, showed that following Cyclone Flora in 1964, peak flows in the agricultural area carried approximately three times more sediment than equivalent flows in the headwaters (Douglas 1973). The larger amount of sediment removed from the lower section of the catchment was attributed to the direct supply of sediment from ploughed fields, to water erosion between the rows of young maize plants, and to the undercutting of stream banks.

The hydrology of streams draining basalt terrains is further affected by the underground drainage of the basalt (Douglas 1973). The deep circulation of groundwater in the basalt of the Atherton Tablelands reduces streamflow at the beginning of the wet season but maintains a steady baseflow during the winter. Therefore runoff per unit area during the dry season at Mareeba, just below the basalt outcrop, can be higher than at Kuranda in the wetter coastal hills (Douglas 1973).

2.2.4 AGRICULTURAL PRACTICES AND FERTILISER APPLICATION

Historical Background:

Landuse has changed considerably over the last 130 years. Before European settlement most of the Atherton Tablelands and the coastal area between Cairns and Mossman were forested. Interest in the economic viability of the North Queensland area was initially stimulated by rainforest timber. Climatic conditions and the perceived fertility of rainforest soils encouraged the expansion of primary industries. Agriculture began in cleared areas in the 1880's. By 1906 much of the wet tropical coastal lowland had been cleared for sugar cane cultivation and the northwest part of the Atherton Tablelands for crops and dairying. By 1918 large areas of the Atherton Tablelands had been cleared for dairying (Pringle 1986). Although land clearing slowed during the 1920's because of difficulties in the more marginal areas, within previously cleared areas there was a marked increase in cultivation and pasture development (Pringle 1986). Agrarian development continued to increase on the Atherton Tablelands and in the Cairns to Mossman Districts (Frawley 1983). Completion of the Tinaroo Dam on the upper reaches of the Barron River in 1958, and the accompanying network of irrigation channels, had two effects on the Tablelands, (1) intense farming methods were now possible, and (2) agricultural expansion spread into the marginal areas of the Tablelands. By 1960, when it became clear that greater capital investment was needed in farming, only remnant forest remained in steeper areas between clearings (Frawley 1983; Pringle 1986).

Current Land Management Practices:

Most agriculture on the Atherton Tablelands takes place on the deeply weathered basaltic soils with a high clay content (Loader 1987). The interrelationship between agricultural practices and geology is shown in Figure 6. Most of these soils have acid extractable phosphorus levels over 20 ppm. These values are considered sufficient for the major agricultural practices of the Tablelands (Loader 1987). Other areas of the Tablelands are deficient in phosphorus (Crosthwaite, 1983, p44), using considerable quantities of phosphatic fertiliser for efficient production. Historical farming practices, however, also control fertiliser application incidental to crop or soil requirements. Only 18% of the phosphatic fertiliser applied to peanut plantations was based on scientific analysis (Loader 1987). Table 2.2 summarises the major use of individual fertilisers in the Barron River catchment.

Table 2.2: Elemental nutrients applied to fields of the Atherton Tablelands. Source: Valentine (1988)

(a) Above Tinaroo Dam

Landuse	*Nitrogen*		*Phosphate*		*Potassium*		*Sulphur*	
	Rate	*Total*	*Rate*	*Total*	*Rate*	*Total*	*Rate*	*Total*
	kg ha^{-1}	*kg*	*kg ha^{-1}*	*kg*	*kg ha-^{1}*	*kg*	*kg ha^{-1}*	*kg*
ORCHARD	*40.0*	*16545*	*12.0*	*4898*	*13.8*	*5667*	*12.7*	*1938*
DAIRY	*51.0*	*475348*	*12.0*	*111738*	*15.6*	*146267*	*9.7*	*90643*
BEEF	*10.3*	*82918*	*5.9*	*47616*	*5.9*	*47572*	*7.0*	*56261*
MAIZE	*86.2*	*230631*	*13.6*	*41092*	*2.4*	*7152*	*7.7*	*23381*
POTATOES	*151.0*	*35947*	*114.3*	*27256*	*93.2*	*22229*	*224.6*	*53568*
PEANUTS	*10.0*	*15116*	*(?)3.7*	*(?)5570*	*1.5*	*2297*	*4.7*	*7073*
SUGAR	*187.0*	*24330*	*54.5*	*7094*	*124.0*	*16130*	*82.0*	*10643*
TOTAL YR^{-1}		*910835*		*245264*		*247314*		*243507*

(?) possible discrepancy in data (see text)

(b) Below Tinaroo Dam

	Nitrogen		*Phosphate*		*Potassium*		*Sulphur*	
	Rate	*Total*	*Rate*	*Total*	*Rate*	*Total*	*Rate*	*Total*
	kg ha^{-1}	*kg*	*kg ha^{-1}*	*kg*	*kg ha^{-1}*	*kg*	*kg ha^{-1}*	*kg*
ORCHARD	*72.4*	*76692*	*13.6*	*14466*	*58.8*	*62334*	*43.3*	*45869*
PEANUTS	*8.9*	*30467*	*26.9*	*92182*	*1.3*	*4439*	*24.4*	*83763*
MAIZE	*88.5*	*263321*	*35.4*	*105324*	*0.4*	*1287*	*13.1*	*39130*
BEEF	*6.2*	*94023*	*4.2*	*64644*	*0.5*	*8357*	*4.2*	*64656*
POTATOES	*147.6*	*55778*	*123.6*	*46720*	*125.2*	*47341*	*181.0*	*68549*
RICE	*181.8*	*86150*	*28.0*	*13310*	*5.3*	*2519*	*28.0*	*13325*
TOBACCO	*130.4*	*167461*	*53.6*	*68863*	*290.0*	*373112*	*32.3*	*41525*
FEED	*23.5*	*38806*	*10.8*	*17917*	*0.4*	*598*	*12.2*	*20064*
SUGAR	*148.0*	*292525*	*28.2*	*55736*	*108.4*	*213987*	*18.3*	*36164*
OTHER	*89.8*	*39999*	*22.6*	*10071*	*23.4*	*10420*	*20.4*	*9084*
TOTAL YR^{-1}		*1145222*		*489233*		*724394*		*422129*

The most extensive agricultural landuse on the Atherton Tablelands is beef cattle grazing (45% of the agricultural land), followed by the grazing of dairy cattle (18%) (Valentine 1988). The higher economic return from the dairy industry supports intensive grazing practices and considerably higher use of fertiliser. In both instances, fertiliser is broadcast directly on to the fields before the onset of the wet season. Fertilisers are applied at the rate of 44 kg P ha^{-1} and 62 kg K ha^{-1} for intensive dairy production.

The most extensively grown crops on the Atherton Tablelands are maize and peanuts. Most farmers growing maize also grow peanuts (Valentine 1988). Both crops are rain grown and soil preparation and planting are closely associated with rainfall (Crosthwaite 1983; Valentine 1988). Fields are prepared by ploughing after harvest (September-November). Maize is planted following the first storm rains and fertiliser applied to the soil at the time of planting (November to January). Peanuts are planted on the first storm rains and grown through the wet season (Department of Primary Industries Note, Anon.). According to Loader (1987), 70% of growers on the Atherton Tablelands fertilise their peanut crops. Nearly all (94%) use phosphorus. The relative profitability of peanuts enables the crop to support extremely high levels of phosphatic fertiliser (Valentine 1988). Fertiliser is always broadcast and incorporated into the soil profile before planting. 66% of growers use other nutrients as well. Valentine's data suggest phosphatic fertiliser applied to peanuts (3.7 kg ha^{-1}) is considerably less than that applied to maize (13.6 kg^{-1} ha) (Table 2.2). Loader's (1987) data suggest this figure should be 370 kg ha^{-1} phosphate. In many cases 'elemental P' is referenced in preference to 'phosphate' and/or fertiliser weight, however, highlighting the difficulties in assessing varying data sources.

Potatoes are the fastest expanding crop on the Atherton Tablelands (L.Loader, Department of Primary Industries, pers.com.), increasing from 696 ha^{-1} in 1987 to 952 ha^{-1} in 1988. Potato growing on the Atherton Tablelands uses the greatest quantities of chemicals with extremely high applications of nitrogen, potassium and phosphate (Valentine 1988; Table 2.2). Approximately 180 tonne P and 240 tonne N were used on potato crops during 1988/89 (Department of Primary Industries note, Anon.). Fertiliser is applied to the soil at the time of planting (Bartholomew, 1981). Summer and winter crops may be planted. Although potatoes only used 1% of agricultural land in 1987 (Valentine 1988), the increasing popularity of this crop, the ability to sustain more than one crop per year, and the need for extremely high inputs of fertilisers, indicates the potential importance of potato farming to the nutrient budget of the Atherton Tablelands.

Orchards use only moderate levels of nitrogen, potassium and phosphate (Table 2.2). However, the recent expansion of tropical fruits (Valentine 1988) suggests higher inputs of fertilisers will be required in the future. Fertilisers are generally applied during the wet season (January-February) but application is not restricted to this period (Valentine 1988).

Sugar cane is the only major crop grown along the coast. Planting begins around May and continues through until September. Phosphatic fertiliser is added to the soil at the time of planting for slow release by subsequent rains. Land management practices also require cane fields to remain fallow for alternating periods. During this period fields are top dressed with nitrogen based fertilisers. Top dressing takes place around November to take advantage of summer monsoons.

Soils in the Mossman-Cairns area are low in magnesium, calcium and potassium, contain a reasonable amount of sulphur and phosphorus and are extremely high in nitrogen (Bureau of Sugar Experiment Stations 1981). Top soils in all regions register high levels of P, suggested by Chapman *et al* (1981) to be due to previous applications of fertiliser. Phosphorus equal to 50% of the applied phosphorus fertiliser is present in the crop. The remainder of the applied phosphorus accumulates in the top soil and is registered in the levels of phosphorus detected by soil analysis (Chapman *et al* 1981).

Soil pH values at approximately 5.2 are considered below optimum in the Mossman to Cairns area (Chapman *et al* 1981). The satisfactory maintenance of soil calcium, magnesium and potassium, is difficult in regions subjected to leaching from high rainfall conditions (Chapman *et al* 1981). Application rates of calcium and magnesium fertiliser are estimated to be less than those removed by the crop, and soil nutrient reserves of these elements are gradually being depleted (Chapman *et al* 1981).

2.3. THE MARINE ENVIRONMENT OF THE STUDY AREA

2.3.1. GEOGRAPHICAL CHARACTERISTICS

In the northern sector of the study area (Figures 1, 2 & 3), the Great Barrier Reef is characterised by a series of ribbon reefs on the outer edge of the narrow, relatively shallow continental shelf. To the east the shelf drops away from depths of less than 50 m to greater than 1000 m within a kilometre of the shelf edge (Hopley 1982). Behind the reef extensive banks of *Halimeda* have developed. In the southern sector, adjacent to the Cairns/Mossman area, a series of ribbon-like reefs occur along the edge of the narrow continental shelf. In this area the shelf drop-off is more gradual than in the northern sector, but depths of 1000 m within 10 km of the shelf crest have been noted (Hopley 1982). Extensive *Halimeda* banks have also formed behind the outer reefs in this location (Wolanski *et al* 1988).

Most reefs in the area lie between 20 and 60 km from the coastline. Major reef development begins around 25 km from the mainland, coinciding with the 36 m isobath. A series of small, relatively close and evenly spaced reefs occupy the outer portion of the continental shelf (Hopley 1982). The inner shelf is comparatively featureless, except for occasional high continental islands close to the coastline, and the low wooded island of Low Isles approximately halfway between the coastline and the 36 m isobath.

Reefs selected for study are adjacent to the Cairns hinterland drained by the Barron River catchment and the short runoff streams between Cairns and Mossman (Figures 2 & 3). Brook Islands Reef, to the south of the major area of study, was included to represent a secondary area with contrasting geological, climatic and agricultural background. No-Name Reef, on the outer shelf of the Great Barrier Reef, 60 km east of the mainland and 300 km north of the mouth of the Barron River (Figures 2 & 3), is adjacent to a mainland area supporting only sparse beef cattle production and considered sufficiently removed from anthropogenic influence to provide an adequate control site.

2.3.2 MORPHOLOGICAL CHARACTERISTICS OF REEFS IN THE STUDY AREA

Reef morphology follows a pattern of maturation associated with depth of the pre-Holocene reef from which modern reef growth has taken place (Hopley 1982; 1989).

Fringing reefs display the shallowest foundations with a progression towards deeper foundations from planar, through lagoonal, crescentic to ribbon reefs (Hopley 1989).

The study area is dominated by planar and crescentic reefs (Hopley 1989) indicative of the relatively shallow underlying pre-Holocene platform. For example, drilling has encountered Pleistocene reef at depths less than 20 m in the study area (see Davies *et al* 1989). Therefore, most of the reefs in the study area have formed extensive reef flats exposed during periods of low tide.

2.3.3 HYDRODYNAMICS

Tides

Semidiurnal tidal exchange produces a significant degree of flushing and mixing of shelf waters (Davis 1978; Hopley 1982). Tidal range in the study area is approximately 2.5 m, induced partly by minor amplification on the shallow continental shelf, with a strong solar influence reflected in relatively high neap to spring tidal variations (Hopley 1982). Currents induced by tidal variations can be significant in shallow areas. Extremely low spring-tides occur during the night in summer (January, February) and during daytime in winter (June, July). Wide expanses of reef flat and living coral are exposed during these tides (Hopley 1982).

Currents

Influence from the dominant southeasterly wind regime, operating along the east coast of Queensland, forces a northwards moving current along the North Queensland coast (Wolanski and Jones 1981; Wolanski and van Senden 1983). Discharge from rivers is subsequently pushed northwards during normal conditions. Thus, reefs in the study area will also be affected by fluvial discharge from southern rivers, driven into the area by dominant northwards moving coastal currents.

2.3.4 WATER MASS STRUCTURE

Temperature

Although latitudinal variation in temperature correlates with air temperature (Walker 1981; Andrews 1983), the greatest seasonal variations occur in a cross shelf transect (Hopley 1989). For example, in the Townsville region of the Great Barrier Reef, inshore waters vary from 19° to >30°C, mid shelf temperatures from 22° to 29°C, and adjacent Coral Sea temperatures between 23° and 29°C (Pickard et al 1977; Hopley 1989).

Salinity

In the southern zone of the lagoon, density cycles are controlled by temperature. However, salinity variations associated with rainfall cycles affect density in the northern sector (Pickard *et al* 1977; Andrews and Pickard 1990). Salinity variations within the open lagoon are primarily non-discharge dependent. However, near land discharge points, salinity is erratic (Wolanski and Jones 1981). In the wet season, salinity close to coastal areas may be reduced to less than 20 ppt. Under conditions of extreme flooding, particularly during cyclonic disturbance, or periods when the dominant southeasterly wind regime disintegrates, river plumes and lowered salinity associated with flooding may extend 40-50 km out to sea (Wolanski and Jones 1981; van Woesik 1991). During the floods of 1991, salinity levels at Great Keppel Island (50 km from the mouth of the Fitzroy River) were in the order of 7 to 10 ppt at the surface, 15 to 28 ppt at 3m, 31 to 34 ppt at 6m and 33 to 34 ppt at 12m (van Woesik 1991).

In relatively open ocean situations, where mixing is almost instantaneous (outer shelf), salinity variations from precipitation are minor (Hopley 1989). Most salinity variations at these locations, are induced by upwellings at the shelf edge (Andrews 1983).

Nutrients

A clear decline in nutrient concentration from mainland to open ocean is apparent across the Continental Shelf. Typical phosphate values are <0.1 μm in tropical open oceans, 0.16 to 0.26 μm at mid-shelf locations, and 0.20 to 0.31 μm along the inner shelf of the Great Barrier Reef (Hopley 1989).

2.3.5 TERRESTRIAL INFLUENCES

Although the Barron River is relatively small compared to some North Queensland river systems (mean annual flow 813,773 Ml compared with 9,926,745 Ml for the Burdekin River) (Hausler 1990), discharge rates over 2,500,000 Ml (Australian Bureau of

Meteorology), with instantaneous flow rates of more than 4,556 m^3 s^{-1} (Hausler 1990) have been recorded. Under normal climatic conditions rainfall in the catchment is intense and strongly seasonal. During cyclonic events, however, the equivalent of one month's 'average' wet season rainfall can fall during a single day. The sudden, intense precipitation associated with such events means interpretation using average data can blur the true situation (Douglas 1973). River discharge is often associated with extreme flooding. Rainfall intensity, often extending for days or weeks, pushes floodwaters and associated sediments far into the marine environment (Wolanski & Jones 1981). Deposition of terrestrial sediments initially takes place close to shore. Resuspension by tides, currents and storms serves to redeposit the sediments further across the continental shelf (Johnson & Carter 1987). Terrestrially derived sediments have been observed across the width of the narrow shelf in the Cairns Section of the Great Barrier Reef (Maxwell 1968; Wolanski *et al* 1986; Johnson & Carter 1987). Thus, on the narrow continental shelf associated with the study area, under extreme conditions, even outer-shelf reefs may be affected by terrestrial influences.

2.3.6 THE DISTRIBUTION OF NUTRIENT RICH WATERS FROM UPWELLING EVENTS

Nutrient upwelling induced by deep ocean currents and the large scale movement of water masses forces nutrient rich waters across the continental shelf (Andrews & Gentien 1982). In some areas of the Great Barrier Reef nutrient input from upwelling events is extensive (Andrews & Gentien 1982). Therefore, in areas where the coastal shelf is narrow, the relative extent of this influence on coral reefs between the outer-shelf and the near-shore zone may be pronounced. This has had an influence on shelf development, especially in the growth of *Halimeda* banks (e.g. Wolanski *et al* 1988).

2.4. CONCLUSIONS

Rainfall in the study area is highly seasonal although heavy downpours may occur during the 'dry' season. Summer monsoons begin around November. Crops planted for economic return are planted to take advantage of precipitation. Thus, when precipitation is greatest the soil has least cover. Within the particular set of climatic, geological, morphological and historical conditions operating in tropical North

Queensland, newly planted fields are exposed to hydrological processes capable of removing considerable quantities of soil.

Finer sediments and sorbed and soluble nutrients are likely to be flushed through the river system and into the marine environment relatively quickly as suspended sediment or solute load during the wet season. Nutrients adsorbed on to heavier material will be considerably slowed.

Variations in base material, bedload, precipitation, agricultural practices, vegetation, anthropogenic inputs, salinity and temperature of the receiving medium, will constantly operate on the sorptive characteristics of the sediments, maintaining the system in a constant state of flux.

Local bathymetry and shallow location of the antecedent platform have encouraged early termination of upward coral growth during the recent Holocene transgression. Therefore, most of the reefs in the Cairns Section of the Great Barrier Reef Lagoon have been at, or near, sea level for a considerable period. The majority of reefs studied are either at, or very near to, maturation, and have subsequently developed extensive reef flats.

Narrowness of the continental shelf in the study area effectively reduces the protective barrier of distance between coastal areas and reefs of the outer-shelf.

The following chapter will pose a number of focussed questions on the nutrient dynamics of the Atherton Tablelands and the coastal strip between Cairns and Mossman. It will also assess the possibility that the nutrient dynamics of the nearby marine environment are closely related to the agricultural practices of the mainland.

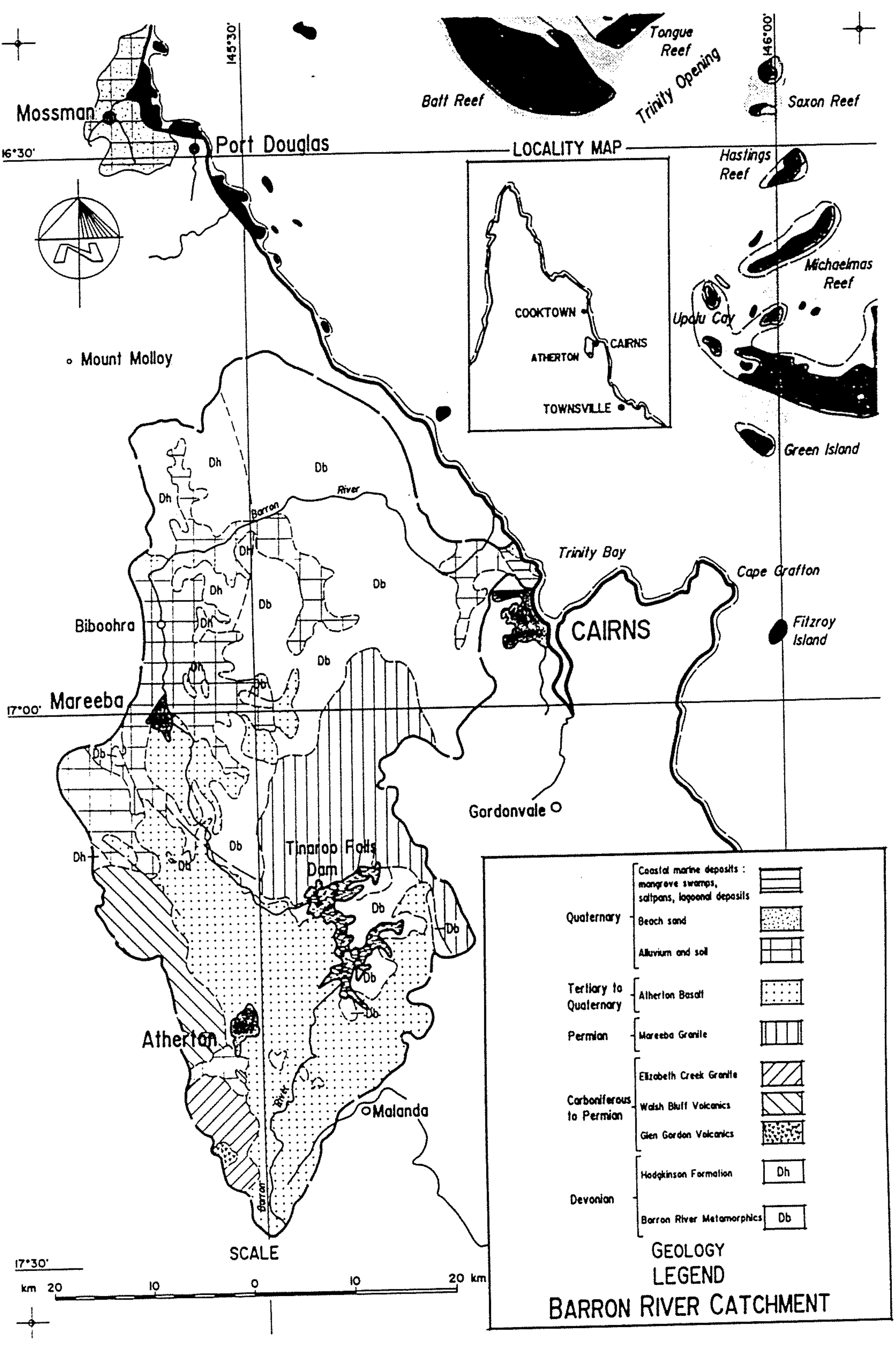

Figure 4: Geology of the study area

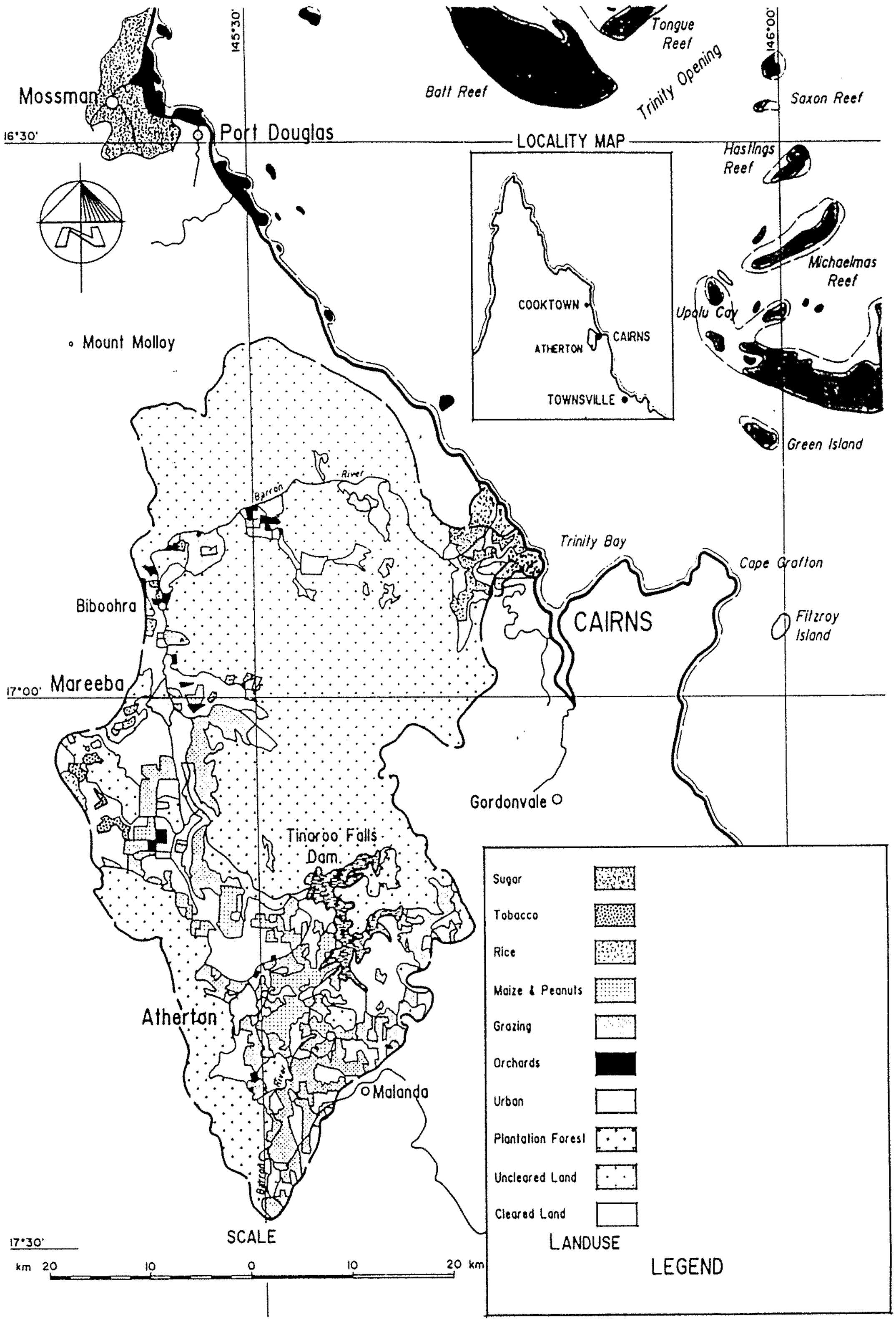

Figure 5: Landuse in the study area (After: Valentine 1988)

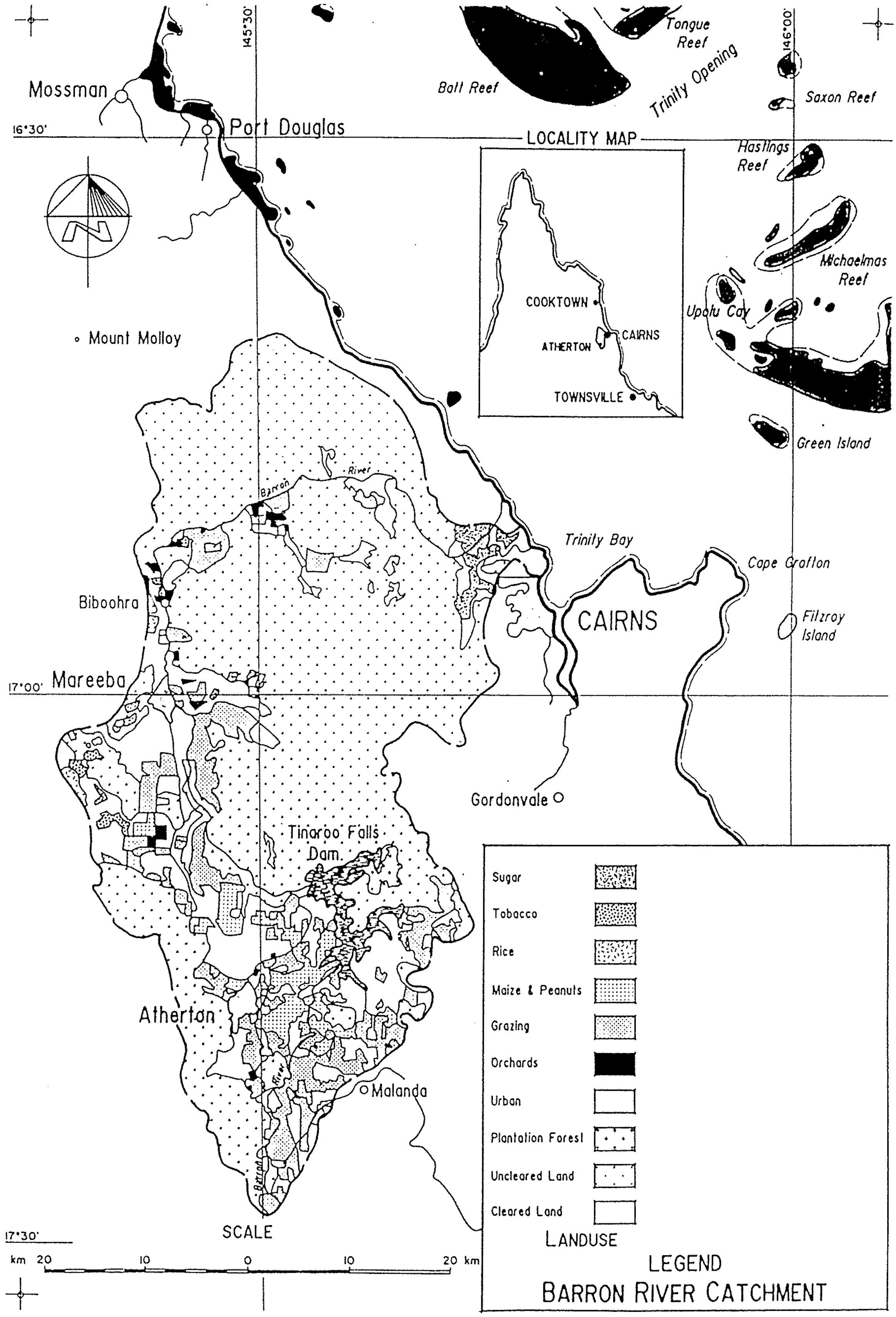

***Figure 6:* Relationship between geology and landuse on the Atherton Tablelands.**

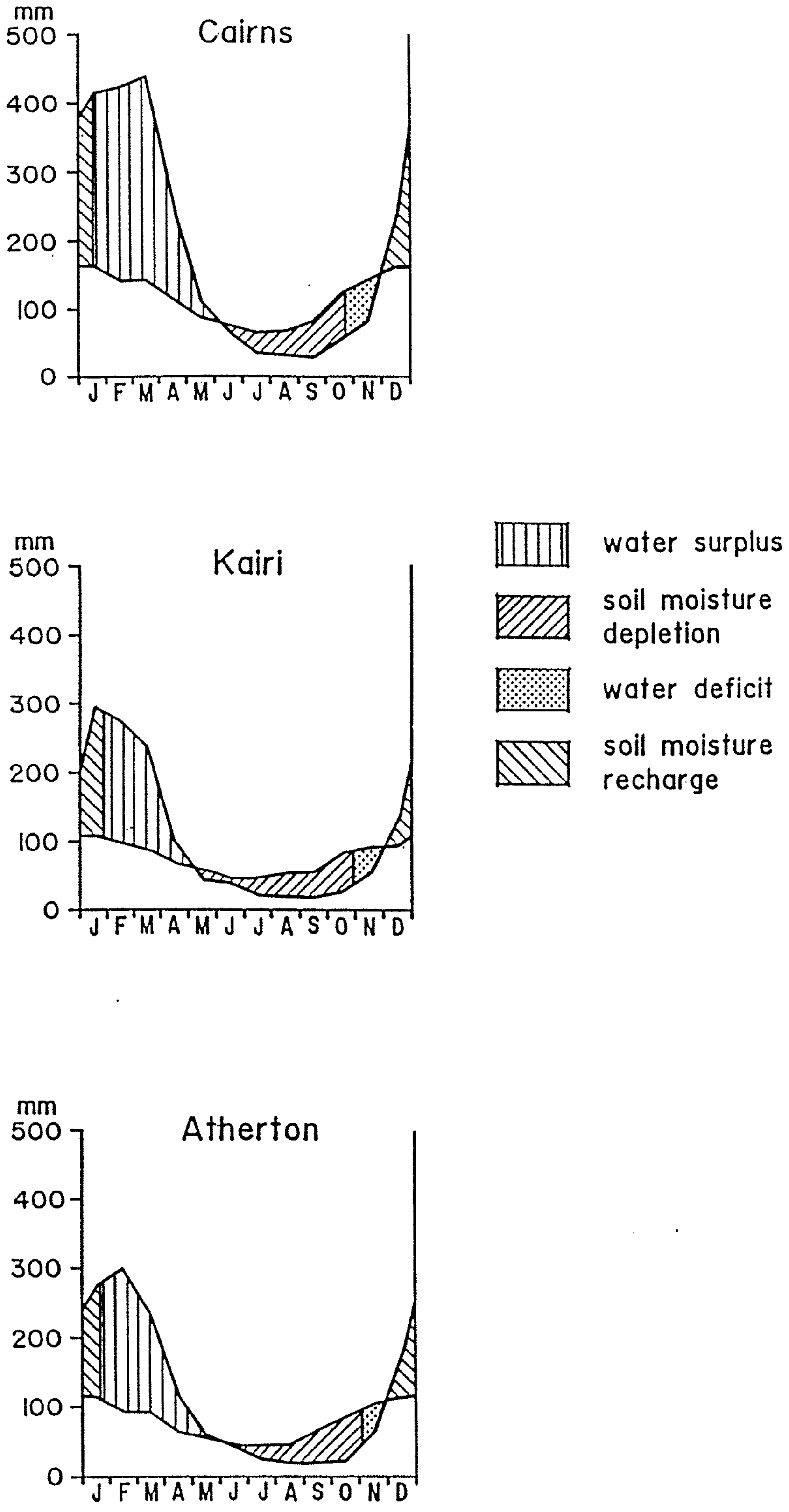

Figure 7: Water balances for selected stations in North East Queensland. (Source: Douglas 1973)

CHAPTER 3

DELIVERY OF NUTRIENTS TO THE GREAT BARRIER REEF - A SERIES OF QUESTIONS

3.1 INTRODUCTION

The potential for nutrient enhancement has been included in much of the debate concerning anthropogenic influence to Australia's Great Barrier Reef (Baldwin 1987; Yellowlees 1990). The major contribution for this enhancement is considered to come from agricultural runoff (e.g. Baldwin *et al* 1987; Brodie 1990).

Unaccountable loss of phosphate from farm soils was strongly contested by agronomists at the 1990 "Workshop on landuse patterns and nutrient loading of the Great Barrier Reef region" (Yellowlees 1990). However, Fish (1969) and Birch (1982) have both reported strong correlations between dissolved phosphate concentration in streams, and the use of fertiliser in adjacent systems. Cosser's (1987) research estimated that around 9,000 tonnes of phosphate was delivered annually into the Great Barrier Reef lagoon, with 20% of that amount transported in solution.

Other researchers have argued that if phosphate and other nutrients were delivered into ocean waters the amount would be minuscule given the size of the receiving medium with any excess quickly used by marine organisms (Furnas 1990; Thomson 1991). While this argument would be true at very large scales, minuscule loading to the ocean as a whole can still translate to locally important additions. Further, it is not yet known what levels of phosphate enhancement the coral organism can tolerate, and some researchers have suggested these levels may be as low 5-10% above ambient (e.g. Connell & Hawker 1987; Bell & Greenfield 1987).

The complexities associated with the removal and transportation of nutrients (e.g. phosphate, ammonia, nitrate, nitrite, silicate) through the fluvial system are many. Yet most of the argument against nutrient enhancement of reef waters has been based on the spasmodic collection of nutrient samples from between-reef marine waters (Furnas, 1990; Thomson 1991). Cosser (1987) argued that delivery of the nutrient phosphate into marine waters via mainland runoff was both episodic and spasmodic. After initial rapid injection, the redistribution of phosphate enriched bottom sediments released the nutrient back into the system over a much longer period (Cosser 1987). Due to the chemical properties, phosphate species (described below) will quickly attach to any suitable receptive particles. Variations in pH or redox potential, either by chemical, biological or physical processes (rainfall, agitation, oxygenation, anaerobic conditions) will potentially remobilise the phosphate into the water column. Spasmodic nutrient sampling under these circumstances could at best describe only the nutrient status of the waters on that particular day. Comparisons of the nutrient status of the waters pre- and post-European influence would be of little value, even if the ambient conditions were known. Therefore, a more effective method of learning the nutrient status of past and present marine waters is necessary.

The ability of massive corals to retain a record of various environmental parameters in their skeleton (e.g. see Knutson *et al* 1972; Druffel 1981, 1982; Schneider & Smith 1982; Isdale 1984; Shen *et al* 1987) suggests these corals may also retain a record of environmental perturbation related to changes in the ambient chemistry, including the nutrient status, of the surrounding water. Previous research suggested that the nutrient most likely to affect the skeleton would be a species of phosphate, either as orthophosphate, $(PO_4)^{3-}$, or a similar species (e.g. Rosenstein 1936; Reitemeier & Buehrer 1950; Simkiss 1964a; Kinsey & Davies 1979). There was little or no literature on either systemic or systematic effects of nitrogen bearing species on crystallisation in aqueous calcium carbonate systems (see Footnote 1, Chapter 1). There was, however, considerable evidence that the addition of phosphate containing species could exert a systematic effect on crystallisation processes (e.g. see Reddy 1977; Reitemeier & Buehrer 1950; Simkiss 1964a). Evidence of the effect of phosphate on calcium carbonate crystallisation processes (Reddy 1977; Reitemeier & Buehrer 1950; Simkiss 1964a) suggested signals from this source could be developed to provide information on the ambient nutrient status of the seawater at the time of deposition. This study, therefore, concentrates on the movement of phosphate through the fluvial system.

Before attempting to interpret any environmental record retained by massive corals, and particularly those that may be related to changes in water quality associated with the use of phosphatic fertilisers, it was first necessary to address several basic questions -

1. is there any connection between land management practices and levels of phosphate in the streams and rivers?

2. could the dissolved phosphate load reach the reefs?
3. Could nutrients be stored and regenerated by near-shore reef flat sediments?

To examine these questions, the study needed to be divided into several components. These are outlined in Section 3.2.

3.2. AIMS AND OBJECTIVES

Previous studies have outlined the movement of dissolved, and adsorbed, phosphate into, and through, the marine environment (e.g. Cosser 1987). However, Douglas (1973) pointed out that the Barron River could discharge 50% of its load in less than 5% of the time. In an area of high intensity rainfall this can translate to the discharge of more than 1.5 million megalitres of water during a single flood event (Australian Bureau of Meteorology, Brisbane). The majority of the phosphate carried by the flood plume is considered to be attached to the sediments (Douglas 1973; Cosser 1987). Recent work, however, has suggested that in some cases a higher proportion of the phosphate load may be in solution (Brodie & Mitchell 1992). Soluble phosphate could conceivably be carried considerably further into marine waters that phosphate attached to sediments. Therefore, when coral reefs are close to a terrestrial environment where high intensity rainfall is combined with heavy use of phosphatic fertilisers, the phosphate in solution may be as important as that attached to the sediments.

Little is known about the tolerance of corals to varying levels of phosphate over different time periods. The most extensive research on the effects of nutrient loading on coral reef ecosystems, that conducted at Kaneohe Bay, did not include the specific effects of individual nutrients on the corals in the bay. The study involved only the long term exposure of the system to elevated levels of nutrients over an extended period (Banner 1974; Smith 1977; Smith *et al* 1981). The work of Kinsey and Domm at One Tree Reef (1974), and reassessed by Kinsey & Davies (1979), also did not differentiate between nutrients. These authors, however, considered the effect on calcification processes was probably caused by the phosphate. Results from both the Kaneohe Bay and the One Tree Reef studies suggests that the influence of nutrients continues after the source of enhancement has been removed, probably through nutrient retention in the sediments (Smith 1977; Kinsey & Davies 1979; Smith *et al* 1981). The possibility that the system and its organisms returns slowly to pre-event conditions, however, cannot be ruled out. In tropical North Queensland, three to four pulses of freshwater input into the marine environment are possible in one wet season (e.g. 1989, Bureau of Meteorology data). If the influence is retentive, or the effect is residual, it is unlikely the system will return to ambient before exposure to an additional pulse. Hence, the effects of short, sharp bursts of elevated levels of nutrients may be significant, but quite insidious and be missed by random sampling. It was considered necessary, therefore, to understand the use of phosphatic fertiliser, and the transfer of phosphate into the fluvial system, in the study area.

For the reasons outlined previously, this study focuses on phosphate. To gain understanding of the phosphate dynamics of the study area, this component of the study was designed to address a series of very specific questions. These questions will examine whether anthropogenically derived phosphate could reach reefs of the Great Barrier Reef Province. The questions asked were those that focussed, short-term studies could elucidate. Four case studies examined the question of soluble phosphate movement through the system

(1) T***he soluble phosphate response of the river to fertiliser application in the catchment*** **-** (i.e. does the application of fertiliser lead to enhanced levels of dissolved inorganic phosphate in the river system?),

(2) T***he soluble phosphate flux of the fluvial system*** **-** (i.e. is the dissolved inorganic phosphate flux in the fluvial system sufficient to influence the nutrient status of shelf waters?),

(3) T***he soluble phosphate concentration of shelf waters*** **-** (i.e. is there a seasonal response in shelf waters that could be related to terrestrial influences?).

(4) T***he potential for reef flat sediments to store and release phosphate*** **-** (i.e. could reef flat sediments act as large phosphate reservoirs, releasing phosphate to the overlying water column when stimulated by suitable environmental conditions?)

Monitoring the terrestrial and marine system over two full years provided information on phosphate seasonality and mobility. This monitoring also included a short, two week period of intense sampling of the Barron River at the beginning of the 1987 wet season. This was done to estimate the response of the fluvial system to initial storm rains after the soils had been subjected to a lengthy dry period. A short-term monitoring programme of reef flat waters (hourly over one tidal cycle), with simulated experimental studies of the sorptivity of the sediments was also conducted to gain some understanding of the phosphate dynamics of near-shore reef flat sediments. Data from these programmes were then compared with climatic data to estimate seasonality, and potential dispersal patterns, of the soluble phosphate load through the marine system.

3.3 THE USE AND BEHAVIOUR OF PHOSPHATE IN NORTH QUEENSLAND

The processes governing levels of dissolved phosphate in natural waters are not clear (e.g. see Fox 1989). A considerable body of evidence shows that phosphate is relatively immobile in some soils (e.g. see Hunter 1991). Other research suggests that under certain conditions considerable quantities can be made available to the fluvial system (e.g. Fish 1969; Cullen *et al* 1978; Yariv & Cross 1979).

Besides the discrete and relatively inert phosphate minerals (e.g. apatite and monazite and xenotime), available phosphate is chemically associated principally with iron and aluminium hydroxides in sediments (e.g. see Kuo & Lotse 1974; Ku *et al* 1978). Uptake by soils (e.g. see Barrow & Shaw 1975; Rajan & Fox 1975; Munns & Fox 1976; Barrow 1983) and by iron minerals (e.g. Crosby *et al* 1983,1984) is well documented and is characterised by adsorption isotherms (Fox 1989). However, interactions with the metal hydroxide portion of suspended particulates can have a significant influence on the concentration of dissolved phosphate in watersheds with large suspended loads. Suspended sediments have been shown to directly influence concentrations of dissolved phosphorus (Fox 1989). Stumm & Morgan (1981) have shown that the pH of water has considerable influence on phosphate solubility, complex formation and sorption processes. Metal oxide surfaces can react with phosphate to form discrete iron phosphate phases if the reaction time is long, or if temperatures or phosphate levels are elevated (Haseman *et al* 1950; Bache 1963). Solid-solution formation on amorphous surfaces of ferric hydroxide suspensions, specifically amorphous ferric phosphate dissolved in ferric hydroxide, is a major process governing concentrations of dissolved phosphate in many river systems (Fox 1989).

The adsorptive behaviour of nutrients (including phosphate) in tropical soils is poorly documented because most of the research on soil mineral sorptivity has been conducted on soils from temperate regions. It is known that the sorptive capacity of sediments for phosphate varies under different regimes, a variation exacerbated by distinctive weather and climatic conditions (e.g. Mackay 1980; Gill 1989). In North Queensland the time scale of climatic variability familiar to temperate areas may be reduced from years or months to days or even hours. Precipitation can be sudden and intense, and followed by extreme temperatures. Soil profiles can wet and dry several times during a single day. The weathering pattern in rock breakdown (even for rocks originally chemically similar) is different in tropical regions than temperate regions. This is due to the high intensity and distribution of the rainfall, and the high, year-round temperatures. The weathering tendency in temperate regimes is towards kaolinite and smectite with relatively limited formation of mixed layer clays and oxyhydroxides of Fe and Al. In wet tropical regions the tendency is towards total breakdown, primarily to oxyhydroxides of Fe and Al. In seasonal monsoonal tropics (North Queensland), the tendency is towards soils containing varying amounts of smectite, kaolinite and hydrated kaolinite (halloysite), illite and abundant mixed layer clays (illite/smectite and kaolinite/smectite), and oxyhydroxides of Fe and Al. The relative proportions of these are dependent upon a variety of factors, including rainfall intensity and distribution, initial rock component, soil permeability and porosity, topography, vegetation, etc. (Mackinnon & Cuff 1992).

Most of the agricultural areas in tropical wet North Queensland exist on soils formed under rainforest or wet sclerophyll conditions. Once cleared, these soils are quickly depleted of their nutrient-rich surface layer. Within two to three years large quantities of replacement nutrients are required to promote the development of agricultural crops. Many soils in the Cairns/Mossman region and adjacent hinterlands now require large amounts of phosphatic fertiliser to maintain viable production (Loader 1987; Moody & Chapman 1990).

Fertilisation practices in North Queensland also follow traditional, established trends (Loader 1987). On some basaltic soils of the Atherton Tablelands, acid extractable phosphate levels are considered sufficient to sustain peanut yields adequately, without additional applications. Yet superphosphate is applied by around 70% of the area's peanut farmers at the rate of nearly 400 kg ha^{-1}, despite a lack of supporting evidence that such practices are necessary (Loader 1987).

Sorptive variabilities in soil profiles have been associated with the continued use of fertiliser (e.g. Fox and Searle 1978; Toreu *et al* 1988; Barrow 1989). In North Queensland many cultivated soils sorb less phosphate than their undisturbed counterparts (Toreu *et al* 1988). Toreu suggests this is linked to previous applications of large amounts of phosphatic fertiliser. Chapman *et al* (1981) attributed high phosphate levels in the top 25 cm of cultivated soils in the Cairns-Mossman cane growing area to the repeated application of phosphatic fertilisers.

In an undisturbed system, phosphate is usually relatively immobile within the soil profile. In North Queensland superphosphate is either broadcast on to fields and pastures, or added to the soil profile at the time of planting. Planting and fertilisation are done to take advantage of the onset of the wet season. In the Cairns/Mossman region and adjacent hinterland, this is sudden, intense, and follows periods of extreme dry (Chapter 2). Erosion of the heavily cultivated soils of North Queensland is a major problem (Kneipp and Bolt 1971; Douglas 1973; Gilmour *et al* 1982; Prove 1987). The amount of phosphate available for removal (either in solution or attached to particulates) will be dependent on the amount present in the system, and the availability of suitable agents of removal (e.g. changes in soil pH, redox potential, Fe mobility and availability, as induced by rainfall and the application of non-phosphatic fertilisers). Changes in redox potential and pH, either from biological, chemical or physical processes, are inevitable as freshwater runoff moves from the land to the sea via the estuarine environment.

3.4. RESULTS AND DISCUSSION - ADDRESSING A SERIES OF QUESTIONS

3.4.1 Question 1: Does the application of fertiliser lead to enhanced levels of soluble phosphate in the river system?

3.4.1.a General:

The approach adopted for this part of the study was to monitor the daily nutrient status of one section of the Barron River in an area of known agricultural use. A section of the river on the Atherton Tablelands near Yungaburra was chosen where superphosphate was broadcast directly on to the fields in anticipation of the wet season (Interviews with Loader, Queensland Department of Primary Industries, 1987). Other studies (e.g. Fish 1969) had shown that in similar areas, stream phosphate levels increased as a response to storm rains. Sampling was programmed to begin at the first suggestion of storm activity on the Atherton Tablelands. Water samples were taken daily from the 3rd to the 19th November 1987. Rainfall and stream discharge data were obtained from the Australian Bureau of Meteorology (Brisbane) and Queensland Water Resources Commission respectively (Appendix A).

3.4.1.b Results:

The results are shown in Appendix B. Soluble phosphate concentration increased with the first storm rains (Figure 8). The relationship deteriorated rapidly as the rains continued and stream discharge increased (Figure 8). This is further displayed in Figure 9 where the regression coefficient drops from $r^2=0.976$ calculated to the period of the initial storm, to $r^2=0.549$ during the second rain period.

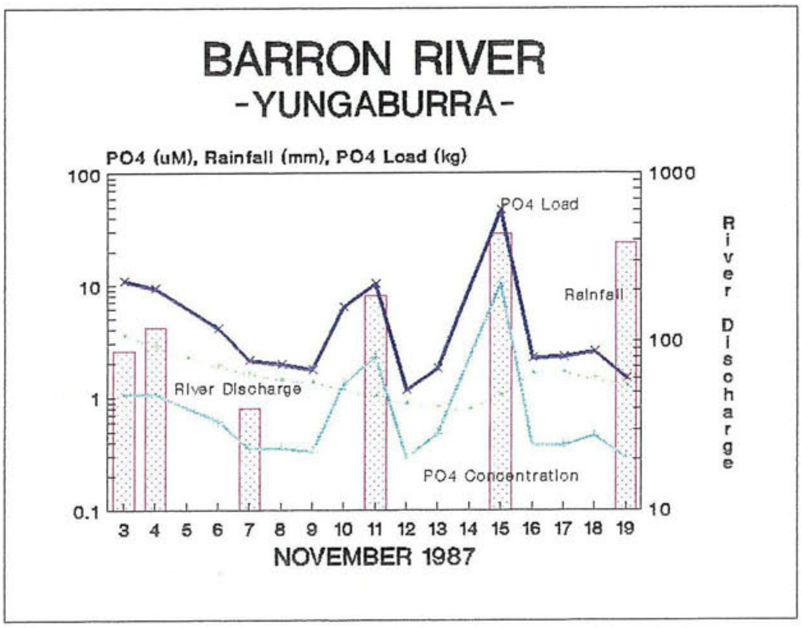

Figure 8: Phosphate values in the Barron River near Yungaburra following the first rains of the season.

3.4.1.c Discussion:

The rapid increase in stream phosphate concentration following the first rains of any significance obviously cannot be attributed solely to the rainfall itself, so other avenues must be considered. Several factors could contribute to the increased stream phosphate levels following rainfall -

(a) high microbial action in the upper soil horizon following a long period of hot, dry weather,

(b) leaching from animal faeces in the immediate area,

(c) naturally occurring phosphate from the basaltic soils (Stephenson 1989),

(d) groundwater seepage,

(e) nutrient enriched runoff.

No attempt was made to partition the various contributions. However, the area next to the Atherton Tablelands sampling site supports extensive crops of maize, potatoes and peanuts. Phosphatic fertiliser is broadcast on to the fields at the rate of around 370 kg ha^{-1} (Loader 1987) before the wet season. Therefore, a rapid increase in stream phosphate concentration at the onset of rainfall, followed by an equally rapid decrease as rainfall continued, or as new water moved into the area from upstream locations, is the most likely possibility. This agrees with studies in New Zealand where dramatic increases in stream phosphate transport (from 0.09 g hr^{-1} to over 800 g hr^{-1}) coincided with superphosphate application and sudden, intense rainfall in the catchments (Fish 1969).

The decrease in phosphate concentration as rainfall continued is probably the result of dilution, although removal of available phosphate from the soil by flushing is also possible. Mitchell *et al* (1990) reported similar reductions in phosphate concentration in the Herbert River system as rainfall increased. These authors attributed the reduced concentrations to a dilution effect.

North Queensland rainfall characteristics are such that storms are localised, with sudden, intense downpours often restricted to areas measuring little more than a few square kilometres. If the major source of soluble phosphate is from fertiliser application, then stream nutrient concentration at a particular site could be expected to respond rapidly to the input of nutrients from the immediate area. This would be followed by an equally rapid decline in concentration as either -

(a) rainfall ceased and water moved into the area from upstream locations, or

(b) available phosphate was flushed from the system.

Clearly, at this location stream nutrient status is a direct response to precipitation, irrespective of the source of enhancement. Historical data, and the results of other research, however, make it probable that current fertilisation practices make the single most significant contribution to phosphate enhancement of the Upper Barron River.

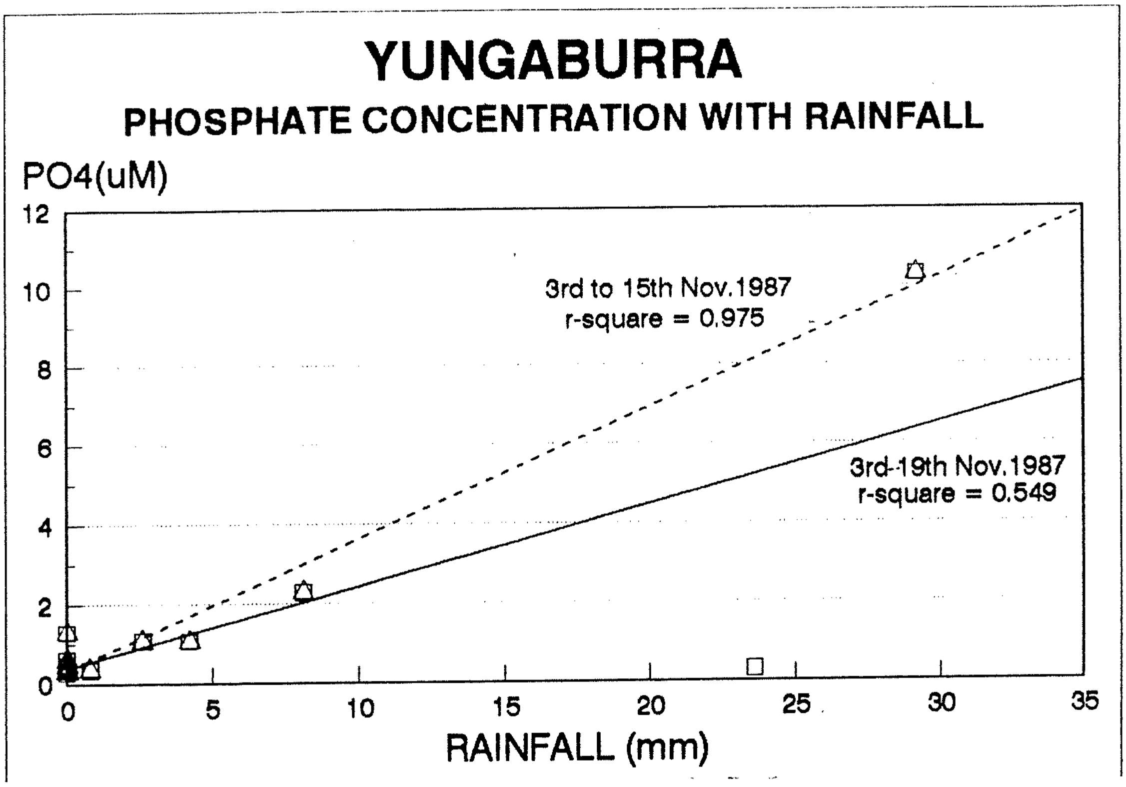

Figure 9: Regressions of stream PO_4^{3-} concentration over rainfall for the short-term dynamic study in the Barron River near Yungaburra, (a) to the first storm rains of the season, and (b) to the second rain period.

3.4.2 *Question 2: Is the soluble phosphate flux in the fluvial system sufficient to influence the nutrient status of shelf waters?*

3.4.2.a General:

The data presented in the short-term dynamic study suggested (Appendix B; Figures 8 & 9) that in localised areas where excess phosphate was available for removal, stream soluble phosphate concentration responded rapidly to precipitation. This response diminished quickly as rainfall continued, probably because of flushing and/or dilution. From the work of Douglas (1973), Gilmour (1981) and the present study, it is proposed that the phosphate concentration of the fluvial system, at any sampling location, will be dependent upon many factors including -

(a) proximity of the date of sampling to a rainfall event,

(b) proximity of the sampling site to the location of a rainfall event,

(c) duration and intensity of precipitation,

(d) the interval between rainfall events,

(e) the height of the groundwater table at the time of precipitation,

(f) runoff and penetration of the water into the soil profile,

(g) soil moisture content before rainfall,

(h) the proportion of groundwater phosphate seeping into the river system, or

(i) the proportion of groundwater phosphate added to the system by irrigation.

Several other issues also need to be considered before trying to extrapolate interpretations to the long-term dynamics of the area.

(1) If stream nutrient enhancement varies with local fertilisation practices, then moderate, persistent, rainfall over the same area of the catchment should slowly flush the system and reduce the amount of phosphate available for later removal.

(2) In areas of high natural phosphate, or in areas with a long history of fertilisation, soil erosion and the scouring and undermining of river banks may add large amounts of particulate adsorbed phosphate to the fluvial system during periods of heavy rain (Chapman *et al* 1981; Toreu *et al* 1988).

(3) Chemical and physical factors (e.g. changing chemistry, pH, sediment type and composition, salinity, agitation) could release/adsorb phosphate from/to host sediments at any point along the river system.

(4) Time is required for phosphate to accumulate in the catchment. Therefore, the interval between successive rainfall events is relevant to both the timing and the amount of phosphate available for delivery to the fluvial system.

(5) In the short-term study, precipitation and stream phosphate concentration were both presumed to represent daily average readings. In the long-term study precipitation data represents averaged monthly readings from the first to the last day of a calendar month.

(6) Samples for nutrient analysis were collected at the beginning of each month and presumed to represent stream nutrient status for a particular month. Rainfall data were averaged for the whole of a particular month. Therefore, proximity of the major rainfall event to the date of sampling will cloud any correlations.

(7) Up-river history will influence the data at down-stream locations.

Statistical correlations between stream phosphate concentration and rainfall data over an extended period will be obscured by the preceding factors. Nevertheless, if nutrient status of the fluvial system is driven by a combination of precipitation, soil types, and agricultural practices, some evidence of these effects should be visible by simple "Time Series Analysis". This should indicate whether the nutrient flux of the system is seasonal and in response to agricultural practices in the area.

A conceptual model of some variables controlling soluble phosphate flux in the Barron/Mossman River systems is shown in Figure 10. Phosphate flux is the result of the interplay between primary input (e.g. rock weathering, groundwater, sewage, fertiliser) and secondary activity (e.g. dilution; adsorption/desorption by river sediments; natural and man-made obstructions; turbidity; vegetation; organisms). The most important generating force responsible for the delivery of land-derived phosphate to the river (both in solution and adsorbed on to sediments) is rainfall. Concentration at any point in the river is controlled by the strength and interaction of the separate forces and influences at any particular time. Therefore, the amount of phosphate available for delivery into the marine environment will be the product of the balance between the varying forces, and the quantity of water moving through the system. The distance the load can be carried through the marine system is dependent on the force of the flow, itself dependent on quantity, intensity and duration of the rainfall, and on the size distribution of the sediments.

The approach adopted for the study of stream nutrient availability was to monitor the nutrient status of the system at several sites along the rivers. These results were compared with rainfall and discharge data from relevant locations. Sampling sites were decided by (a) accessibility throughout the year (some areas of the catchment are inaccessible during the wet), and (b) continuity of flow (some streams stop flowing for months during the dry season). Twelve sampling sites were initially established in the Barron River catchment. Additional sites were added as access was granted by land-owners. By mid-1987 nineteen sites had been established within the two catchment areas (Figure 3, p.8) and sampling was carried out monthly (except during periods of major flooding) until April 1989. Samples were analysed at the Australian Institute of Marine Science. Samples for August and September 1987 were lost by the analytical laboratory.

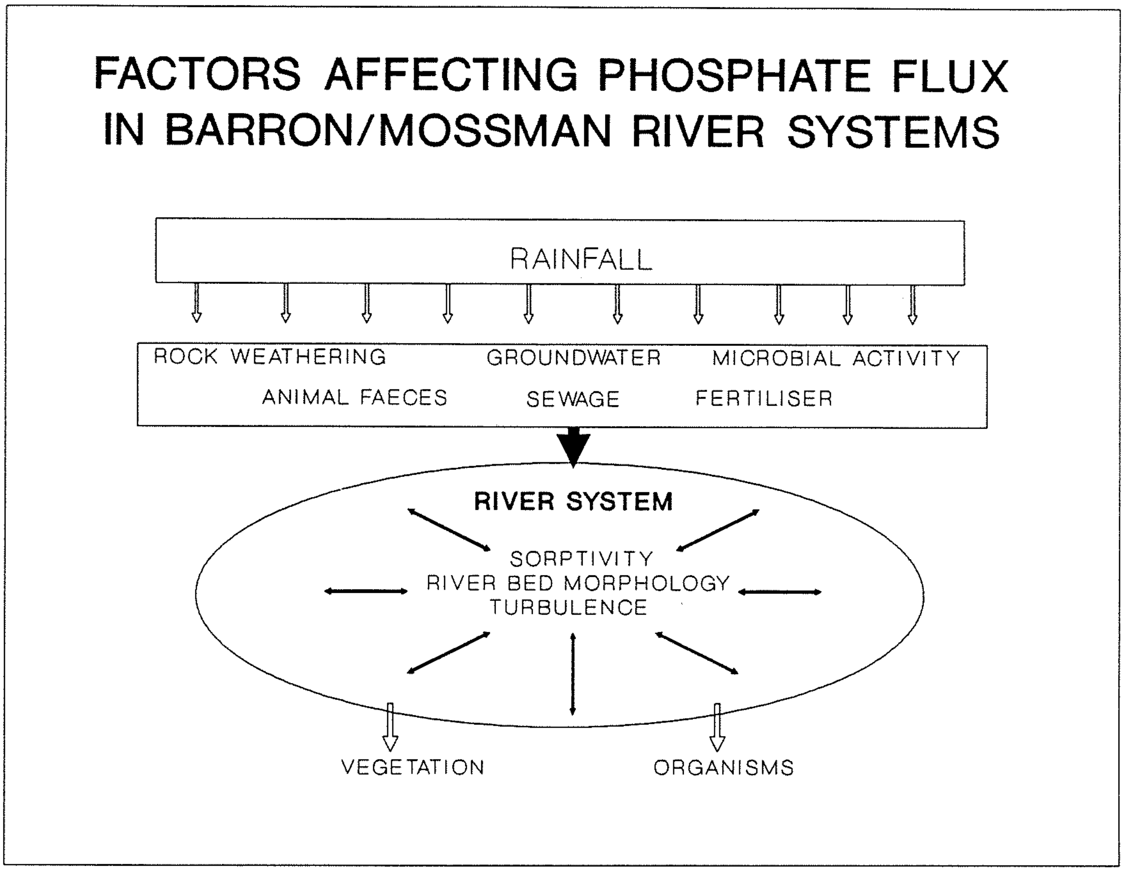

Figure 10: A conceptual model of some forces that affect stream phosphate flux in the Barron/Mossman River systems.

3.4.2.b Results:

General:

Results from the nutrient sampling programme are shown in Appendix D.

For interpretative purposes the sampling sites have been grouped according to agricultural practices (Table 3.1). The different agricultural practices are closely associated with the geology (Figure 6), climate and geography of the area (Chapter 2).

Table 3.1: Breakdown of the Barron\Mossman River catchments into areas of similar land management practices.

AREA	SAMPLING SITE	LANDUSE	CLIMATE	SOURCE OF WATER SUPPLY
AREA A SOUTHERN TABLELANDS	(1) MALANDA (2) YUNGABURRA	MAIZE, PEANUTS, POTATOES DAIRYING, CATTLE	- SOME FROSTS - SEASONAL RAINFALL - HEAVY IN SUMMER	- RAINFALL. - SOME IRRIGATION DURING WINTER
AREA B LAKE TINAROO	(3) LAKE TINAROO	BASE OF LAKE TINAROO OVERFLOW. SOME CATTLE. STATE FOREST.	- SOME FROSTS - SEASONAL RAINFALL - HEAVY IN SUMMER	- RAINFALL.
AREA C MID TABLELANDS	(5) EMERALD CREEK, (6) EDMUND KENNEDY BRIDGE, (7) GRANITE CREEK.	ORCHARDS, SMALL CROPS, PEANUTS CATTLE	- COOL WINTERS - HOT SUMMERS - REDUCED SUMMER RAINFALL.	- RAINFALL. - IRRIGATION.
AREA D NORTHERN TABLELANDS	(8) BIBOOHRA (9) BILWON	ORCHARDS, CATTLE,	- COOL WINTERS - HOT SUMMERS - REDUCED SUMMER RAINFALL	- IRRIGATION
AREA E EASTERN TABLELANDS	(10) DAVIES CREEK. (11) CLOHESY RIVER. (12) KOAH	SMALL CROPS, SOME ORCHARDS, CATTLE	- COOL WINTERS - HOT SUMMER - HEAVY RAINFALL ON RANGES. - DRY ON TABLELANDS - MOST RAINFALL IN SUMMER	- RAINFALL. - IRRIGATION.
AREA F COASTAL RANGES	(13) MYOLA (KURANDA)	SMALL CROPS. URBAN.	- COOL WINTERS - MODERATE, HUMID SUMMERS - HEAVY SUMMER RAINFALL	- RAINFALL
AREA G COASTAL STRIP - CAIRNS AREA	(14) FRESHWATER CREEK (15) LAKE PLACID (16) THOMATIS CREEK	SUGARCANE, URBAN	- MILD WINTERS - HOT, HUMID SUMMERS - HEAVY SUMMER RAINFALL	- RAINFALL
AREA H COASTAL STRIP - MOSSMAN AREA	(17) STH MOSSMAN RIVER (18) COOYAH BEACH (19) NEWELL PT	SUGARCANE URBAN	- MILD WINTERS - HOT, HUMID SUMMERS - HEAVY SUMMER RAINFALL	- RAINFALL

Reliance on statistical analysis for the interpretation of this form of data is both restrictive and deceptive. Presently available statistical packages are unable to incorporate the many factors outlined above (Coomans, Mathematics Department, James Cook University of North Queensland, pers.com). Adherence to such methods would provide untrue, or at best inadequate, interpretation of the interplay between environmental factors. Therefore, while statistical analysis has been explored (Appendix G), interpretation for this discussion will rely upon graphic presentation. Assessment includes only areas where stream discharge data was applicable to, reliable, or provided a reasonable indication of, the relative area. Rainfall and stream discharge data from the Mossman area were unreliable and South Mossman, Cooyah Beach and Newell Point were excluded from this examination. Data presented in the graphs cover the period October 1987 to April 1989. Changes in the scale of the Y axis have been made to adapt to the magnitude of the variables at different sites.

Soluble phosphate concentration (Figure 11 and Appendix D):

No significant correlations were found between stream phosphate concentration and rainfall at the relevant locations in the Barron/Mossman River Catchments (Appendix G). Figure 11, however, shows the strong seasonal association between PO_4^{3-}concentration, soluble phosphate load (the product of concentration and discharge), rainfall, and stream discharge rates at the appropriate locations. Soluble phosphate concentrations at all locations were extremely variable throughout the sampling period. Highest concentrations occurred during the summer rainy season. Except in the drier western catchment (Biboohra, Bilwon area), secondary enhancement also occurred around August/September, coinciding with minor rainfall. Winter enhancement is highest in the coastal area (Lake Placid, Freshwater Creek, Thomatis Creek).

Soluble phosphate load (Figure 11):

The soluble phosphate load mimics the soluble phosphate concentration at all sites except Tinaroo. Tinaroo Dam (and the associated Lake Tinaroo) effectively restricted the amount of phosphate transported through the system when lake waters were low. At all sites the soluble phosphate load increased significantly during the April 1989 flood.

Rainfall, discharge and phosphate load:

During the 1988/89 climatic year, 49% of the rain fell during March/April with 69% of the total discharge occurring during the same period. Five days in April 1989 accounted for over 50% of the total river discharge (Appendix C). In the March/April 1988/89 period

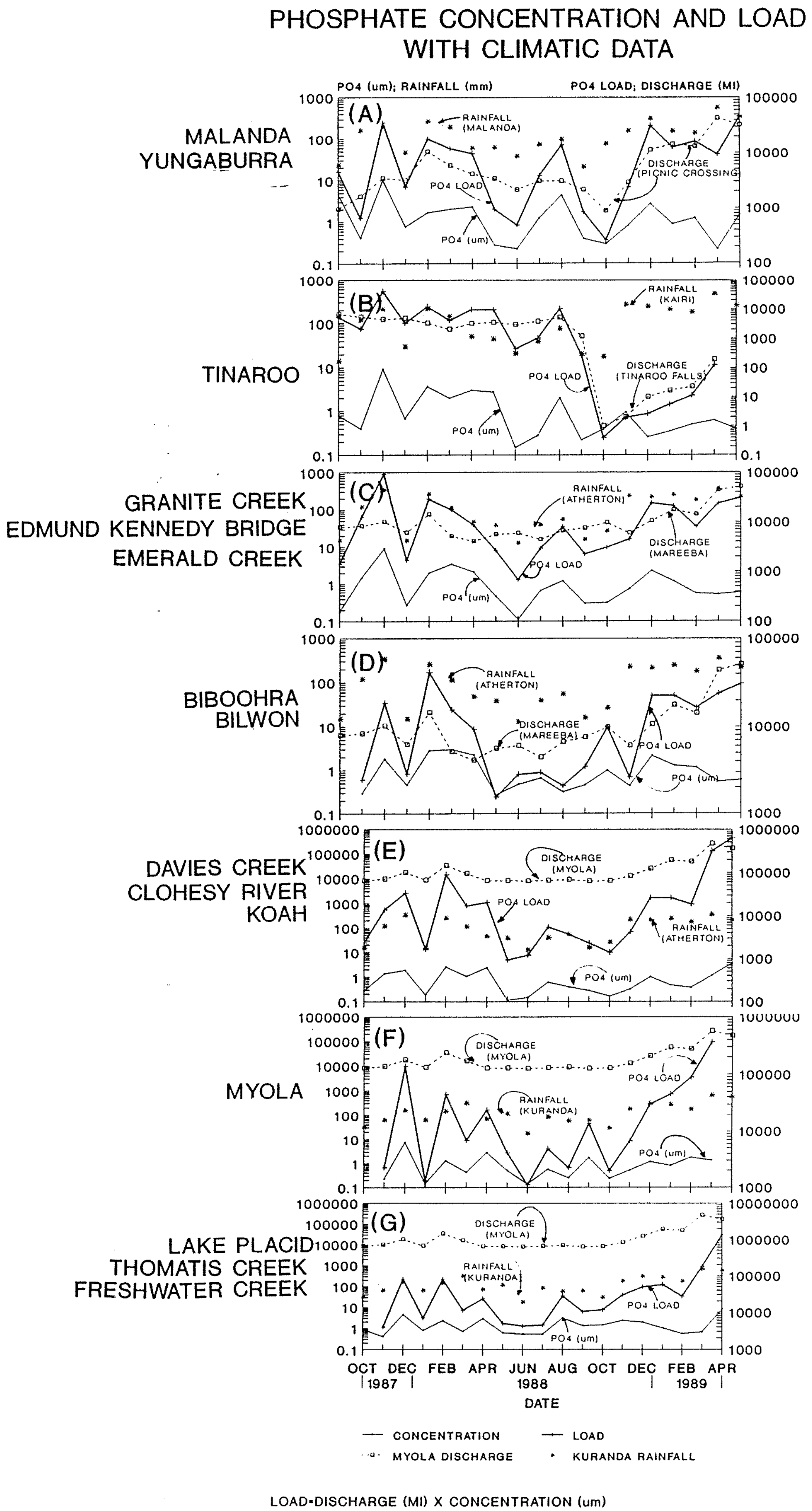

Figure 11: Soluble phosphate concentration and total phosphate load with climatic data. Sampling sites are grouped and the data averaged according to the land management practices of the area. Changes in the scale of the Y axis have been made to adapt to increases in the magnitude of the variables at different sites.

87% of the annual soluble phosphate load was transported across the coastal plain (measured at Lake Placid, the first sampling site after the Myola Stream Discharge Station). 77% of this load was carried during the April flood. The dissolved load transported through Lake Placid in April 1989 was equal to an estimated 57 tonnes of phosphate.

3.4.2.c Discussion:

Douglas (1973) and Cosser (1987) estimated that less than one fifth of the total phosphate load is transported in solution with the greater proportion carried attached to sediments. Using this estimate of a 5:1 ratio of adsorbed to soluble phosphate, the total phosphate load moving through the Lake Placid sampling site for the month of April 1989 was approximately 285 tonnes. The dissolved portion of superphosphate fertiliser is approximately 10% (Chapter 4, Table 4.1). The remaining 90% is unidentified supporting medium. If all figures remained constant during April 1989, and the total amount of soluble phosphate was released from the fertiliser, the equivalent of approximately 2,850 tonnes of superphosphate would have been moved through Lake Placid during April 1989. This estimate is substantially higher than the industry estimated usage (1,810 tonnes) for the total sugarcane district of the Far Northern Statistical Division during 1988 (Pulsford 1990). Cosser (1987) estimated a total phosphate load of about 9000 tonnes was delivered annually to the Great Barrier Reef lagoon from the far North Queensland region. This figure is also considerably higher than the industry estimated usage. Considerable confusion is caused by the inconsistent use of elemental phosphorus and product weight (e.g. 10kg of superphosphate contains <1kg of elemental phosphorus) which could explain why fertiliser usage quoted by farmers and suppliers (Valentine 1988; Pulsford 1990) is considerably higher than industrial estimates. Apart from the obvious confusion caused by the indiscriminate use of the term 'phosphate', there are several possible explanations for the discrepancies -

(1) alienation of residual phosphatic fertiliser from the soil profile (Fox & Searle 1978; Toreu *et al* 1988; Barrow 1989),

(2) remobilisation of adsorbed phosphate from river sediments (Cosser 1987),

(3) floodwater intrusion into unknown sources,

(4) the addition of naturally occurring phosphate from the soil profile,

(5) changes in the degree of partitioning between particulate phosphate and soluble phosphate during periods of peak flow.

The latter suggestion agrees with Brodie & Mitchell's (1992) results. During the period of the 1991 Fitzroy River floods, particulate P measured in the water column around the Keppel Group was almost negligible. Dissolved PO_4^{3-} reached values of 1.8 μM 50 km from the mouth of the flooding Fitzroy River. The results suggested that during periods of peak flood phosphate was released from the host sediments. In this situation, the solution load may represent most of the total phosphate load being transported by the flood plume into the sea. If this is the case, the dispersal of phosphate from the river into the marine environment may need to be reconsidered. For example, if high levels of dissolved phosphate are delivered into the oceans under conditions of accelerated discharge, then the area of localised influence will be extended outwards to the limit of the plume. Reduction of phosphate concentration by mixing and the processes of dilution will take longer. Terrestrially derived phosphate, carried by the plume, will be moved further into the marine environment than would be otherwise anticipated.

In terrestrial soils phosphate adsorption is increased by the presence of clays and oxyhydroxides (Stumm & Morgan 1981). These fine clays are readily removed from the soil profile and transported through the river system (Douglas 1973). Tropical rainforest soils cleared for agriculture are particularly susceptible to erosion (Douglas 1973). These phosphate enriched fine sediments are rapidly transported into the marine system by river discharge. Thus, the probability of a coral reef coming into contact with terrestrially derived phosphate is limited only by the force, direction, duration and phosphate content of a river plume. While most of the dissolved phosphate fraction will be quickly and easily dispersed in the larger basin context, some of the load will be adsorbed by the reef sediments. Purely chemical considerations suggest that carbonate sediments alone should strongly adsorb phosphate (DeKanel and Morse 1978). The combined presence of carbonate sediments, terrigenous material (particularly the fine clays), increased concentrations of soluble phosphate, and a substrate adequately suited to sediment retention, may significantly influence the amount of phosphate able to be held by the reef and its sediments.

3.4.3 Question 3: Is there a seasonal response in shelf waters that could be related to terrestrial influences?

3.4.3.a General:

Several generating forces introduce nutrients to the waters of the Great Barrier Reef, including mainland runoff (Walker & O'Donnell 1981; Revelante & Gilmartin 1982; Sammarco & Crenshaw 1984; Cosser 1987; Gagan *et al* 1987), and deep ocean upwellings (Andrews & Gentien 1982; Crossland & Barnes 1983). Planetary wave perturbations in the East Australian Current produce a 90 day oscillatory intensification that pumps nutrients to the shelf break from a bottom Ekman layer (Andrews & Gentien 1982). Oscillatory longshore currents and steady onshore winds then move the nutrients inshore and advect them poleward through the outer reef zone (Andrews & Gentien 1982).

Nutrient input from mainland runoff is variable, both spatially and temporally. Quantity and eventual distribution of mainland derived nutrients is dependent on nutrient availability, and the force and direction of the transporting medium. Ability to reach the reef is controlled by the discharge potential of the flood plume, the strength and direction of winds and currents, and the distance to the reef. In the Cairns section of the Great Barrier Reef, the reef tract occupies the entire, narrow, continental shelf (Figure 1), a distance of less than 50 km. Evidence that reefs are influenced by fluvial runoff includes the incorporation of terrestrial fulvic acids into the skeletons of massive corals (Isdale 1984; Boto & Isdale 1985), terrigenous sediments trapped in coral skeletons approximately 20 km offshore (Davies & Hughes 1983), and the direct observation of river flood plumes (Wolanski & Jones 1981; Wolanski and van Senden 1983).

Three approaches to the study of phosphate dynamics in the Great Barrier Reef lagoon were adopted -

(a) ***Nutrient sampling of the Great Barrier Reef lagoon in areas adjacent to the mouths of the Barron and Mossman Rivers.*** Results from the marine and terrestrial monitoring programme were divided into a wet/dry seasonal component. Wet season was decided by the distribution of rainfall on the nearby mainland (Appendix C). Concentrations for the different periods were ranked and assigned values of "1" to "5". For example, in the marine section, "1" = $<0.2\ \mu M\ PO_4^{3-}$ (presumed ambient), "2" = 0.2-$0.4\ \mu M\ PO_4^{3-}$, and so on to "5" = $>0.8\ \mu M\ PO_4^{3-}$. All values are presumed representative of surface waters (-0.50 m) in waters -5-10 m deep, on the leeward side of the reef.

(b) ***Nutrient profiles across the two environments (terrestrial and marine).*** Values were plotted from sites along the Barron River and its tributaries and profiles produced to examine possible relationships between the two systems. Sites from the Mossman section were added to the seaward end of the profile to complete the terrestrial representation. Inshore marine sites were plotted closest to coastal sites and other sites after these according to distance from the coast. Profiles covered the periods when adequate marine data were available.

(c) ***The phosphate dynamics and characteristics of reef flat sediments.*** These were examined to assess their potential to supply nutrients to overlying waters. This approach is discussed in section 3.4.4.

3.4.3.b Results:

Sampling locations are shown in Appendix A. Results from all sites sampled are shown in Appendix E.

Marine phosphate concentration within the study area was extremely variable, both spatially and temporally. Occasional extreme values (up to 6.1 μM PO_4^{3-}, Moore Reef, April 1988) were recorded (Appendix E). Very high values (4.0 μM PO_4^{3-}) were recorded at Low Isles in early September 1988. Average marine phosphate levels were 0.37 μM PO_4^{3-}, after removal of all extreme values over 1.0 μM.

Table 3.2: Pearson's Product Moment correlations for stream phosphate concentration at the South Mossman River and Newell Point sampling sites, and phosphate concentration at Low Isles (after removal of the outlier). All terrestrial samples were taken early in the month (within the first three days). Low Isles samples were taken (a) early in the month, and (b) mid-month.

SAMPLING SITE	*(a) LOW ISLES (Sample taken early in the month)*	*(b) LOW ISLES (Sample taken mid-month)*
SOUTH MOSSMAN (Sample taken early in the month)	*r = 0.7779 ** *(n = 10)*	*r = -0.4271* *(n = 9)*
NEWELL POINT (Sample taken early in the month)	*r = 0.6986 #* *(n = 10)*	*r = 0.0068* *(n = 9)*
** Significance Level = 99%* *# Significance Level = 95%*		

Statistical analysis (Pearson's Product Moment Correlations) showed a significant correlation between sample results from Low Isles (Appendix E) and the adjacent South Mossman River and Newell Point sites (Appendix D) when sampling was done at approximately the same time (Table 3.2). There was no correlation between the results from the Low Isles mid-month sampling and terrestrial samples taken earlier in the month (Table 3.2).

The seasonal (wet/dry) results are shown graphically in Figure 12 and summarised below -

(a) ***Summer, wet season:*** Concentrations in the rivers are higher during this period. In the marine area near-shore to mid-shelf values are also higher in the summer.

(b) ***Winter, dry season:*** Concentrations in the upper Barron River catchment are lower during the dry, winter period. Values are high in the northern sugarcane areas (South Mossman River, Newell Creek, Cooyah Beach), and in the inshore areas of Low Isles and at the Cairns Leads (Figure 12). Values decreased in the near-shore to mid-shelf areas (Green Island, Upolu Cay, Arlington Reef, Michaelmas Cay).

Results from the nutrient profiles also show a seasonal relationship (Figure 13) -

(a) ***December 1987 (Figure 13; data taken from Appendices D & E):***
High concentrations of soluble phosphate were recorded in the upper Barron River catchment. The first major storms were recorded three days before sampling. Relatively small amounts were present in the drier areas of the catchment, and only limited amounts in the streams draining cane growing areas. Soluble phosphate in the marine environment was only slightly above values suggested as ambient for tropical waters (0.2 μM PO_4^{3-}).

(b) ***April 1988 (Figure 13; data taken from Appendices D & E):***
At the end of the wet season phosphate values in the streams and rivers draining the Atherton Tablelands were moderate. All sampled reefs likely to be affected by the plume of the Barron River displayed high levels of soluble phosphate. There was relatively little enhancement in streams draining cane growing areas, and Low Isles (adjacent to the coastal sugarcane fields) displayed only moderate levels of soluble phosphate.

(c) ***August/September 1988 (Figure 13; data taken from Appendices D & E):***
Streams and rivers draining the upper reaches of the Barron River recorded only background levels of soluble phosphate. Coastal streams draining sugarcane areas recorded extremely high concentrations of soluble phosphate. PO_4^{3-} values in the water column around Low Isles and at the Cairns Leads are high. Values of PO_4^{3-} at other sampled marine sites are considerably lower than those recorded during the April sampling period. The elevated level at Yungaburra (Site 2) may be an artefact, but corresponds to a localised winter planting of potatoes.

3.4.3.c Discussion:

Data for this study were collected from many different locations in the marine section of the study area (Appendix E). Samples were taken monthly over a two year period. From the results, it is not possible to demonstrate a definitive case for or against nutrient enhancement of the Great Barrier Reef lagoon. Average marine phosphate levels are high (0.37 μM PO_4^{3-} calculated after removal of all extreme values over 1.0 μM) when

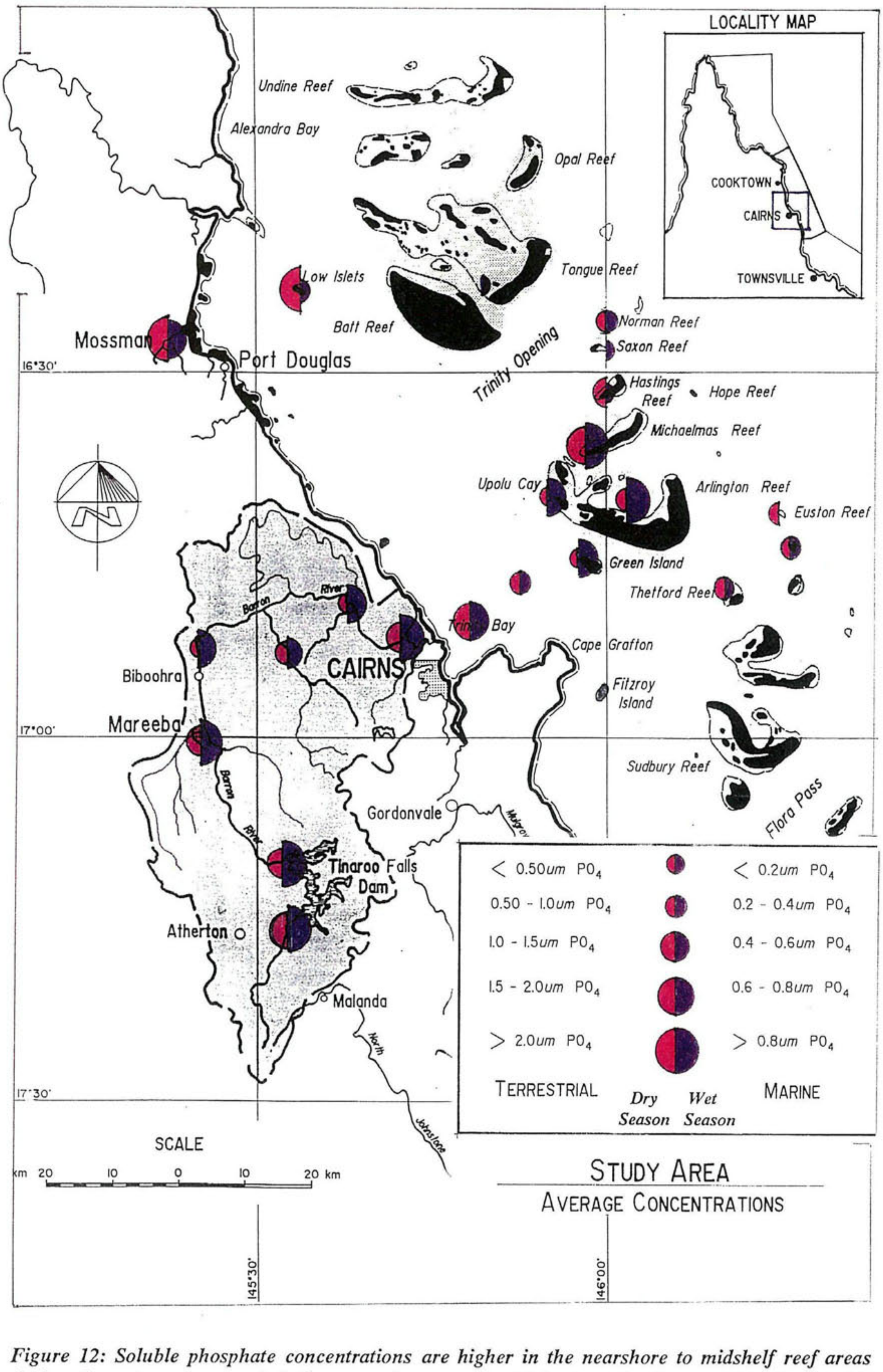

Figure 12: Soluble phosphate concentrations are higher in the nearshore to midshelf reef areas during the wet, summer period. Concentrations are also high along the Barron River during this same period. During the cane planting season concentrations are high at the nearshore sites of Low Isles and the Cairns Leads.

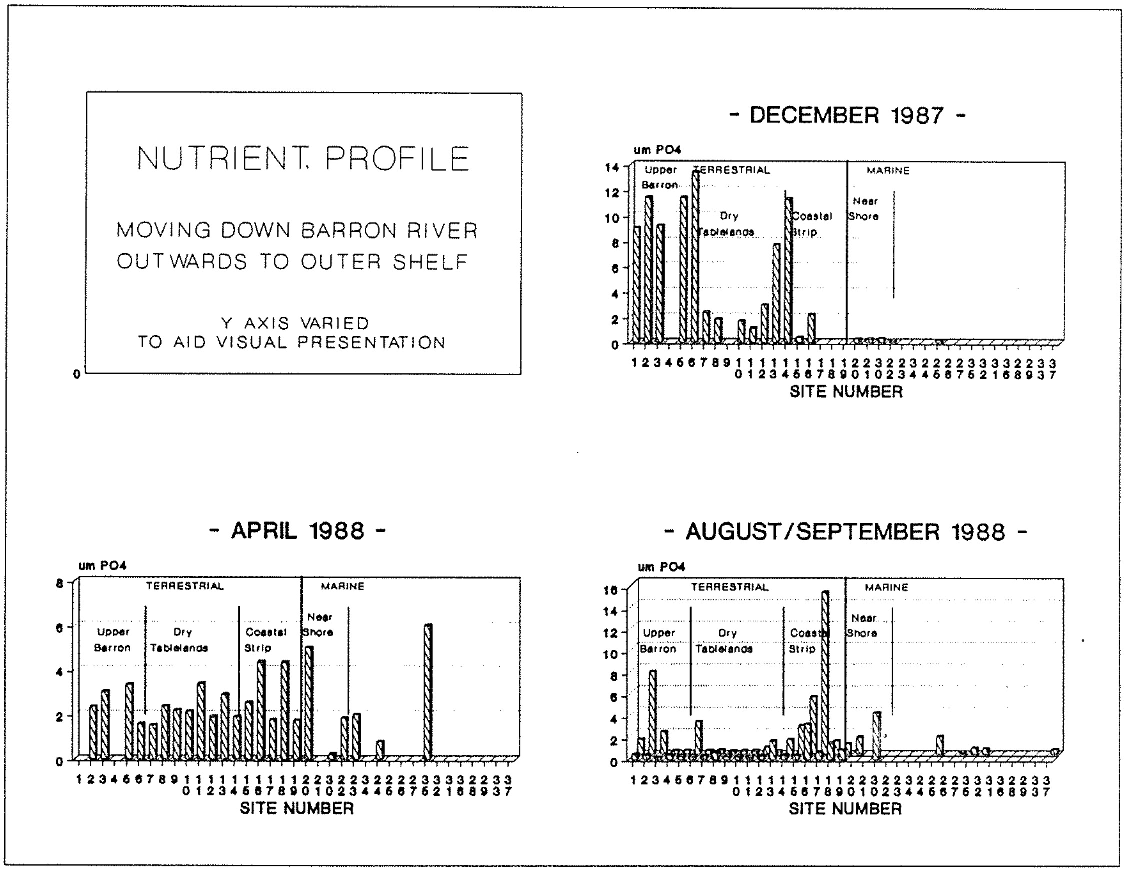

Figure 13: Nutrient profiles for selected months.

compared with values quoted by Entsch *et al* (1983) (0.05-0.20 μM Soluble Reactive Phosphate). Without unequivocal knowledge of ambient values before European settlement, however, phosphate enhancement from anthropogenic influence cannot be concluded.

Even if such data were available, comparative assessment would still be difficult. Individual phosphate values were occasionally high. These values can neither be excluded nor assigned to anthropogenic influence. For example, the elevated levels at Michaelmas Cay may be due to bird droppings flushed into nearby waters. However, the bird population on this cay is reasonably constant while the soluble phosphate concentrations fluctuate (Appendix E). Shallow waters extend considerable distances around the Michaelmas Cay reef. Therefore, the higher values are probably a combination of factors that could include the remobilisation of nutrients from sediments by agitation, pH change associated with rainfall events, or tidal pumping (Entsch *et al* 1983). It is possible to apply the same argument to Low Isles in September 1988. Low Isles also has a migratory bird population that arrives on the Island late August each year. At Low Isles, however, the extreme values were not recorded during any other sampling period, even though sampling at this site was predominantly fortnightly. Enhanced concentrations were also found in streams draining sugarcane farms on the adjacent coastline immediately before the time of sampling.

Timing is an important factor when assessing terrigenous inputs into near-shore areas. This is suggested by the strong positive correlation between the results from Low Isles and those from the adjacent rivers when the sampling periods coincided. In addition, Brady *et al's* sampling programme around Green Island (September 1988 to April 1990, Brady *et al* 1990) was as erratic as the sampling conducted for this programme. Brady *et al's* results contained no episodic excessive enhancement. However, examination of Brady *et al's* data set at an overlapping period with the results from this programme (Appendix F), shows similar values during the sampling period 04/3/1989 (approximately 0.2 and <0.1 μm phosphate respectively). Samples collected for this programme on 18/3/1989, displayed particularly high values (1.9 μm PO_4^{3-}) following excessive rainfall and peak river discharge on the mainland. Values had returned to presumed ambient levels by the next sampling trip, 10/4/1989. Monthly sampling would have missed these enhanced values. It is suggested that a seasonal component exists in both the terrestrial and marine systems. The link is consistent with (a) seasonal land management practices and river phosphate concentrations, and with river discharge and ocean phosphate levels. Brodie & Mitchell (1992) reported soluble phosphate levels of 1.8 μM 50 km seaward from the mouth of the Fitzroy River following freshwater input associated with the January 1991 flood. Discharge from the Barron River was extremely high at the end of the 1988/89 wet season (268,368 and 171,636 megalitres in March and April respectively, compared to 34,354 and 16,076 megalitres the previous year; Appendix C). Observations on the 25th April 1989, five days after the second major flood event of the season, showed the plume extending north past Low Isles (50 k north of the Barron River mouth) and east past Upolu Cay. Although no samples were taken at this time, it is proposed, by extrapolation from the results of the terrestrial monitoring programme, that significant levels of phosphate were contained in this plume.

3.4.4 Question 4: Could reef flat sediments act as phosphate reservoirs, releasing phosphate to the overlying water column when stimulated by suitable environmental conditions?

3.4.4.a General:

It was shown above that the injection of phosphate into the marine waters of the study area is rapid, episodic and spasmodic. These results agree with Cosser's (1987) research. Cosser, however, extended his argument to suggest that the initial, rapid, injection of phosphate was followed by a slower redistribution of enriched bottom sediments. In Kaneohe Bay, Smith *et al* (1981) found that after the initial input of nutrients, changes to community composition and increased biomass production led to secondary enhancement of the system. The production of particulate organic matter in the system, fallout to the sediments, and oxidation, produced an active, short-lived, additional nutrient reservoir.

It was argued above that if the major proportion of the phosphate in the flood plume was in solution (as suggested by Brodie & Mitchell 1992), then the spatial distribution of phosphate through marine waters could be considerably extended. Under this scenario reef flat sediments within the flood plume could receive, adsorb and store phosphate for redistribution at a later time. If this is the case, then a major source of additional nutrients could be made available to the system from the sediments held by that reef.

It was hypothesised, therefore, that well-developed reef flats in the path of a river plume, could trap additional phosphate. Whether in solution or attached to terrestrially derived sediments, this additional phosphate will provide an additional supply of phosphate to the sediment and interstitial water reservoir of that reef.

To examine this hypothesis, Low Isles, a planar, low wooded island reef (Figure 14), was chosen for the study. This reef was selected for its accessibility, proximity to the mainland, and the documentation of the island's features by several workers including Rasmussen (1986).

The surface of the Low Isles reef is made up of several geomorphologically distinct areas. These areas contain varying amounts of coral shingle, fragments of coral and other marine organism, fine carbonate sediments, terrigenous material and living coral and algae (Rasmussen 1986). Morphological characteristics include sediment retaining features such as shingle ramparts, moated pools, seagrass beds and an extensive mangrove system (Figure 14) (e.g. Hopley 1982). Evidence of terrestrially derived material in the sediments has previously been documented (e.g. Fairbridge & Teichert 1948; Rasmussen 1986; plus anecdotal evidence from E. Lone, Low Isles Lighthouse Keeper and I. Bennett, Marine Biologist).

It is beyond the scope of this study to examine phosphate uptake and release by different organisms, the adsorptive properties of phosphate to different surfaces, or phosphate movement through and across different surfaces. The primary and secondary influences of a phosphate reservoir on the reef community are determined by a number of parameters and must be recognised. However, it has to be presumed that any influence on the coral skeleton will come from phosphate that is in solution. This does not presume that the phosphate has not undergone several chemical or biological processes. Nor does it presume that the phosphate has not been recycled, both across the reef and through the reef flat sediments. For this particular section of the study, the total amount of phosphate held by the system is of little consequence if it is not easily released into the water column, even though it may be recycled through the system at some later stage. Therefore, while the nutrient recycling capabilities of reef organisms are recognised, such an understanding should be obtained from other sources (e.g. Pilson & Betzo 1973; Di Salvo 1974; Smith *et al* 1981; Atkinson & Smith 1983; Andrews & Muller 1983; Entsch *et al* 1983; Atkinson 1981 in Atkinson 1987a).

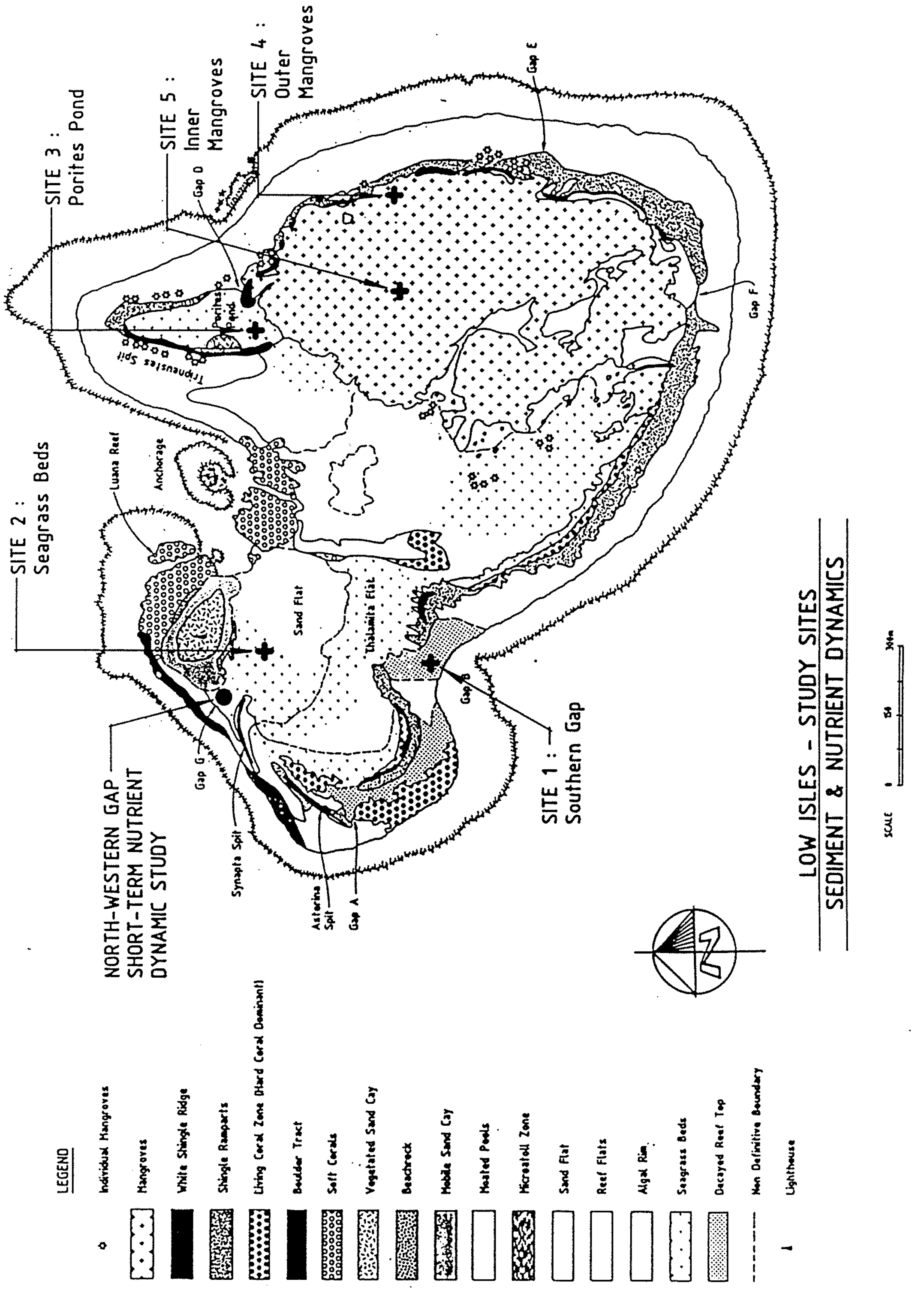

Figure 14: Location of sampling sites on Low Isles, Great Barrier Reef.

The focus of this segment of the study is the amount of phosphate adsorbed by the sediments and made available in solution to the system by the physical and chemical processes operating on an exposed near-shore reef flat. Laboratory experiments, therefore, were designed to mimic the effects of those processes on the top 10 cm of sediment and did not include any contributions from biological factors (Appendix A). However, other research has shown that phosphate concentration in the sediments increases with depth in the sediment profile (Thorstenson & MacKenzie 1974; Krom & Sholkovitz 1977; Rosenfeld 1979; MacKenzie *et al* 1981; Smith *et al* 1981; Pacey 1985), and that these sediments are made available to the surface layer by bioturbation. Therefore, for comparative purposes, deeper sediments from the mangrove area were included in the study.

If the sediments of the Low Isles reef flat were acting as a phosphate reservoir, then elevated levels of phosphate should also be present in (a) the interstitial waters, and/or (b) pools within the reef framework (Entsch *et al* 1983; Andrews & Muller 1983). If this was the case, then normal tidal pumping through the porous reef framework should produce elevated levels of phosphate in the water column immediately above. It was also possible that tidal agitation, accompanied by midday heating of the shallow waters moving over the reef sediments, could be sufficient to stimulate release of phosphate from the sediments. This process could probably be examined by assessing the phosphate concentration of samples taken from the water and the underlying sediments at approximately the same time. A programme of nutrient and sediment sampling from the same location, at the same time, over one full tidal cycle was planned to examine these two possibilities.

In summary, the study to be presented here has one primary objective - to assess whether the retention of phosphate on the Low Isles reef flat is enhanced by the presence of terrestrially derived sediments. To examine this, the study was divided into three parts -

1. A mineralogical assessment of the reef flat sediments, type and source (terrestrial or marine),

2. A sediment desorption study that involved the collection of sediment samples from the reef flat. These samples were then subjected to a series of desorption experiments designed to simulate the physical processes likely to be encountered on the reef flat (Appendix A), and

3. A field based study at one location on the reef flat. This involved the hourly collection of water (surface and 10 cm from the bottom) and sediment samples over one tidal cycle to provide *in situ* data for comparison with the laboratory results. Water and sediment samples were collected simultaneously (water first) from the main drainage gap on the northwestern side of the reef flat (Figure 14). The samples

> were analysed for soluble phosphate concentration, and the sediments subjected to desorptive studies (see Appendix A for the methods used). The site had to be accessible for water sampling throughout the tidal cycle.

The study contained several flaws which need to be explicitly stated. The experiments were designed to release phosphate from the sediments under simulated conditions known to operate on a tropical reef flat exposed at low tide. However, no provision was made for the normal biological processes of removal or addition that would take place if the sediments remained on the reef flat. The results represent only the amount of soluble phosphate that could be released at one point in time if all the physical and chemical processes were jointly operative. The results, therefore, are not directly comparable to other studies where interstitial or pooled water has been measured *in situ*. The results of the programme, however, should provide an estimate of the pool of soluble phosphate that is potentially available to the system, plus or minus biological activity. This should be sufficient to examine the relationship between phosphate retention and the sediments of a near-shore reef flat.

3.4.4.b Results:

3.4.4.b(i) Mineralogical assessment of the reef flat sediments.

Results are shown in Table 3.3 and Appendix H.

The highest proportion (~76%) of terrigenous sediment (defined as quartz + feldspar + kaolinite[1] + illite/smectite and other smectite based mixed layer clays; see Chapter 2) was found in samples taken from the top sediments of the outer mangrove area. This was followed by the lower sediments of the outer and inner mangroves (~71% and ~70% respectively), the top sediments of the inner mangroves, the seagrass beds, and the Porites Pond (~67% each). The lowest proportion of terrigenous material (~63%) came from the Southern Gap sample. Quartz + feldspar minerals were more abundant in samples from the seagrass beds and the outer mangrove area, followed by the bottom sample from the inner mangrove area, the Southern Gap and the Porites Pond. Lowest quartz + feldspar values were found in the top sample from the inner mangrove area.

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[1] The term kaolinite is used to signify clay minerals of the dioctahedral, 1:1. kandite group, and thus may include kaolinite *sensu stricto*, nacrite, hydrated kaolin, and halloysite.

*Table 3.3: **Assessed mineralogy of the Low Isles sediments. Mineralogy detected using X-ray Diffractometry on the <63 micron portion of the sediments. Values are qualitative (see Methodology, Appendix A). Percentages were obtained by proportionalising the class data.***

LOCATION	*QUARTZ %*	*FELDSPAR %*	*CALCITE %*	*ARAGONITE %*	*GYPSUM %*	*KAOLINITE %*	*ILLITE/ SMECTITE %*	*MIXED LAYER CLAYS %*	*TERRIGENOUS MATERIAL %*
SEAGRASS BEDS	*5 (~19%)*	*3 (~12%)*	*3 (~12%)*	*5 (~19%)*	*1 (~4%)*	*3 (~12%)*	*3 (~12%)*	*3 (~12%)*	*~67%*
PORITES POND	*3 (~12%)*	*2 (~7%)*	*5 (~19%)*	*5 (~19%)*	*0 (n.d.)*	*3 (~12%)*	*4 (~16%)*	*4 (~16%)*	*~63%*
SOUTHERN GAP	*4 (~16%)*	*3 (~12%)*	*5 (~19%)*	*4 (~16%)*	*0 (n.d.)*	*2 (~7%)*	*4 (~16%)*	*4 (~16%)*	*~67%*
INNER MANGROVE (TOP)	*3 (~12%)*	*1 (~4%)*	*2 (~7%)*	*2 (~7%)*	*5 (~19%)*	*5 (~19%)*	*4 (~16%)*	*4 (~16%)*	*~67%*
INNER MANGROVE (BOTTOM)	*5 (~19%)*	*2 (~7%)*	*3 (~12%)*	*4 (~16%)*	*1 (~4%)*	*3 (~12%)*	*4 (~16%)*	*4 (~16%)*	*~70%*
OUTER MANGROVE (TOP)	*4 (~16%)*	*3 (~12%)*	*0 (n.d.)*	*2 (~7%)*	*5 (~19%)*	*4 (~16%)*	*4 (~16%)*	*4 (~16%)*	*~76%*
OUTER MANGROVE (BOTTOM)	*5 (~19%)*	*3 (~12%)*	*3 (~12%)*	*4 (~16%)*	*1 (~4%)*	*3 (~12%)*	*3 (~12%)*	*4 (~16%)*	*~71%*

Table 3.4: Soluble phosphate concentrations released from the <63 micron portion of the Low Isles sediments following six sequential treatments - in freshwater at 26oC + agitation; in saltwater at 26°C + agitation; in saltwater at 40°C + agitation; and in saltwater at 60°C + agitation. Four sub-samples were taken from the <63 micron portion of each sediment sample from each location and each sub-sample allocated to a different treatment. Each sample is presumed to represent a potential area of phosphate retention. Therefore, the concentrations measured after six sequential treatments have been proportionalised to suggest the contribution each area makes to the phosphate reservoir of the Low Isles reef flat.

SITE	*26°C Freshwater wash per 100 g of sediment*	*26°C Saltwater wash per 100 g of sediment*	*40°C Saltwater wash per 100 g of sediment*	*60°C Saltwater wash per 100 g of sediment*	*TOTAL FROM ALL WASHES*
	µM PO_4^{3-}	*µM PO_4^{3-}*	*µM PO_4^{3-}*	*µM PO_4^{3-}*	*µM PO_4^{3-}*
Seagrass Beds	*12.15 (3%)*	*35.50 (8%)*	*50.75 (13%)*	*35.75 (8%)*	*134.15 (7.7%)*
Porites Ponds	*60.50 (14%)*	*33.80 (7%)*	*17.08 (4%)*	*29.53 (6%)*	*140.91 (8.1%)*
Southern Gap	*17.63 (4%)*	*58.05 (12%)*	*58.08 (15%)*	*51.78 (11%)*	*185.54 (10.7%)*
Mangroves -Inner (Top)	*139.55 (33%)*	*114.95 (25%)*	*114.20 (29%)*	*160.40 (35%)*	*529.10 30.4%*
Mangroves -Inner (Bottom)	*22.18 (5%)*	*64.28 (14%)*	*60.48 (15%)*	*47.18 (10%)*	*194.12 (11.2%)*
Mangroves -Outer (Top)	*94.75 (23%)*	*91.75 (20%)*	*60.00 (15%)*	*74.95 (16%)*	*321.45 (18.5%)*
Mangroves -Outer (Bottom)	*71.90 (17%)*	*67.60 (15%)*	*34.15 (9%)*	*59.05 (13%)*	*232.70 (13.4%)*
TOTAL SOLUBLE PHOSPHATE REMOVED BY EACH TREATMENT	*418.66*	*465.93*	*394.74*	*458.64*	*TOTAL 1737.97*
PROPORTION OF TOTAL REMOVED BY THIS TREATMENT	*24%*	*27%*	*23%*	*26%*	*100%*

The samples from the Porites Pond contained the highest proportion of marine sediment (defined as calcite + high magnesian calcite + aragonite) (~38%). This was followed by samples from the Southern Gap (~35%), the seagrass beds (~31%) and the bottom mangrove sediments at both sites (~28%). Lowest levels came from samples in the top mangrove sediments (~14% inner mangrove site; ~7% outer mangrove site).

The largest amounts of gypsum ($CaSO_4.2H_2O$) came from the top mangrove sediment samples (approximately 19% of the <63 micron fraction at each location).

3.4.4.b(ii) *Release of soluble phosphate from the sampled sediments:*

The sediments were sieved and a set amount of solution added to a standardised weight of the <63 micron sediment fraction (Appendix A). The soluble phosphate concentration of the resulting supernatant was then measured. The results, therefore, are expressed as μM as extracted from a standardised weight of sediment.

The quantity of soluble phosphate released from the sediments under laboratory conditions, was highly variable, with quantity released closely linked to sediment type. The largest quantity of phosphate came from the surface samples of the inner mangrove area (30.4%) and the lowest from the Seagrass Beds (7.7%) (Table 3.4, p.58).

The response to the four treatments was also highly variable. The sediment samples from the Porites Pond and the Outer Mangroves (both top and bottom) released higher proportions of soluble phosphate during the freshwater/agitation treatment (43%, 29% and 31%, respectively, of total obtained from all treatments from each site). The Seagrass Beds and the Southern Gap released higher proportions of phosphate during the 40°C saltwater/agitation treatment (38% and 31%, respectively, of total from these sites). The surface sediments of the Inner Mangrove area released most phosphate during the 60°C saltwater/agitation treatment (30%). The bottom sediments of the Inner Mangrove area were the only samples to release most phosphate during the 26°C saltwater/agitation treatment (33%).

Table 3.5: Pearson's Product Moment Correlations for phosphate concentration released from the sediments of Low Isles Reef Flat, under controlled treatments designed to simulate environmental conditions.

MINERAL	*26oC Freshwater wash per 100 g of sediment*	*26°C Saline wash per 100 g of sediment*	*40°C Saline wash per 100 g of sediment*	*60°C Saline wash per 100 g of sediment*
QUARTZ	*-0.4897*	*-0.1368*	*-0.2272*	*-0.4104*
FELDSPAR	*-0.3898*	*-0.4028*	*! -0.6033*	*! -0.6039*
CALCITE	*-0.5061*	*! -0.6820*	*-0.4593*	*-0.4823*
ARAGONITE	*-0.5367*	** -0.8349*	** -0.7709*	*! -0.7261*
GYPSUM	** 0.7777*	*# 0.8754*	*! 0.7154*	** 0.7989*
KAOLINITE	*# 0.8702*	** 0.7847*	*! 0.6841*	** 0.8399*
ILLITE/SMECTITE	*0.2788*	*0.3520*	*0.3205*	*0.2786*
MIXED LAYER	*0.4599*	*0.4701*	*0.0897*	*0.2955*

n = 11
! = 95% SL
** = 99% SL*
 # = 99.9% SL

Sediment type was a major factor in determining the quantity of phosphate released during treatment. Pearson's Product Moment Correlations (Table 3.5) show a strong positive correlation between the amount of phosphate held by the sediments, and (a) evaporative components (gypsum), and (b) kaolinitic components -

(a) Gypsum content was highest in the surface sediments of the mangrove area (an estimated 19% of the <63 micron fine fraction from both Inner and Outer mangrove areas). Samples from this area also released the highest soluble phosphate values during all treatments (30.4% Inner Mangrove area and 18.5% Outer Mangrove area).

Samples from the Porites Pond (0%), the Southern Gap (0%) and the Seagrass Beds (~4%) contained the lowest quantities of gypsum. Small amounts of phosphate were found in the samples from these sites (Porites Pond 8.1%; Southern Gap 10.7%; Seagrass Beds 7.7%; see Table 3.4, p.58).

(b) Kaolinite content was highest in the surface sediments of the Inner and Outer Mangroves (~19% and ~16% of the <63 micron sediment fraction respectively). Large quantities of soluble phosphate were released from the surface samples from these sites (30.4% and 18.5% total contribution), with most phosphate released

> during the 26°C rainwater/agitation treatment (Inner Mangroves 26%, Outer Mangroves 29% of their total phosphate load).
>
> By contrast, kaolinite content was lowest in the sediments of the Southern Gap (~7% of the <63 micron sediment fraction). These samples released only low levels of soluble phosphate (10.7% total contribution) with only 9% total phosphate load released during the 26°C rainwater/agitation treatment.

In the mangrove area, the top sediments released the highest proportion of soluble phosphate under all treatments -

Total contribution Inner Mangroves - 30.4% top, 11.2% bottom
Outer Mangroves - 18.5% top, 13.4% bottom.

The surface sediments of the Inner and Outer Mangrove area together contained nearly half (48.9%) of the soluble phosphate released during laboratory experiments. This proportion increases to 73.5% when the bottom sediments are included.

3.4.4.b(iii) Short-term, in situ, phosphate dynamic study of reef flat waters and underlying sediments.

Results are shown in Table 3.6.

The site chosen for this section of the study was in the approximate centre of a major drainage channel on the Low Isles reef flat. The area never dries completely and sediment cover is relatively thin when compared to the mangrove area. During this study low tide occurred around 1.45 pm. Flow direction changed and water flowed back onto the reef flat, through the drainage channel, approximately one hour after this. Wind speed was <3 knots (<6 km/h^{-1}) during the study. Water samples were taken approximately 5 cm from the top and 10 cm from the bottom of the water column immediately before collection of a sediment sample. Soluble phosphate concentrations at the bottom of the water column were on average higher than those at the surface. Surface samples were usually just above detection limit with values rising above 0.2 μM PO_4^{3-} during only three of the eleven sampling periods. On the other hand, values in the bottom samples were above 0.2 μM PO_4^{3-} on several occasions with two extreme values of 2.88 and 32.00 μM PO_4^{3-}.

Analysis of water samples taken from both depths in the water column generally produced concentrations that were higher after the turn of the tide. Phosphate values at the bottom of the water column increased rapidly as the tide turned, rising to 2.88 μM PO_4^{3-} immediately before, and 32.00 μM PO_4^{3-} immediately after, the tide changed (Table 3.6). The concentration of phosphate in the sample taken at the next sampling period (3.30 pm, Table 3.6), was slightly elevated, but decreased in later samples as the water level rose over the reef flat (Table 3.6).

Table 3.6: Soluble phosphate concentrations released from the <63 micron portion of the Low Isles sediments of the Northern Gap following six successive treatments - Freshwater at 26°C; Saltwater at 26°C, 40°C and 60°C.

TIME AND FLOW DIRECTION	*26°C Fresh water wash per 100 g of sediment*	*26°C Saline wash per 100 g of Sediment*	*40°C Saline wash per 100 g of Sediment*	*60°C Saline wash per 100 g of Sediment*	*PO_4^{3-} concentration Top of water column*	*PO_4^{3-} concentration Bottom of water column*
	µM PO_4^{3-}	*µM PO_4^{3-}*	*µM PO_4^{3-}*	*µM PO_4^{3-}*	*µM PO_4^{3-}*	*µM PO_4^{3-}*
E->W 8.30	*39.50*	*77.60*	*71.20*	*72.80*	*0.02*	*0.04*
E->W 9.30	*36.38*	*75.78*	*86.23*	*70.90*	*0.02*	*0.30*
E->W 10.30	*38.00*	*76.20*	*83.70*	*68.23*	*0.42*	*0.14*
E->W 11.30	*79.80*	*104.90*	*121.30*	*116.05*	*0.08*	*0.05*
E->W 12.30	*15.53*	*36.30*	*35.10*	*36.78*	*0.04*	*0.01*
E->W 13.30	*41.28*	*76.76*	*93.40*	*104.44*	*0.16*	*2.88*
E->W 14.30	*7.68*	*42.75*	*31.85*	*29.25*	*0.05*	*32.00*
W->E 15.30	*31.88*	*70.40*	*81.24*	*69.28*	*0.16*	*0.41*
W->E 16.30	*22.40*	*55.30*	*50.75*	*58.88*	*0.59*	*0.56*
W->E 17.30	*15.96*	*23.24*	*27.48*	*28.36*	*0.04*	*0.61*
W->E 18.30	*8.80*	*17.33*	*9.58*	*8.38*	*0.67*	*0.31*

3.4.4.c *Discussion*

3.4.4.c(i) *The relationship between sediment mineralogy and phosphate retention on the Low Isles reef flat:*

Clearly, the sediments of the Low Isles reef flat contain considerable amounts of phosphate. However, the amount held is extremely variable across the reef flat and is closely correlated with sediment mineralogy (Table 3.5). Distribution of the sediments varies with reef flat hydrodynamics and the settlement pattern of the sediments, with the finer terrigenous particles settling predominantly in the sheltered mangrove environment (Table 3.3).

The sediment samples from the Mangrove Park (inner and outer mangrove areas; see Figure 14) contained the highest concentrations of phosphate (Table 3.4, p.58). These sediments also contained the highest terrigenous content, particularly the illite/smectite mixed layer clays, and the highest quantities of gypsum (Table 3.3). The surface samples from this area contained higher concentrations of phosphate. These samples also released very high amounts of phosphate during the freshwater treatment (~140 μM PO_4 and ~95 μM PO_4 inner and outer mangrove areas respectively).

On Low Isles the Mangrove Park covers 41.5 ha (Rasmussen 1986), or nearly half the reef flat, and makes up around 80% of the reef flat sediments (estimated on a one-dimensional plane), excluding the cay. Approximately 70% of the <63 micron fraction of the surface sediments of the mangrove area is terrestrially derived. Together the samples from the inner and outer mangrove area produced nearly half (48.9%) of the soluble phosphate released during the laboratory experiments. The depth of the Mangrove Park sediments, however, is considerable. For example, bores put down by Marshall & Orr (1931) at various points on the reef platform noted sediments of grey coralline mud at least 15 ft (approximately 4.5 m) deep.

In the extensive study on the effects of sewage discharge and diversion in Kaneohe Bay, Smith *et al* (1981) excluded reef flat sediments from the major part of their study. These authors argued that the relatively thin loose sediment veneer of the reef flat was not quantitatively as important in nutrient storage and cycling as the thicker and spatially more extensive sediment of the lagoon. That argument may not be viable within the Great Barrier Reef and is particularly invalid in the study area. While some reef flat sediments form only a thin veneer across the reef, many reefs have well-developed reef flats with extensive areas of deeper sediments protected behind shingle ramparts. In the northern sector of Australia's Great Barrier Reef, many protected areas on mature reef flats have developed extensive mangrove systems. Decaying organic matter from vegetation and reef organisms is abundant in mangrove areas and considerable amounts of phosphate will be added to the system as secondary enrichment (Smith *et al* 1981). Sulphate reducing bacteria associated with mangrove sediments aids the decomposition of organic matter, increasing the concentration of dissolved phosphate in shallowly buried sediment pore waters (Thorstenson & MacKenzie 1974; Krom & Sholkovitz 1977; Rosenfeld 1979; Pacey 1985). Biochemical reactions influence pH and alkalinity (Boudreau & Canfield 1988). Within the reef framework the water is put under partial pressure by tidal forcing (Burton & Walter 1990). Such conditions operate to release phosphate from the sediments and the organic matter retained in the framework. While the newly released nutrients may reattach quickly to new surfaces, it is possible that tidal pumping will -

(a) change the chemical composition of the pore water leading to further changes in the sorptive capacity of the sediments in the reef profile, and

(b) force nutrient enriched pore water upwards through the reef framework and onto the overlying reef flat.

While this would suggest that any phosphate in the system should increase with depth in the sediment column (a process previously noted by other researchers; e.g. see Thorstenson & MacKenzie 1974; Krom & Sholkovitz 1977; Rosenfeld 1979; MacKenzie *et al* 1981; Smith *et al* 1981; Pacey 1985), in this study the highest quantities of soluble phosphate were released from the top sediment samples in the mangrove area (Inner Mangroves - 30.4% top, 11.2% bottom; Outer Mangroves - 18.5% top, 13.4% bottom). While this was surprising, it is probably explained by the high proportions of gypsum and mixed layer clays in the top mangrove sediments.

The surface samples from the mangrove area contained extremely high levels of gypsum ($CaSO_4.2H_2O$), the origin of which is problematical. Either it is an artefact caused by drying the sample, in which case the absence of halite ($NaCl$) cannot be explained, or it is formed *in situ* by the evaporation of marine waters in the upper layers of the mangrove sequence. Gypsum precipitation will occur when seawater has been concentrated by approximately 1.5-3.0 times, dependent upon the presence or absence of sediment (Pomeroy 1987).

In the Low Isles Mangrove Park, the surface sediments are persistently exposed to evaporative processes. Only trace amounts of gypsum were found in areas continually covered with water. If the amount present was due only to sample preparation, then it would be reasonable to expect similar, or greater, amounts in samples taken from beneath the surface of the water. In these areas the amount of saltwater present in the sample would be greater, producing larger amounts of gypsum during the drying process. Regardless of the source, PO_4^{3-} is not structurally dissimilar to SO_4^{2-} and can replace it in limited amounts within the gypsum structure, providing a coupled substitution can occur and charge neutrality maintained. Agitation, or inundation by either fresh or dilute salt water, will readily dissolve the gypsum, releasing the included phosphate ions back into the water column. This explains the strong correlations between gypsum and the experimental results from all treatments (Table 3.5). This is an important point. If additional phosphates are being added to the marine system by anthropogenic cause, and if these phosphates are being stored in the sediments of near-shore reef flats, then the results from this study suggest that phosphate will be easily remobilised to the water column during periods of rainfall, agitation, or inundation by dilute saltwater.

The processes of phosphate dynamics outlined above are natural components of a complex system. In near-shore areas terrestrially derived materials will also contribute to the dynamics of a particular system. Phosphates have a strong affinity for organics, terrestrially derived clays, and sulphate containing evaporative minerals such as gypsum (Yariv & Cross 1979). Anthropogenically derived phosphate could be expected to adsorb rapidly onto the naturally occurring sediments of near-shore reef flats. Exposure to rainfall, turbulence or inundation by dilute saltwater is common on mature reef flats in the northern sector of the Great Barrier Reef Lagoon. In these areas reef flats are exposed twice daily at all but neap tides.

The results from this segment of the study show that under such circumstances, phosphates stored by the sediments will be more susceptible to remobilisation than the sediments of the deeper areas between reefs. They could, therefore, form an important source of additional phosphate to the local reef community and explain such anomalies as periodic algal blooms. In Kaneohe Bay the most conspicuous effects of the increased nutrients were increased biomass, productivity, and altered community structure (Smith *et al* 1981). Research at Low Isles cannot benefit from the before and after experimental situation of Kaneohe Bay, and without quantitative ambient data, any suggestions of community alteration can only be qualitative. However, documented evidence suggests that many changes have taken place on Low Isles (e.g. increased algal cover; the spread of the seagrass beds and mangrove park; rapid decline of coral cover on the reef flat; increased numbers of herbivores and filter feeders). Morphological processes alone cannot explain these variations. This leads to the conclusion that the changes may have an anthropogenic signature, possibly related to the increased delivery of nutrient enriched terrigenous sediments (Fairbridge & Teichert 1948; I. Bennett 1973; Rasmussen 1986).

3.4.4.c(ii) The short-term, in situ, phosphate dynamic study of reef flat waters and the underlying sediments:

The site chosen for this section of the study was in the approximate centre of a major drainage channel on the Low Isles reef flat. The area never dries completely and sediment cover is relatively thin (<10 mm) when compared to the mangrove area (>1 m in some areas). Low Isles reef exchanges material with the ocean through tidal advection over the reef, tidal pumping through the reef structure, and turbulent diffusion on and around the reef. Rate of tidal inundation over the reef is rapid, particularly during periods of extreme high tide. The reef flat is exposed twice daily except during neap tides, with a maximum exposure time of around four hours during periods of extreme low water. Drainage off the reef flat is retarded by shingle ramparts around the perimeter of the reef, patches of living coral and algae, and piles of loose or cemented rubble on the surface of the reef. Therefore, some water is retained in scattered pools even during the lowest tides. Reef flat exposure during daylight hours occurs predominantly in winter when skies are clear, daytime temperatures are around 26°C, and evaporation is high (125-225 mm mo^{-1}; Australian Bureau of Meteorology). Tidal inundation back over the reef edge commences approximately one hour after the turn of the tide.

During this study low tide occurred around 1.45 pm. Change of flow direction through the drainage gaps commenced approximately one hour after this. Wind speed during the study was <3 knots (<6 km h^{-1}). Water samples were taken approximately 5 cm from the top and 10 cm from the bottom of the water column immediately before collection of a sediment sample. Soluble phosphate concentrations at the bottom of the water column were on average higher than those at the surface. Surface samples were usually just above detection limit with values rising above 0.2 μM PO_4^{3-} during only three of the eleven sampling periods. On the other hand, values in the bottom samples were occasionally above 0.2

$\mu M\ PO_4^{3-}$ with two extreme values of 2.88 and 32.00 $\mu M\ PO_4^{3-}$.

Analysis of water samples taken from both depths in the water column generally produced concentrations that were higher after the turn of the tide. Phosphate values at the bottom of the water column increased rapidly as the tide turned, rising to 2.88 $\mu M\ PO_4^{3-}$ immediately before, and 32.00 $\mu M\ PO_4^{3-}$ immediately after, the tide changed (Table 3.6). Water entering the sampling site at this time would have been a mixture of new water from outside the reef, and water forced through the reef structure. The amount of phosphate measured by the laboratory desorption studies was particularly low when the 32.00 $\mu M\ PO_4^{3-}$ concentration was collected (2.30 pm, the first sampling period after tide change (Table 3.6), suggesting that at least some phosphate came from remobilisation from the sediments, induced by agitation as the tide changed. The concentration of phosphate in the sample taken at the next sampling period (3.30 pm, Table 3.6), increased slightly, but the concentration decreased in the later samples as the water level rose over the reef flat (Table 3.6). The results of this *in situ* study suggest, therefore, that a relationship exists between phosphate attached to, or within, the reef sediments, and soluble phosphate in the overlying water column.

Pools of nutrient enriched waters in reef sediments have been reported previously. Entsch *et al* (1983) noted soluble phosphate pools in outer-shelf reef sediments with concentrations of phosphate in the interstitial water 30 - 50 times higher than in the overlying water. Andrews and Muller (1983) also reported elevated levels of soluble phosphate in the water within the open framework of the same reef. High levels of interstitial phosphorus (70.9 $\mu g\ g^{-1}$) have also been found in the coarse marine sands of an estuarine ecosystem (Congdon & McComb 1980). Congdon & McComb suggested that the accumulation of phosphorus in these sands was probably due to the trapping of riverine silts and phosphorus by seagrasses in the area. In the terrigenous muds of the same estuarine ecosystem, Congdon & McComb (1980) reported interstitial and total phosphorus concentrations of 118.3 and 1280.8 $\mu g\ g^{-1}$ respectively. These authors again suggested that the high levels were probably due to the trapping effects of marine flora. Other data from the same ecosystem linked high concentrations of total phosphorus to the quantity of organic material in the sediments. The rapid rise in phosphate concentration in the shallow water column as the tide turned (<30 cm at this sampling period), and the accompanying drop in soluble phosphate released from the sediments, suggests that the elevated concentration of soluble phosphate in the water column came from the underlying sediments. Clearly, agitation induced by tidal action contributed to the increased levels of phosphate in the water column, but Andrews & Muller (1983) have outlined the effects of tidal pumping through the reef structure in open ocean reef systems. Given the amount of phosphate shown to be retained by the sediments (Table 3.4, p.58), tidal pumping undoubtedly contributed to the phosphate concentration of the overlying water. The increase as the tide changed is probably explained by this factor.

The amount of phosphate desorbed from the drainage gap sediment samples during the freshwater/agitation treatment in this section of the study was reasonably high (up to nearly 80 μM PO_3; median value 31.88 μM PO_3; mean value 30.65 μM PO_3). These values, however, are considerably less than the amount released by the surface samples of the Mangrove Park (inner mangroves ~140.0 μM PO_3; outer mangroves 95 μM PO_3). There is also a large difference in the thickness of the sediment layer between the two areas. The sediments of the northern drainage gap (Figure 14) are generally <10 cm thick. In the Mangrove Park the sediment layer ranges from <10 cm on the outside of the Park to at least 2 m towards the interior. On the western edge of the Park surface sediments are superficial but are trapped to an unknown depth by decaying honeycomb rock (Figure 14). It was also shown in Table 3.3 that the sediments of the Mangrove Park had a higher terrigenous component than the sediments of the drainage gaps. Therefore, the amount of phosphate likely to be remobilised into the water column by tidal forcing and agitation from wind, waves and tidal movement, could be expected to be considerably greater from the Mangrove Park sediments than from the northern drainage gap (Table 3.6).

Kinsey & Domm (1974) and Kinsey & Davies (1979) demonstrated experimentally that calcification processes could be altered by the addition of elevated levels of nutrients. Other researchers have noted that elevated phosphate concentrations alter carbonate mineral precipitation kinetics (Mucci 1986; Burton & Walter 1990). Kinsey & Davies (1979) believed the reduction in calcification processes was probably caused by the phosphate levels in their experimental pools, although these researchers considered that the phosphate loading used by them (2.0 μM) was excessive. However, the results produced above show that the phosphate concentration of the shallow waters of the Low Isles reef flat increased to over 2.0 μM PO_4 as the tide turned and increased further to over 30 μM PO_4 as the direction of tidal flow changed and water flowed back over the reef flat. Whether the increased concentrations are the result of tidal forcing, agitation of the sediments, or a combination of both, is largely irrelevant to this segment of the study. What is important is that phosphate concentrations on the reef itself were elevated to over the level of 2.0 μM PO_4 considered by Kinsey & Davies (1979) to be excessive. It is also clear from the results that these concentrated levels returned quickly to values presumed to be closer to ambient, but this segment of the study was conducted on a clear, wind-free day. From the laboratory results it can be presumed that these concentrated levels would increase during rainfall, excessive heat, or high energy events. It should also be reiterated at this point that the tolerance of the corals to the spasmodic introduction of elevated levels of phosphate is not known. Further, Kinsey & Davies (1979) noted that the effects of nutrient enhancement continued long after the source of the enhancement had been discontinued.

3.5 CONCLUSIONS

The study presented in this chapter had three primary objectives -

1. to examine whether any connection existed between stream phosphate enhancement and land management practices,
2. to examine whether the dissolved phosphate load reached the reefs, and
3. to examine whether nutrients could be stored and regenerated by near-shore reef flat sediments.

The study employed several different methods to gather information on phosphate transport from agricultural areas to coral reefs. Data from phosphate monitoring programmes were used, together with climatological data, to estimate load, seasonality and the movement of phosphate from the land to the sea. Simulated phosphate desorption studies examined the potential for near-shore reef flat sediments to release phosphate to the overlying water column. The conclusions formed from the results of these studies are summarised below.

1. Stream phosphate enhancement and land management practices.

The Barron and Mossman River systems display many features of a manipulated agricultural system, including rapid response of stream phosphate concentration to rainfall. Theoretical considerations of the processes of phosphate sorptivity were shown to be inapplicable to the two catchments because of climate and the interaction with land management practices. While other studies have shown that phosphate remains relatively stable in the soil profile, this study suggests that these factors are of little importance in the Barron/Mossman River area. In this region the sorptive capacity of the soil profile is altered by high temperatures, and sudden, intense rainfall (often following periods of extreme dry). Soils of the area can wet and dry the soils several times during a single day. Overland flow, soil erosion, high water tables, intensive farming, and the practice of using rainfall to incorporate fertiliser, contribute to the movement of significant quantities of soluble phosphate from the land to the rivers. It was demonstrated that the levels of phosphate in the Barron River at Yungaburra increase rapidly following rainfall, dropping off as river discharge increases and dilution takes place.

2. ***Soluble phosphate in the fluvial system and the phosphate status of shelf waters.***

The phosphate flux of river systems varies according to the hydrology, geology, geomorphology and land management practices of the study area. The catchments of the Barron and Mossman River systems have been significantly altered for agricultural purposes and one obvious source of soluble phosphate input from such a situation was shown to come from agricultural fertiliser. An additional, but unknown, contribution will also come from natural weathering processes and groundwater seepage, but this contribution is considered relatively small in comparison.

An association was shown between land management practices in the catchments and phosphate concentration of the rivers although this was blurred by the monthly sampling procedure. The short-term dynamic study explained that phosphate concentrations rise and fall rapidly in response to rainfall and are easily missed by monthly sampling. Turbulence, stream vegetation, stream bed morphology and sediment type were also shown to influence the concentration of phosphate in the water column at any location.

Phosphate concentration in the streams and rivers is generally higher in the coastal areas of the Barron and Mossman River systems. Lack of major agriculture in the upper catchment of the Mossman River suggests that the elevated downstream concentrations are caused by high levels of phosphate applied to the sugarcane farms, rather than migration from up-river areas.

Large obstructions such as the Tinaroo Dam restrict the movement of phosphate from the upper reaches of the river during periods of diminished flow. However, the rapid increase in phosphate concentration as the dam overflowed suggests this is a temporary barrier and possibly supplements stream phosphate levels by agitation or desorption of phosphate enriched bottom sediments during periods of peak flow.

The quantity of phosphate delivered to the ocean from the land is the result of both concentration and the amount of water moving down the river. Both depend on rainfall, but with an upper limit imposed by complex solubility criteria. Empirical consideration of the appropriate phosphate equilibrium may indicate that only under extremely high phosphate concentrations do the river waters approach saturation with respect to apatite [$Ca_5(PO_4)_3(OH)$]. Thus, under more usual conditions, the phosphate levels in the rivers are dependent upon the amount available for transfer.

Nearly 90% of the annual soluble phosphate load transported by the Barron River was carried during the March/April 1988/89 flood period (pp.42 & 44), with approximately 80% of this load carried during the April flood. The dissolved load transported through Lake Placid in April 1989 was estimated to be equivalent to 57 tonnes of phosphate when calculated as PO_4^{3-}. According to the 5:1 ratio of adsorbed to soluble phosphate proposed by Douglas (1973) and Cosser (1987), the total load was equivalent to 285 tonnes of phosphate when calculated as PO_4^{3-} This is the equivalent of approximately 2,850 tonnes of superphosphate, a figure substantially higher than the industry estimated usage (1,810 tonnes) for the total sugarcane district of the Far Northern Statistical Division during 1988 (Pulsford 1990). Based on the findings of Brodie & Mitchell (1992), the phosphate in solution probably made up most of the phosphate load during flood events. The results of these researchers suggests the proportion of dissolved phosphate may be closer to 80% rather than 20% during flood events. This estimate provides a more realistic calculation of the total amount of phosphate (approximately 71 tonnes of phosphate calculated as PO_4^{3-}, or approximately 710 tonnes of superphosphate) transported through the river system. However, it also implies that reefs in the flood plume will receive greater quantities of phosphate during the initial rapid injection period than was previously believed. Under these circumstances the distribution of soluble phosphate through marine waters will be restricted only by the force, direction, duration and phosphate content of the river plume.

Other studies have shown that the fresh/saline interface acts as an efficient flocculating and settling agent for both soluble phosphate and sediment load (Milliman 1990). During periods of peak flow the breakdown of the estuarine salinity barrier allows considerably more phosphate to be transported further into marine waters before flocculation and/or settling occurs. Flocculation will be delayed by a layer of freshwater overlying the seawater. Dispersal of the soluble phosphate load through the marine system will be controlled by river carrying capacity, and the presence or absence of suitable settling or flocculating agents. It is suggested, therefore, that movement of the soluble load will follow the flood plume, extending the influence of terrestrially derived phosphate considerable distances through the marine environment.

3. *Reef flat sediments as phosphate reservoirs.*

Low Isles displays many features of a mature, near-shore coral reef, including a well-developed rampart system, mangrove colony, seagrass beds, and a high proportion of terrestrially derived material rich in kaolinitic material and illite/smectite mixed layer clays. Studies in terrestrial sedimentology demonstrate the capacity of such clays to sorb phosphate. Gypsum, formed by evaporation, is an additional viable phase for storing phosphate and, upon dissolution, releases it back into the water column in a soluble form. The highest amount of soluble phosphate desorbed from the sediments during laboratory simulation experiments came from (a) areas of high terrigenous content, and (b) surface areas exposed to daily evaporative processes.

The primary source of the phosphate in the sediments was considered to come from the land during periods of increased river discharge. This primarily occurs during the austral summer, but heavy rain events also occur during the winter period. Winter rainfall coincides with sugarcane planting on the coastal strip and a correlation was shown between phosphate concentration in the waters around Low Isles and stream concentration on the nearby mainland immediately after such an event.

Most of the soluble phosphate released by the sediments in the laboratory experiment came from the surface layer. This was probably due to the high proportion of fine terrigenous sediments in the surface layer. These fine sediments are created by the downward migration of larger particles and the selective reworking of the fine sediment layer by tides, currents and wave action.

Phosphate exchange between the sediments and the overlying water column was implied to be associated with tidal ebb and flow. Particularly high concentrations in the water column (32.0 μM PO_4^{3-}) coincided with lowered concentrations in the underlying sediments during flow reversal as the tide turned. The most likely cause of this effect is tidally induced agitation of the sediments. Tidal pumping through confined spaces in the reef framework probably contributed to the enhancement (2.8 μM PO_4^{3-}) that took place as the tide turned. The large area (approximately 50 ha) of relatively deep, terrestrially enriched, sediments of the mangrove area (over 1 m deep in the interior), clearly act as a phosphate reservoir, contributing significantly to the amount of soluble phosphate available to the Low Isles reef system.

General:

A direct relationship between phosphate levels in the rivers and the sea could not be established during this study. However, the results suggest that unless nutrient monitoring is done often, and in a wide variety of locations, this is an inefficient method of establishing water quality and its potential to impact on coral reefs. The results indicate that there is sufficient circumstantial evidence to suggest that considerable quantities of phosphate are being delivered into the marine environment and that the effects of this delivery should be detectable in the skeletal properties of near-shore corals.

The literature suggests that elevated levels of phosphate may affect the skeletal architecture and calcification processes of the coral (e.g. Reitemeier & Buehrer 1950; Simkiss 1964a; Reddy 1977). Examination of the possible interaction between phosphate and the coral skeleton is the subject of the next Chapter. Examination of coral skeletal material laid down pre- and post-European influence will be explored in Chapters 5, 6 and 7.

CHAPTER 4

EXAMINATION OF THE PHYSICAL EFFECTS OF ENHANCED LEVELS OF PHOSPHATE ON EXPERIMENTAL CORALS

4.1 INTRODUCTION

Numerous researchers have demonstrated the sensitivity of the growing coral to variations in the marine environment (e.g. Houck *et al* 1977; Smith *et al* 1979; Schneider & Smith 1982; Muir 1984; Isdale 1984; Shen *et al* 1987; Lea *et al* 1989; Linn *et al* 1990). Used with the chronological record retained by the massive corals, this sensitivity strengthens the argument towards using coral skeletal material for the reconstruction of environmental records. To date most proxy environmental records have been recovered from variations in the chemical composition of the coral skeleton (e.g. Houck *et al* 1977; Smith *et al* 1979; Druffel 1981, 1982; Druffel & Suess 1983; Schneider & Smith 1982; Muir 1984; Isdale 1984; Shen *et al* 1987; Lea *et al* 1989; Linn *et al* 1990). Other researchers have noted differences in the nature of the density bands and attributed these to environmental factors (Knutson *et al* 1972; Barnes & Devereux 1988; Barnes & Lough 1989,1991). Experiments in related areas have shown that precipitation of calcite crystals can be hindered by the introduction of relatively small amounts of phosphate (Reitemeier & Buehrer 1950; Benton *et al* 1983). In an on-site experimental situation, Kinsey & Davies (1979) noted significant decreases in calcification processes following the introduction of elevated levels of nutrients to a microatoll pool. These researchers considered the results were probably a reaction to phosphates rather than nitrates.

For this study, therefore, it was hypothesised that -

(a) if the sensitivity of the coral was such that environmental change could be recorded in both the chemical and physical properties of the skeleton, and

(b) if calcification processes could be measurably altered by the elevation of the phosphate concentration of the water column, then

(c) by analogy, the physical parameters of the coral skeleton should also be affected by increasing the supply of phosphate to the growing coral.

4.2 ESTABLISHING THE EXPERIMENT

The experiment was established for two reasons -

(1) to assess whether the decreases in calcification processes noted by Kinsey & Davies (1979) were the result of phosphate enhancement, and

(2) to examine the effect of elevated levels of phosphate on the architecture of the coral skeleton.

4.2.1. Selection of experimental corals

Two genera of corals were originally selected for experimentation -

(a) ***Porites***: Previous research has demonstrated the ability of massive species of corals such as *Porites* to provide a record of past environmental changes. The fine grained, relatively even growth habits of the *Porites* coral established -the usefulness of this species of coral as a paleoenvironmental indicator. Interpretation of isotopic and geochemical variations of the dated bands shows a correlation between these factors and environmental changes.

(b) ***Acropora***: There were two reasons for selecting this coral -

  (1) The rapid growth habits of *Acropora formosa* make this a particularly suitable species for experimentation.

  (2) *Acropora* species contribute large quantities of material to the reef framework. The species are also aesthetically pleasing. Hence, the social and economic value to reef management cannot be overlooked.

4.2.2. Establishing the experimental aquaria

4.2.2.a Location of aquaria

The experimental aquaria were established in an open outdoor position at the Orpheus Island Research Station. The aquaria were placed inside a fibreglass raceway and the ends given special attention to ensure equivalent operating conditions of light and temperature. All main feeder lines to the aquaria were placed underground to reduce temperature fluctuations from exposure to the sun. Shade cloth covered the top and sides of the tanks to replicate oceanic conditions at a low water tidal depth of approximately two metres. Shade cloth also covered all above ground minor feeder lines to the aquaria.

4.2.2.b Water supply to the aquaria

Ninety litre polyurethane tanks were fitted with drainage tubes just below the upper rim of the bins. Unfiltered seawater from deeper water, 50 metres past the reef edge, was pumped to a header tank before introduction to the experimental area through 50 mm black irrigation pipes. Seawater was distributed by individually controlled 15 mm irrigation hoses attached to 30 mm polythene piping. To maximise circulation inside the aquaria, water was introduced to the bottom of each tank, along the entire length of the tank, by holes drilled into a piece of irrigation tubing similar in length to the tank. To chemically age the aquaria, seawater was allowed to run through all pipes and tanks for two weeks before the experimental corals were placed into the tanks. Unfiltered seawater was pumped into each 90 litre aquarium at a rate designed to provide an hourly turnover.

4.2.2.c Coral collection and establishment in the experimental aquaria

Because of the geomorphology and the geographical location of Orpheus Island (the eastern side of the island is exposed to relatively open ocean water; the western leeward side runs parallel to the mainland and is influenced by runoff, both from the mainland and from the island) water quality differs considerably on either side of the island. Aquaria water for the Research Station is pumped from the bay on the western (mainland) side of the island. To reduce stress and maximise control conditions, the experimental corals were collected from the mainland side of Orpheus Island as close to the water intake as possible under existing Great Barrier Reef Marine Park Authority Permit Regulations.

Care was taken to avoid unnecessary handling of the corals. Sunscreens and insect repellents were avoided before, and during, all handling procedures. Branches of *A.formosa* from the same colony were collected by scuba divers at 2-3 metre low-water tidal depth, placed into polyurethane tanks on board the boat, and transported to the experimental location immediately after collection. Several small *Porites* colonies of less than 200 mm diameter were collected in tanks from areas as near to the *A.formosa* stand as possible, transported to the experimental location and placed into the prepared aquaria.

The collected *Porites* samples continually died under experimental conditions and subsequently this section of the experiment had to be abandoned. The *A.formosa* presented very few problems if experimentation was restricted to the winter period when stress levels from spawning, extreme temperatures and salinity variations were reduced.

Polyurethane lattice mats were placed into the base of the aquaria as a holding platform for the stands of *A.formosa*. Branches of *A.formosa,* averaging approximately 40 actively growing growth tips, were placed into the lattice holding platforms. Care was taken to ensure that -

(a) no coral tip was less than 100 mm below water level,

(b) no overcrowding took place, and

(c) no tip could touch the sides of the aquaria during the growth period.

Early experimental attempts suggested the existence of a rapid sympathetic reaction within the corals similar to the "shut-down-response" described by Antonius (1977. Traumatisation to any part of the co-existing aquarium colony resulted in an immediate sympathetic response from the entire experimental community. Corals showing any signs of stress were immediately removed from the experimental tanks.

Algal growth inside each aquarium was removed weekly by suction. The use of lattice holding platforms meant disturbance to the coral was reduced during the cleaning process.

4.2.2.d Establishing temporal indicators using Alizarin Red

Following collection and removal to the experimental location, the corals were allowed to settle for seven days. Alizarin Red dissolved in UV filtered seawater according to the formula suggested by Lamberts (1974) was then added to all tanks as a chronological indicator. Water supply to the aquaria was stopped during the staining period and the corals allowed to rest in the Alizarin for three hours. To avoid pooling or ponding of the Alizarin during the holding period, air was supplied to each aquarium from the main system at the Orpheus Island Research Station. Water supply was returned to the aquaria and the Alizarin allowed to flush slowly out of the system. A further 48-hour settling period was allowed before nutrient introduction.

4.2.2.e ***Introduction of enhanced phosphate concentrations to the experimental corals.***

Commercial superphosphate (see Table 4.1 for composition) was dissolved in UV filtered seawater, allowed to settle, then syphoned off through 0.45 μ Sartorius filters before analysis. The known concentration of supernatant solution was initially added to the tanks by a drip system designed to maintain concentration within individual tanks of two, 4 and 4 μM PO_4^{3-}. Previous analysis had shown that average PO_4^{3-} values around the host corals were 0.4 μM PO_4^{3-}. Each enhancement occupied two aquaria and two aquaria remained free of enhanced phosphate levels as controls.

Table 4.1: ***Superphosphate analysis according to the label of the commercial brand "Superphosphate"***

Phosphorus 'P' (water soluble)	***7.0%***
Phosphorus 'P' (citrate soluble)	***1.5%***
Phosphorus 'P' (citrate insoluble)	***0.5%***
TOTAL	***9.0%***
Sulphur 'S' as Sulphates	***10.0%***
Calcium 'Ca' as Superphosphate	***20.0%***

To avoid algal growth, supernatant phosphate solution was stored in black tanks. The phosphate solution was fed to the experimental aquaria through black tubing. Constant aeration to the supernatant holding tanks kept the solution well mixed.

Water samples were taken daily from all tanks. Averaged values for the experimental aquaria were close to the 2.0, 4.0, and 8.0 μM PO_4^{3-} values originally envisaged. Control tanks averaged 0.5 μM PO_4^{3-}, relatively close to the Bay status previously established at 0.4 μM PO_4^{3-}

4.3. ***RESULTS***

The *A.formosa* colonies were harvested after a twelve-week winter growth period and returned to the laboratory for subsequent measurement and analysis.

4.3.1 *External characteristics:*

Where skeletal linear extension of the *A.formosa* branches occurred, extension increased rapidly following the addition of superphosphate solution at all but the highest levels (8.0 μM PO_4^{3-} of nutrient enhancement (Plate 1:a,b,c,d; Table 4.2). In aquaria containing 8.0 μM PO_4^{3-} solution, coral mortality was extensive and linear extension of the surviving corals reduced to between 2 and 4 mm. At 4.0 μM PO_4^{3-} extension advanced rapidly (range 15-20 mm), but skeletal circumference thinned considerably. At 2.0 μM PO_4^{3-} linear extension was enhanced compared to the controls (range 9-14 mm) with a decrease in diameter similar to that shown in the higher phosphate concentrations.

Table 4.2: ***Average measurements of actively growing tips from experimental <u>A.formosa</u> over a twelve weeks period.***

Concentration	*Avg. linear extension*	*Avg. circumferenc e*	*No. of growth tips*
Control	*9 mm*	*31.42 mm*	*n=12*
2.0 μM PO_4^{3-}	*12 mm*	*18.54 mm*	*n=11*
4.0 μM PO_4^{3-}	*18 mm*	*16.66 mm*	*n=13*
8.0 μM PO_4^{3-}	*3 mm*	*12.55 mm*	*n= 4*

4.3.2 *Internal characteristics:*

Tips were removed from the actively growing portion of the coral immediately past the Alizarin Red indicator using a diamond tipped saw. The tips were then examined for internal morphological variations using a Tracor Northern Image Processing Package fitted to a JEOL JXA840A Scanning Electron Microscope.

Substantial alteration to the internal morphological structure of the skeleton accompanied the linear extension of the experimental corals noted above (Plate 2:a,b,c). The extension rate of the 8.0 μM PO_4^{3-} enhanced sample did not yield sufficient skeleton for examination using Scanning Electron Microscopy.

4.3.3 Examination of crystallographic distortion using X-ray Diffractometry (XRD)

Following the methods outlined in Appendix A for X-ray Diffractometry (XRD), individual growth tips were crushed and analysed for changes to the crystallographic structure.

No significant crystallographic changes could be detected in the skeletons of the experimental corals.

Studies by Reitemeier & Buehrer (1940) and Simkiss (1964a) noted disturbance to crystal formation following the addition of enhanced phosphate concentrations to the medium surrounding the precipitating calcareous material. Although the lack of evidence of crystallographic distortion cannot be adequately explained at this time, there are two possible reasons that need to be explored -

(1) ***Insufficient material.*** The crystallographic examination was exploratory. While the literature suggested there may be some disturbance of the aragonite crystal, the results reported in the literature referred to the experimental precipitation of crystals in an aqueous solution. Therefore, the reaction of a biologically controlled organism incubated in a solution containing elevated levels of phosphate could not be presumed. Individual analysis of each growth tip was, therefore, the preferred option. From examination of Plates 1:a,b,c,d and 2:a,b,c, clearly while linear extension was enhanced, this was at the expense of the internal structure of the skeleton. Thus, very little skeletal material was available for analysis. Although X-ray densitometry requires very small amounts of material, it is possible that the lack of results was due to the limited amount of skeleton.

(2) ***Sample preparation.*** Again, the analysis was exploratory and the technique innovative. The samples were not cleaned of organic material. The technique was later refined and extended to other corals. Subsequent examination of *Porites* material showed that the youngest material gave unpredictable results.

An extension of the experimental programme outlined above is presently being conducted in a joint project between the Chemistry and Zoology Departments of James Cook University of North Queensland. These experiments include the skeletal development of the giant clam, *Tridacna gigas.* Results detected significant variations in the X-ray powder diffraction pattern from the aragonite skeleton following the addition of controlled levels of phosphate (Belda *et al* 1993)

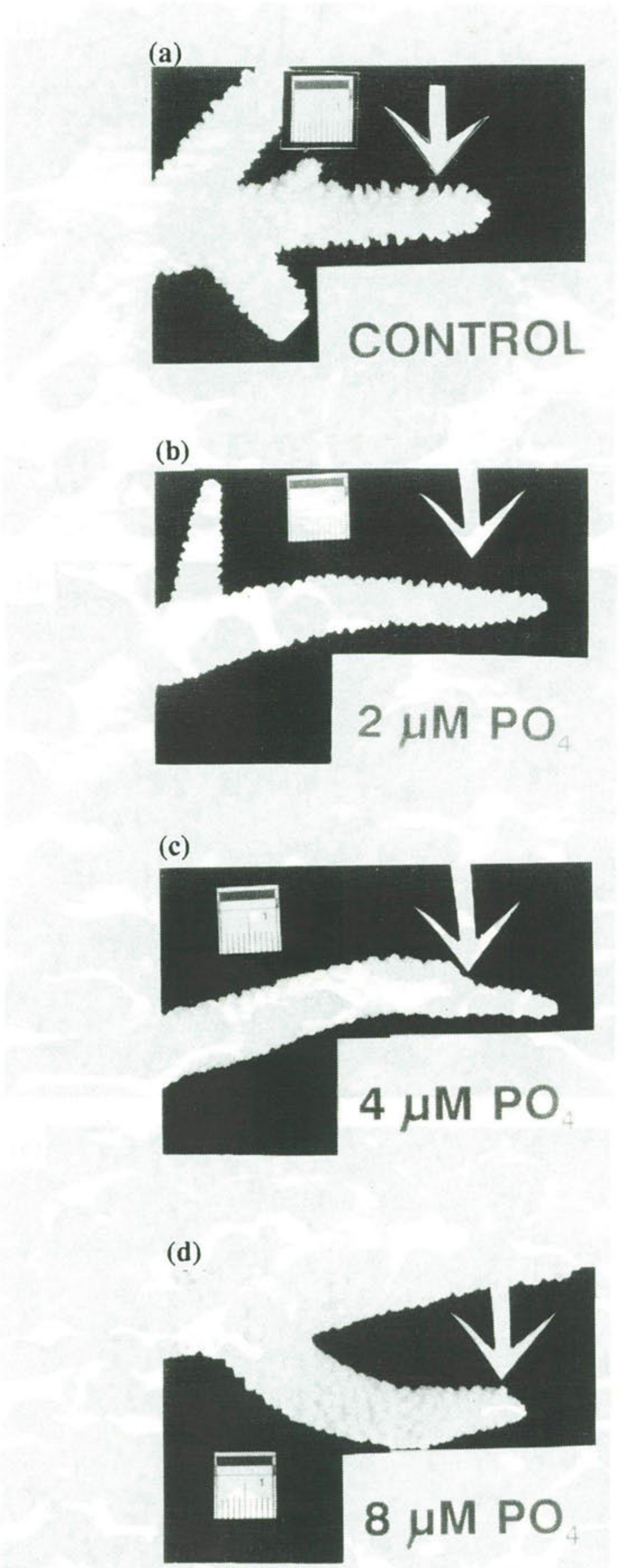

Plate 1: Linear estension of actively growing *Acropora formosa* growth tips under controlled experimental conditions. Arrow indicates beginning of experiment. (a) Control (b) 2 $\mu M\ PO_4$ (c) 4 $\mu M\ PO_4$ (d) 8 $\mu M\ PO_4$.

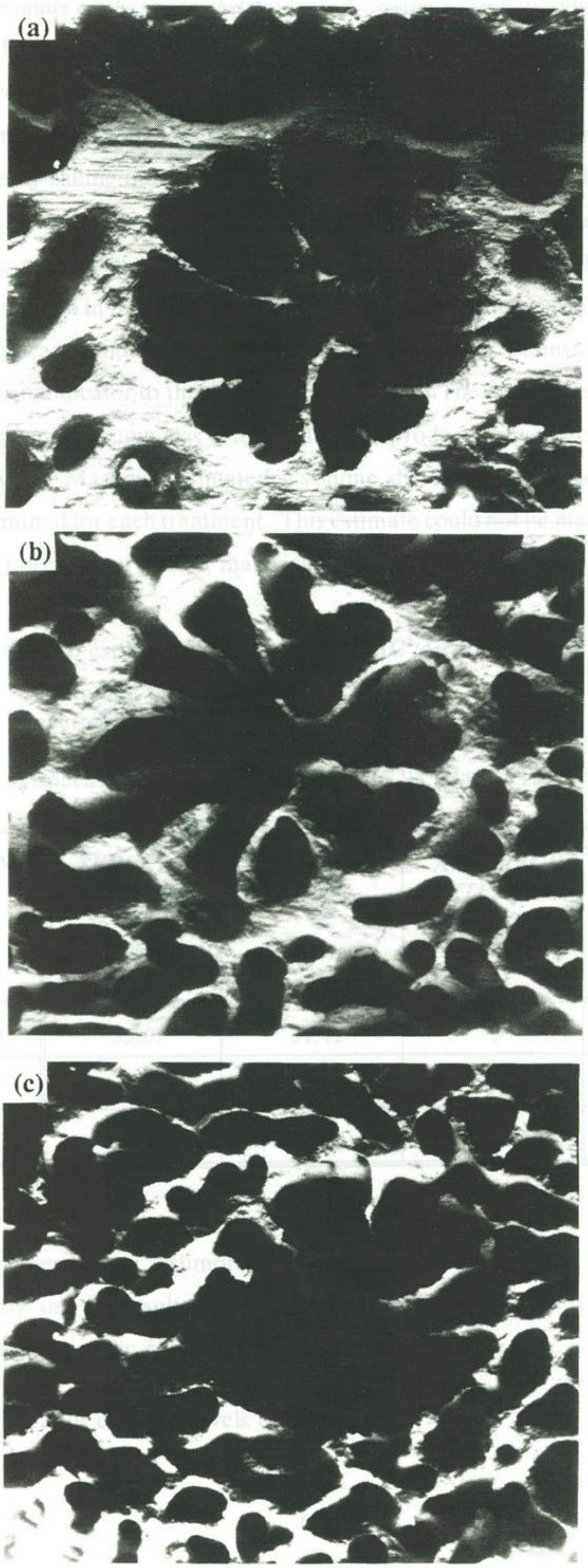

Plate 2: Internal morphological changes of *Acropora formosa* growth tips following the addition of varying levels of PO_4. (a) Control (b) 2 μM PO_4 (c) 4 μM PO_4.

4.3.4 Estimate of change in skeletal mass following phosphate enhancement.

The ratio of skeletal material/voids was estimated using photographic overlays of the type used for vegetation cover. Estimates were made from the SEM photographs of the exposed planar surface of the experimental corals. Differentiation between skeleton and void was made by calling indentations 'voids' and the remainder 'skeleton'. The ratio of skeletal material to voids was made by estimating the coverage of the deep indentations as a proportion of the whole area. Only a pre-set, equal amount of each skeleton was included in the estimation. Circumference was measured halfway between the Alizarin indicator and the end of the growth tip. Linear extension was measured from the Alizarin indicator to the end of the growth tip. The results were then averaged for each treatment. Volume was estimated as the product of average linear extension and average radius. Mass was estimated as volume, divided by the proportion of skeletal material determined for each treatment. This estimate could not be made for Treatment 4 (8 μM PO_4^{3-}) because of lack of material.

The equation used to estimate skeletal mass was $(C^2/4\pi)ESG$. Where -

C = estimated **C**ircumference;
E = average linear **E**xtension;
S = % **S**keletal material/100,and
G = specific **G**ravity of Aragonite @ 2.94 (Battey 1972)

TREATMENT	*SKELETAL MATERIAL 'S' %*	*CIRCUMFERENCE 'C' mm*	*AVGERAGE EXTENSION 'E' mm*	*ESTIMATED SKELETAL WEIGHT (gm)*
CONTROL	*55.07*	*31.42*	*9*	*1.147*
2.0 μM	*45.80*	*18.54*	*12*	*.443*
4.0 μM	*39.72*	*16.66*	*18*	*.362*

Although there were many assumptions made for these estimations, all samples were treated similarly and the results are considered comparable. Three conclusions can be tentatively drawn from the results of the experiments -

(1) calcification processes may be depressed by around 50% following the introduction of elevated levels of phosphate,

(2) the external morphology of the corals is changed to what would be expected from quiet, protected waters (e.g. see Done 1982),

(3) exposure to elevated levels of phosphate may interfere with the ability of the coral skeleton to withstand normal levels of physical stress.

4.4 DISCUSSION

The results show that under controlled experimental conditions, elevated levels of phosphate cause significant alteration to the external and internal morphology of the coral skeleton. It is acknowledged that the levels of phosphate enhancement were high and that it is unlikely that such levels would surround growing corals for any extended period under natural conditions. However, significant alteration was already apparent at the lowest level of enhancement (2 μM PO_4^{3-}), suggesting that interference began at considerably lower concentrations. Extrapolation from the laboratory experiments of Reitemeier & Buehrer (1950) suggests that disturbance may take place as low as 0.6 μM PO_4^{3-}. Benton, Cuff & Elliott's (1983) research also suggested that calcium carbonate precipitation was severely inhibited at levels of around 0.6 μM PO_4^{3-} (Cuff, pers.com).

Although the decrease in calcification processes associated with the morphological changes (up to 50%) is important for the structural development of the total reef system, the implications for reef maintenance and survival are considerably more extensive. The effect on the internal porosity of the branching coral used in this experiment suggests susceptibility to damage by the physical processes associated with storm events will be exacerbated. Therefore, the path of damage caused by tropical cyclones could widen under conditions of elevated nutrient levels. If calcification processes are also affected by elevation of the phosphate concentration in the water column, then initial skeletogenesis following recruitment of any calcium carbonate producing organism could be expected to be hampered. Tomascik (1991) has also reported reduced larval recruitment in areas exposed to increased levels of nutrients. Thus, in severe instances, reef regeneration could be seriously impeded following a catastrophic event.

Other secondary effects of phosphate enhancement also need to be considered. Observations made during this experiment suggested that the corals were constantly stressed by the presence of the phosphate. Coral mortality followed minor environmental disturbance tolerated by the control corals. This mortality usually occurred between two and four days after the event (changes in salinity, temperature, etc.). Although the levels used in the experiment were higher than could reasonably be expected in the waters around coral reefs, the results suggest that corals are less able to tolerate environmental change in the presence of enhanced levels of phosphate, and that this influence may not immediately be apparent. In addition, Kinsey & Davies (1979) noted that nutrient related effects continued for at least one month after the contaminant was removed. The results from the phosphate monitoring programme reported in Chapter 3 show that nutrient spikes are relatively frequent. If a time lag does exist, near-shore corals may not have time to return to ambient before the second impact is felt. Therefore, a cumulative effect may be operational. This would be more likely to occur if elevated levels of phosphate were held in the reef sediments.

The results of Chapter 3 and this Chapter suggest that coral skeletal material may be affected by phosphate variation in near-shore waters. The possibility that this variation may be related to anthropogenic influences is explored in the following chapters by examining the temporal record retained in the geomechanical and geochemical properties of the annual density bands.

CHAPTER 5

GEOCHEMICAL RECORDS RETAINED BY MASSIVE CORALS

(A)

MICRO-ENVIRONMENTAL (LOCAL OR INTRA-REEFAL) ASSESSMENT OF THE GEOCHEMISTRY OF THE CORAL SKELETON.

5.1 INTRODUCTION

Chapter 3 suggested that significant quantities of phosphate entered the marine environment via mainland runoff through the Barron River (e.g. an estimated 57 tonnes of dissolved phosphate during the flood event of April 1989). It was further suggested that most of this phosphate had an agricultural origin, a proposition supported by the research of Fish (1969), Birch (1982) and Cosser (1987). The impact of nutrients (including phosphate) on the marine environment is known to be complex and often insidious (e.g. Banner 1974; Kinsey & Domm 1974; Smith 1977; Kinsey & Davies 1979; Smith *et al* 1981). Storage, biomass production, re-enrichment of sediments and remobilisation can continue after the initial input has taken place (Banner 1974; Kinsey & Domm 1974; Smith 1977; Kinsey & Davies 1979; Smith *et al* 1981), and at considerable distance from the point of origin (Cosser 1987). Indeed, it was shown in Chapter 3 that unless nutrient monitoring was done continuously and in a variety of locations it was unlikely to produce useful information. This suggests that it would be difficult to detect whether nutrient content of marine waters had increased post-European influence, even if good quality ambient data existed. It is possible that the calcium carbonate skeleton of long-lived massive corals has the potential to 'bridge the gap' in the understanding of environmental conditions pre- and post-European influence (Dunbar & Cole 1992).

It is now well recognised that the chemistry and morphology of calcium carbonate skeletons are affected by the chemical composition of the surrounding seawater (e.g. Chave 1954, 1965; Chillingar 1956, 1962; Pilkey & Goodell 1963; Weber 1973; Houck *et al* 1977; Smith *et al* 1979; Druffel 1981, 1982; Schneider & Smith 1982; Druffel & Suess 1983; Muir 1984; Isdale 1984; Shen *et al* 1987; Lea *et al* 1989; Linn *et al* 1990). Research into the use of corals as proxy indicators of environmental and climatic variation has accelerated over the past few years. Sessions at the American Geophysical Union meetings in 1991 and 1992, a special issue of the journal *Coral Reefs* (Montaggioni and Macintyre 1991), and a workshop on "*Coral Paleoclimate Reconstruction*" (reported in Dunbar & Cole 1993) were dedicated to the use of corals and coral reefs as recorders of environmental variation. Yet, while correlations between environmental parameters and the chemistry and morphology of the coral skeleton have been shown (e.g. Druffel 1981, 1982; Schneider & Smith 1982; Druffel & Suess 1983; Isdale 1984; Shen *et al* 1987; Lea *et al* 1989; Linn *et al* 1990), use of the proxy record to hindcast environmental conditions has been restricted by the ambiguity of many results. Whether the ambiguities are caused by endogenic or exogenic factors has not been resolved.

Exogenic influences (physicochemical factors) are the environmental parameters, primarily controlled by climate and global oceanography. Such global influences may be approximately regular and qualitatively predictable (seasonal temperature differences), or periodic but irregular (perturbations in the Southern Oscillation Index). Other influences may be controlled by global conditions, but their effects will be constrained to a smaller area or region within that system (e.g. local rainfall and river runoff associated with weather events). Within these global and regional systems, other events can be completely unrelated to weather or climatic influences and restricted to an extremely localised area (e.g. sewage discharge). Endogenic biological or species effects have also been noted (e.g. Weber 1973; Schneider & Smith 1982). Therefore, sclerochronological interpretation of the chemical and morphological variations in the coral skeleton, which may be a response to environmental change, may be clouded by different scales of influence. These effects may, or may not, be superimposed on to undocumented endogenic effects.

Chapter 6 will focus on the ability of *Porites* skeletons to record environmental variation that may have an anthropogenic signal. It will do this by comparing the results of chemical and morphological analysis of *Porites* samples taken from seven locations within the study area.

However, collection of coral cores for geochemical analysis is both costly and time consuming. Because the extent of geochemical variability within and between reefs is largely not known, it is necessary to first establish whether a single core from an individual location represented that location. To do this, sample cores were removed from the centre of eight *Porites* colonies from seven different reefs (No Name, Hastings, Upolu, Batt, Thetford, Green Island and Brook Island Reefs). This included two samples from the same reef approximately 100 m apart (Green Island Reef). It was attempted to ensure that all cored samples were removed from the same species of *Porites*. However, the difficulties of species identification are such that, while microscopic examination was conducted, each sampled colony can only be presumed to be *Porites lutea* (Veron, Australian Institute of Marine Science, *pers.comm.*). The core samples from each *Porites* were prepared for analysis according to the methods outlined in Appendix A. The results from the two Green Island samples were then statistically compared, both with each other and with the other samples.

This Chapter examines the local (or intra-reefal) variability in the chemical composition of the coral skeleton. The study concentrates on the major element in the coral skeleton (calcium), and on the two trace elements that have attracted most attention as paleoenvironmental indicators (strontium and magnesium).

5.2. ANALYSIS

5.2.1 ***Procedure:***

To examine the extent of intra-reefal variability, individual cores were removed from the centre of two actively growing *Porites* colonies at Green Island Reef. Each density couplet was analysed through one entire core sample. Concentrations of calcium, strontium and magnesium were analysed using Atomic Absorption Spectrometry (AAS) according to the procedures outlined in Appendix A. A review of the relevant characteristics of the various elements analysed is given in Chapter 6, Section 6.2. Part of the second core was selected at random from the older section of the coral skeleton (presumed by density couplet counting to pre-date major environmental change either on the mainland or at Green Island). This was then analysed for a twenty-year period (1883-1902) using similar techniques. The results from these two sample sets were statistically compared with results from the same period for sample sets taken from No Name, Batt, Upolu and Brook Islands Reefs. The coring process missed the vertical growth axis in the samples taken from Hastings and Thetford Reefs. Therefore, material before the turn of the century was not available for these two reefs.

5.2.2 Statistical Analysis

All statistical analyses were carried out using JMP statistical computer software (Version 2, SAS Institute). The dependent variables in this study were weight-percent calcium, strontium, magnesium, potassium and sodium. All variables were tested for the assumptions of normality (Shapiro-Wilk test, Zar 1984) and equality of variance (Bartlett's Test, Zar 1984).

Multivariate outliers were identified by Mahalanobis distance (Tabachnick & Fidell 1983) of each point from the multivariate mean. This method of estimating outliers is best used to identify data input errors, or for the identification of outliers. Outliers may be important in their own right, but may, if left in the data set, produce incorrect, or false, estimates of the base structure of the data set. It is, therefore, a useful tool in that it identifies outliers which may incorrectly bias the results, and as such allows outliers to be removed or retained, depending on the focus of the examination. All outliers were checked for data input errors, found correct, and were not excluded from statistical examination.

The composition of each sample set was analysed by multivariate analysis of variance (MANOVA) using Pillia's Trace test statistic (Tabachnick & Fidell 1983). Canonical Discriminatory Analysis (CDA) was employed to identify significant variation over location. CDA is an ordination technique employed to compare group means based on a variety of predictor variables on a reduced space 2-D display (Tabachnick & Fidell 1983). Variables selected for multivariate analysis were those most likely to be associated with environmental parameters (calcium, strontium and magnesium). The CDA plot presents multivariate 95% confidence ellipsoids around each centroid mean (multivariate least-square means) (Mardia *et al* 1979). Biplot rays show the directions of the original response variables in the reduced test space.

Analysis of variance (ANOVA; Zar 1984) identified significant variation in the concentration of individual elements among locations. Means comparisons using the Tukey-Kramer HSD test (Zar 1984) differentiated locations based on the relative amounts of each element.

5.3. RESULTS

The results from geochemical analyses using Atomic Absorption Spectrometry are shown in Appendix H. MANOVA results are described in the text and the resulting CDA biplot is displayed in Figure 15. Analysis of variance results are presented in Appendix I and displayed where appropriate within the text. Interpretation of the results will follow in section 5.6.

(a) Multivariate Analysis:

MANOVA detected a significant Pillai's Trace statistic for the effect of location ($F=21.2199$; $Dfn=15$; $Dfd=315$; $P<0.001$). The discrimination of locations including both Green Island sample sets is presented in Figure 15. Canonical axes 1 & 2 (Can 1 & Can 2) accounted for 86.9% and 12.5% of the total multivariate variation respectively. The third canonical axis was found to have little discriminatory power.

CDA resulted in no significant difference in the two Green Island sample sets as their 95% ellipsoids overlap. These two sample sets at the same location were discriminated from all other locations. The sample set replicates from Green Island are primarily discriminated from the other sample sets on the bases of higher levels of strontium. Calcium in this analysis, as shown by its small vector length, has little discriminatory power. The Brook Island sample set is discriminated from the other locations by low levels of strontium and magnesium. The sample sets from Upolu and No Name Reefs are not discriminated from each other. The Batt Reef sample set is discriminated from the other sample sets primarily by high levels of magnesium.

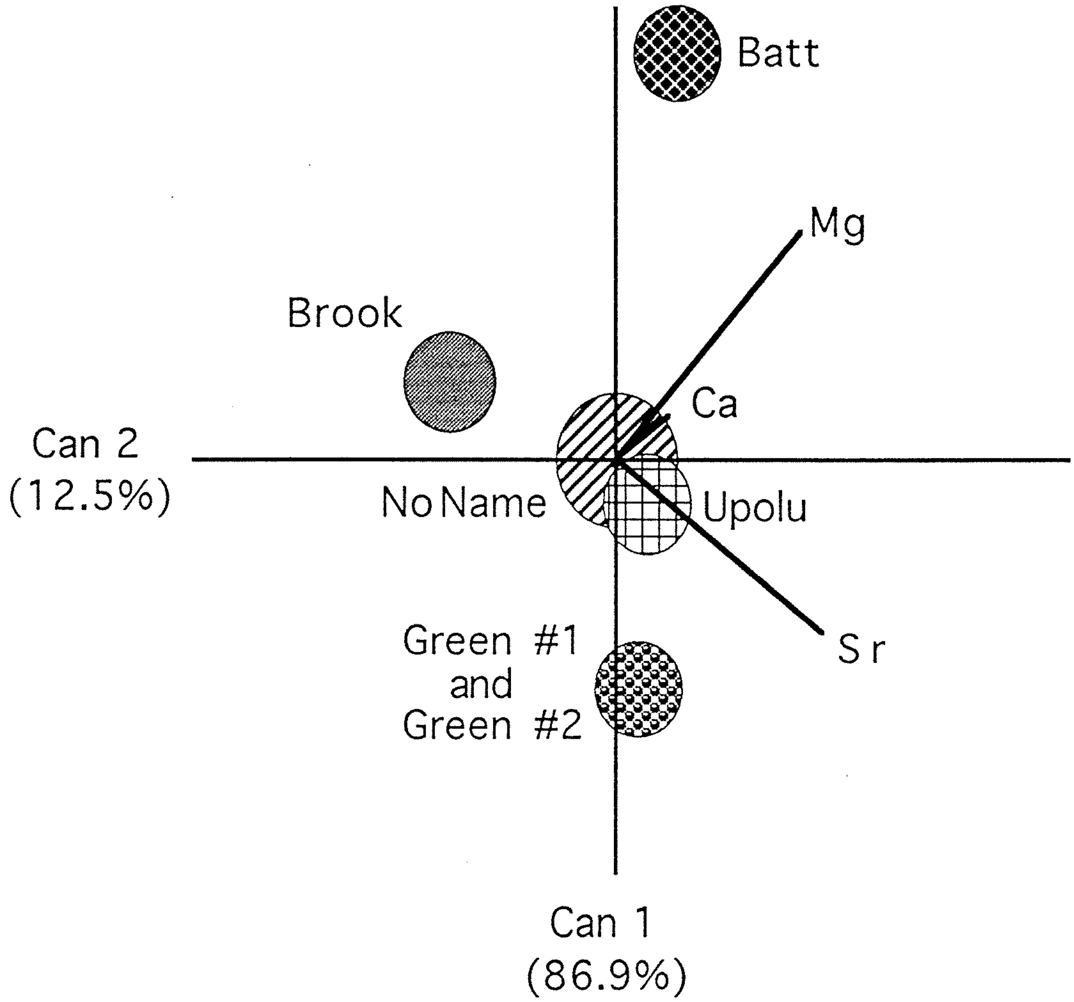

Figure 15: Biplot of multivariate centroid means with associated 95% confidence ellipsoids on the first two canonical axes exploring variation in chemical composition among locations, for the period 1883-1902.

(b) Univariate analysis (ANOVA):

ANOVA's revealed significant ($P < 0.001$) differences among sites for all variables analysed. Comparison of means showed significant variation in the chemical composition of the sample sets among locations. This difference was inter-reefal, with no significant difference between the two Green Island sample sets for any of the variables examined (Appendix H).

(i) Calcium:

Percentage calcium varied significantly between locations (F=16.8275, P<0.001, Appendix I). Comparison of means showed that only the sample set from Batt Reef differed significantly from the other sample sets (Figure 16).

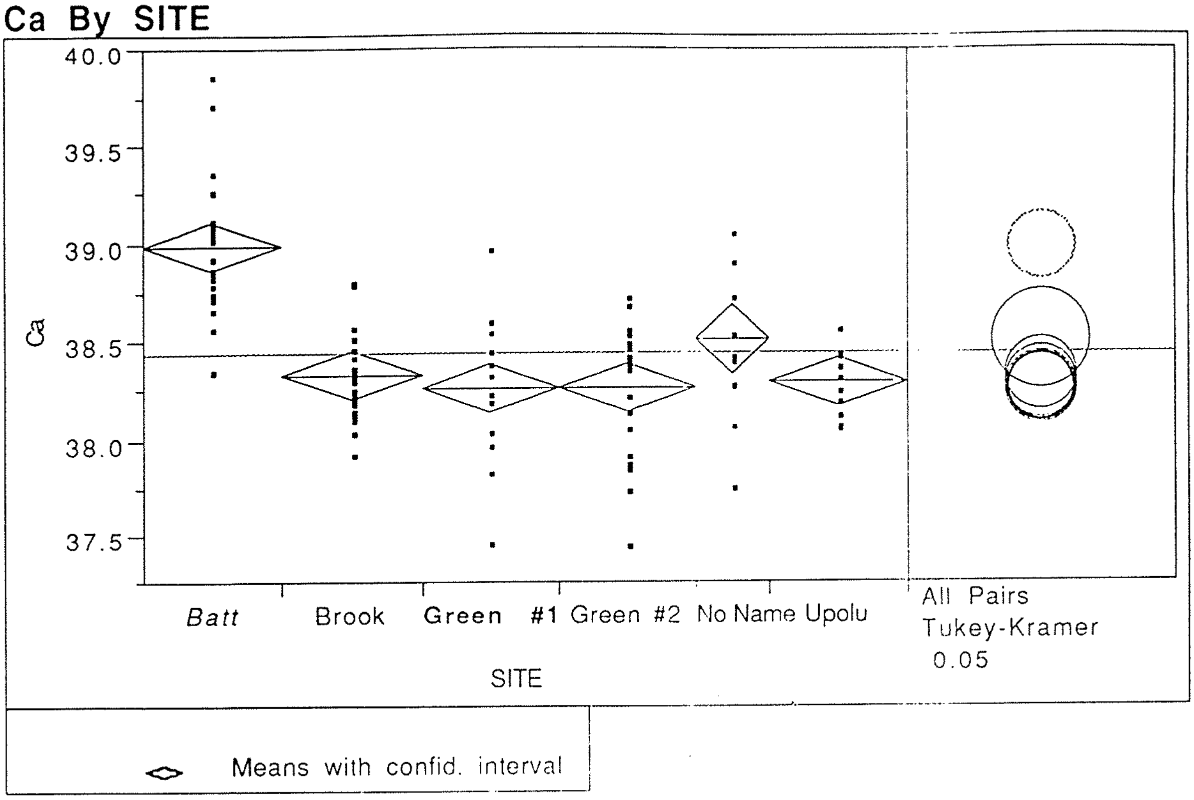

Figure 16: Graph showing mean calcium levels over time (1883-1902) for each location ± 95% confidence intervals. Means comparisons presented were assessed using Tukey-Kramer HSD Test (α=0.05).

*(ii) **Strontium:***

Percentage strontium varied significantly between locations (F=99.5505, P<0.001, Appendix I). Comparison of means failed to detect a significant difference between the two sample sets from Green Island, but identified these two sample sets as significantly different from all other sample sets (Figure 17). Tukey-Kramer HSD Test failed to detect a significant difference among all other samples.

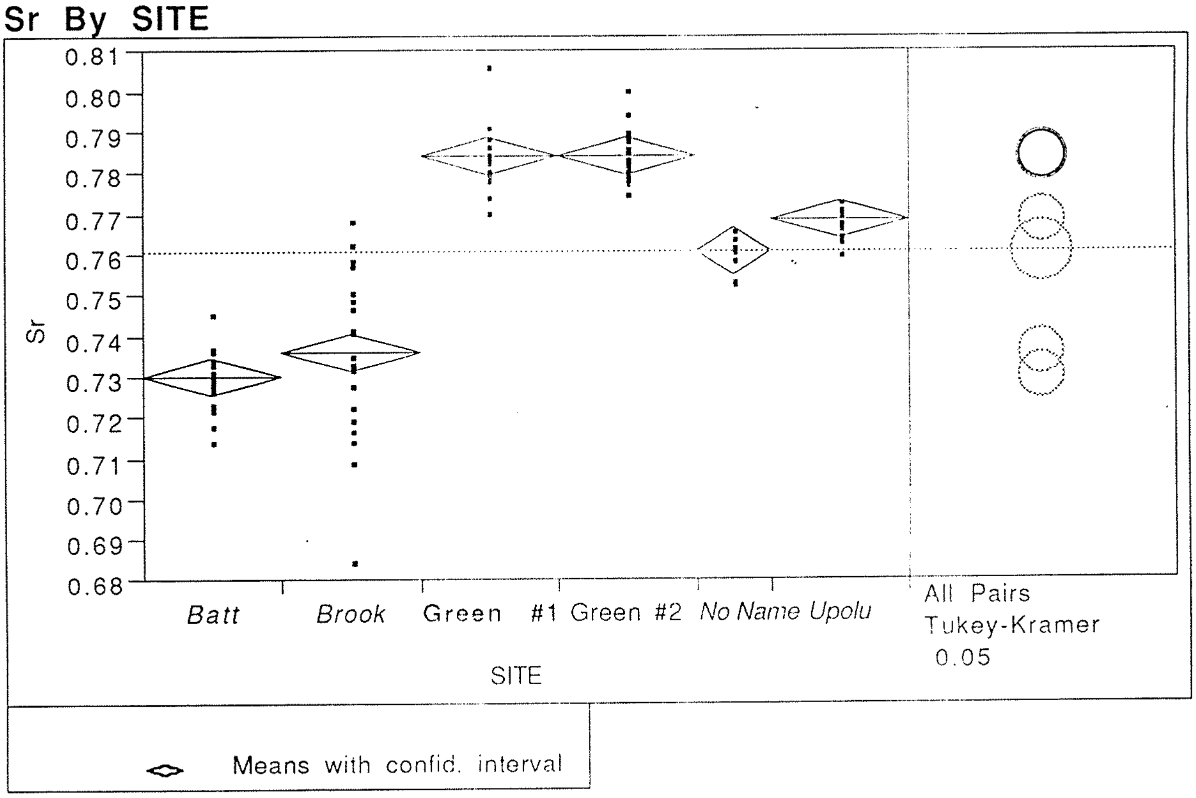

Figure 17: Graph showing mean strontium levels over time (1883-1902) for each location ± 95% confidence intervals. Means comparisons presented were assessed using Tukey-Kramer HSD Test (α=0.05).

(iii) Magnesium:

Percentage magnesium varied significantly among locations (F=110.9287, P<0.001, Appendix I). Tukey-Kramer HSD Test failed to detect a significant difference between the two sample sets from Green Island, but identified these two sample sets as significantly different from all other samples. No significant difference could be detected among the sample sets from No Name Reef, Upolu and Brook Island Reefs. The sample set from Batt Reef was significantly different from all other sample sets (Figure 18).

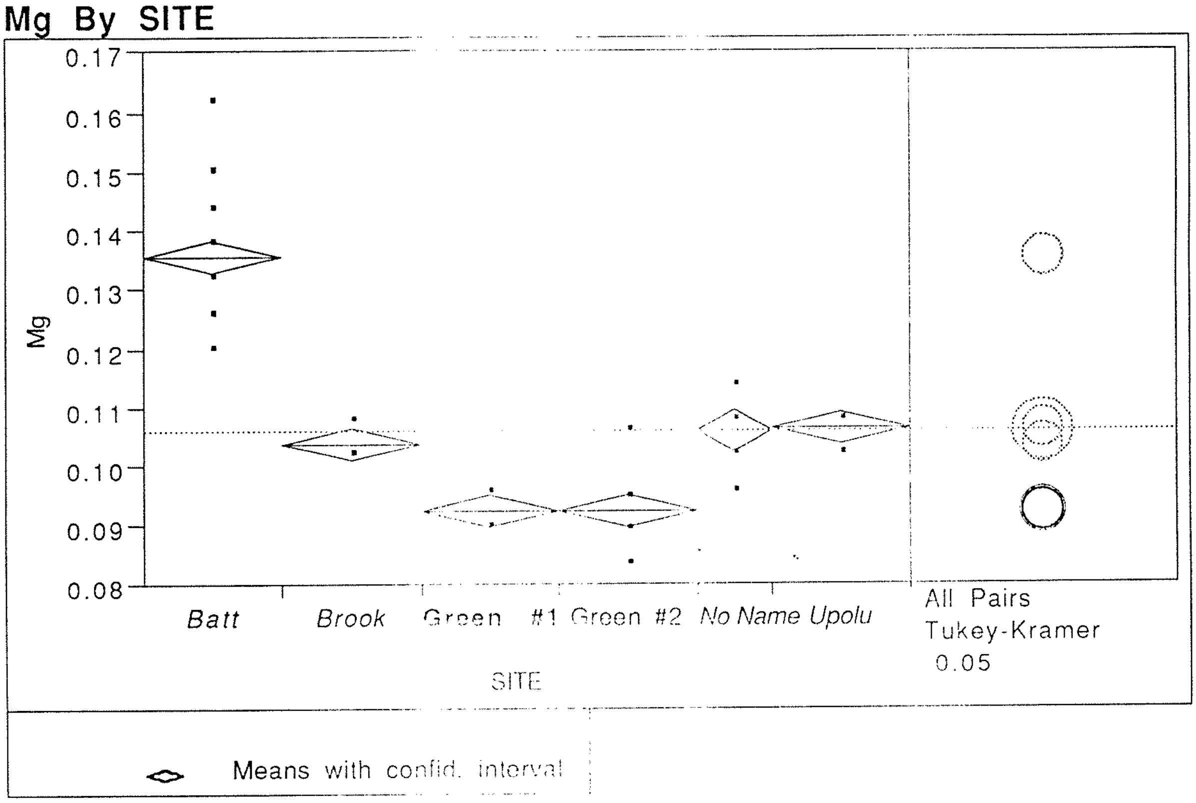

Figure 18: Graph showing mean magnesium levels over time (1883-1902) for each location ± 95% confidence intervals. Means comparisons presented were assessed using Tukey-Kramer HSD Test (α=0.05).

5.4. *DISCUSSION*

(a) Multivariate analysis:

This statistical analysis of chemical data covered a single twenty-year period considered to pre-date any major human impact. Data from six locations was incorporated, including two closely located sample sets from Green Island. The results suggest that with respect to the three elements most frequently used for the reconstruction of paleoenvironmental information from calcium carbonate material (calcium, strontium and magnesium), the two sample sets taken from the same reef (Green Island #1 and #2) are not significantly different from each other. From the statistical tests carried out, the geochemistry of the two sample sets from Green Island can be considered uniform.

(b) Univariate analysis:

While intra-reefal uniformity can be shown statistically, when each element is examined individually, inter-reefal relationships are less clear. For the three elements used in this section of the study (calcium, magnesium and strontium), only the sample set from Batt Reef was consistently and significantly different. This sample set contained many hiatuses and boring algae and will be discussed further in Chapter 6.

Inter-reefal comparison shows -

(1) For the element calcium (Figure 16), only the Batt Reef sample set is significantly different from the other locations.

(2) Strontium content (Figure 17) falls into three groups, with each group significantly different from the others -

  (a) the two Green Island sample sets (not significantly different from each other),
  (b) the Batt Reef and Brook Island samples, and
  (c) the sample sets from Upolu and No Name Reef (not significantly different from each other).

(3) Magnesium concentration (Figure 18) also falls into three groups, though these groupings are less defined, and in two cases are different from the strontium groupings:

  (a) The two sample sets from Green Island are not significantly different from each other.
  (b) The sample set from Batt Reef is significantly different from all other sites.

(c) The sample sets from the Brook Islands, No Name Reef and Upolu Reef are not significantly different from each other.

In addition, inconsistencies in the annual record suggest that localised, micro-environmental conditions exist and should be recognised when attempting to reconstruct environmental records from the coral skeleton. An example of these inconsistencies is shown in Figure 19.

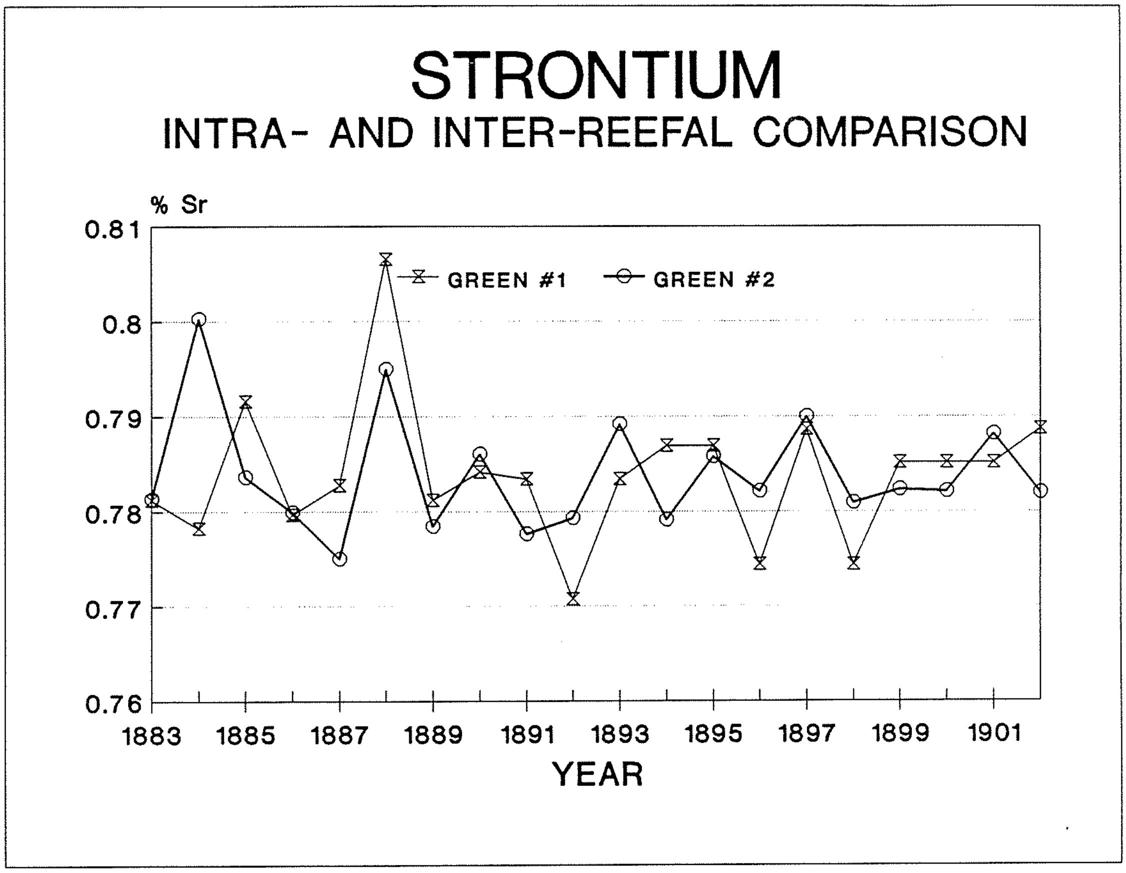

Figure 19: Localised variations in the timing and intensity of the strontium concentration in the Green Island Porites core.

(c) General:

Based on group membership of the variables calcium, strontium and magnesium (Figure 15), this analysis clearly shows that the sample sets examined in this study are separated by their location on the continental shelf. Groups of samples from the inner- and inner/mid-shelf locations (Green Island, Batt Reef, Brook Islands) are isolated from the mid-shelf and outer-shelf sample sets (Upolu Reef and No Name Reef respectively), but are also isolated from each other. However, while there is no clear discrimination between the mid- and outer-shelf sample sets, the contribution of the various elements to each sample set varies with location. This suggests that each reef is an entity, interacting with the environment in an interplay unique to that area.

5.5 CONCLUSIONS

The study considered a micro-environmental, or intra-reefal, comparison of two sample sets from the same reef with sample sets taken from a number of other reefs over a twenty-year period. From the results it is concluded that the uniformity of the two Green Island sample sets is such that single core comparisons, proven to be statistically representative (with minor micro-environmental disturbance), allows inter-reefal, comparative examinations to be based on examination of a single core.

CHAPTER 6

GEOCHEMICAL RECORDS RETAINED BY MASSIVE CORALS

(B)

REGIONAL VARIABILITY AND HUMAN IMPACT?

6.1 INTRODUCTION

Chemical and morphological variations in the skeleton of annually banded massive corals (Knutson *et al* 1972) have previously been used to reconstruct historical evidence of environmental variability over time (e.g. Druffel 1981, 1982; Schneider & Smith 1982; Druffel & Suess 1983; Isdale 1984; Shen *et al* 1987; Lea *et al* 1989; Linn *et al* 1990; Druffel & Griffin 1993; Dunbar & Cole 1993). In an historical perspective, therefore, use of the coral skeleton to hindcast environmental conditions operating at the time of skeletal formation, should be limited only by the age of the coral skeleton. This Chapter examines the possibility that variations in water quality, particularly those associated with increased phosphate availability, are reflected in the chemical properties of the coral skeleton and that variations in these properties provide useful information on anthropogenic influence.

To examine this possibility, core samples were removed from reefs at varying distances from the coast. The samples were taken across the width of the Continental Shelf, primarily in the Cairns section of the Great Barrier Reef Marine Park. For the reasons stated previously (Chapters 1,2 & 3), reefs selected for sampling were adjacent to, and radiating out from, the mouth of the Barron River (Green Island, Thetford, Upolu, Batt and Hastings Reefs). Two additional samples were taken, one to the north of the study area in a location presumed to be relatively pristine (No Name Reef), and another to the south of the study area (Brook Islands Reef) for geographical contrast.

Width of the Continental Shelf differs considerably along the Queensland coast. Descriptive terms "inner-, mid- and outer-shelf" infer a commonality of distance along the length of the Continental Shelf. These terms lack any linear connection when a "mid-shelf reef" in one area is further from the shore than an "outer-shelf reef" in another. Use of such terms is particularly ambivalent when the research is examining terrestrial influences. For this study, the Continental Shelf has been graded according to Maxwell's (1968) isobaths -

(1) coast to 16 fathom isobath - inner-shelf,
(2) between 16 and 22 fathoms isobaths - mid-shelf, and
(3) from the 22 fathom isobath to the edge of the shelf - outer-shelf.

Table 6.1: ***Period covered by each sample set and the location of the sample sets on the Continental Shelf.***

Sampling Location	*Shelf Location and Legend*	*Period Covered by the Sample Set*
No Name Reef	*# Outer-shelf*	*1892-1987*
Hastings Reef	*#* Outer/mid-shelf*	*1913-1987*
Thetford Reef	** Mid-shelf*	*1930-1987*
Upolu Reef	** Mid-shelf*	*1827-1987*
Batt Reef	**@ Inner/mid-shelf*	*1814-1987*
Green Island Reef	**@ Inner/mid-shelf*	*1876-1987*
Brook Islands Reef	*@ Inner-shelf*	*1853-1987*

To examine regional variability in the study area, individual cores were removed from the centre of seven actively growing *Porites* colonies at No Name, Hastings, Batt, Upolu, Thetford, Green Island and Brook Islands Reefs. Each core was slabbed and density couplets defined by X-radiography (Knutson *et al* 1972). Each couplet was then presumed to represent one year of growth. The samples were dated by counting the density couplets backwards from the time of collection (Table 6.1). The sample was then sub-sampled by dissecting each dated couplet from the remainder of the set.

Each sample (presumed to represent one annual growth increment) within the complete sample set, was then analysed for percent calcium, strontium, magnesium, potassium, sodium and iron using Atomic Absorption Spectrometry (AAS) according to the procedures outlined in Appendix A.

6.2 CHARACTERISTICS OF THE ELEMENTS ANALYSED

The ionic radii used throughout the text are generally for ions in 6-fold coordination and are taken from Henderson (1982), who tabulated the values obtained by Shannon and Prewitt (Prewitt 1980, reported in Henderson 1982).

Besides the elements most frequently used for the reconstruction of paleoenvironmental information (calcium, magnesium and strontium), this study will consider briefly other elements easily detected in the coral skeleton. These elements have been indirectly associated with changing environmental conditions (potassium, sodium and iron). The locations of these three elements in the aragonitic coral skeleton are not known, and variations in the concentration of these trace elements in coral skeletons have received little attention. Variations could conceivably be related to where the elements are held in the skeleton and associated material. Such elements could be held within the organic matrix, in which case there is no direct reason to presume incorporation into the carbonate skeleton will be environmentally controlled. However, many researchers (e.g. Chillingar 1953; Chave 1954; Chillingar 1956; Mitchell 1961) suggest environmental and/or chemical associations related to variations in the seawater column may indirectly affect the concentration of these elements in the structure of the coral skeleton.

6.2.1 Calcium:

Approximately the top 100 m of surface open ocean water is supersaturated with respect to calcium carbonate (Turekian 1968; Berner 1976, 1978). Yet most of the $CaCO_3$ found in marine sediments is derived from the biogenic secretion of skeletal carbonates and not from a simple inorganic precipitation (e.g. Milliman 1974a). Two explanations to account for the lack of inorganic precipitation have included -

(1) the coating of precipitating nuclei with non-nucleating organic material caused by the ingestion and defecation of sedimentary particles by marine organisms,

(2) the poisoning of potentially favourable nuclei with various substances obtained from seawater (Simkiss 1964b; Pytkowicz 1965; Chave & Suess 1970; Berner *et al* 1978).

The most commonly implicated substances inhibiting the spontaneous precipitation of calcium carbonate are magnesium (Pytkowicz 1965; Bischoff 1968; Berner 1975), dissolved organic compounds (Chave & Suess 1970), and phosphate (Simkiss 1964b; Pytkowicz 1973; Berner *et al* 1978; Mucci 1986; Walter 1986; Burton & Walter 1990). By inference this suggests that -

(1) the calcium carbonate content of the coral skeleton will vary with the addition of organic compounds, either by the reduction of the amount precipitated per unit volume (see Chapter 4), or by changing the composition of the carbonate phase itself, and/or

(2) the crystallography of the aragonitic material will be modified by the addition of crystal 'poisons' (Simkiss 1964b).

6.2.2. Strontium:

Strontium is the major trace element in seawater with an abundance of approximately 8 ppm. Because of its abundance in carbonate phases, and its relative ease of analysis using comparatively simple techniques (including Atomic Absorption Spectrometry), strontium has attracted attention as a possible source of environmental and ecological information (Weber 1973).

Strontium has a similar ionic radius to calcium (0.118 nm and 0.1 nm respectively) and can readily substitute for calcium in the aragonite lattice where the cation is in a relatively large 9-fold co-ordination site. It is less able to enter a calcite based structure where the 6-fold co-ordination metal atom site prefers the incorporation of divalent ions with an ionic radius of less than 0.1 nm. Consequently, calcite based structures, including high magnesian calcites, tend to have strontium concentrations appreciably below that of aragonite.

Laboratory experiments have shown that the incorporation of strontium into aragonite is temperature dependent (Kitano *et al* 1971; Houck *et al* 1977) with the concentration of the strontium in the skeleton negatively correlated to the temperature of the water (Weber 1973). However, while temperature is considered the primary control on the concentration of strontium in aragonite, other factors need to be considered. For example, growth kinetics, changes in the competing activities of calcium and strontium, and related changes in the distribution coefficient have also been shown to influence the strontium content of calcium carbonates (see Kinsman 1969; Kitano *et al* 1971; Houck *et al* 1977; Weber 1973; Smith *et al* 1979; Schneider & Smith 1982).

Therefore, correlations between strontium content and environmental parameters have not been consistent. Skeletal strontium content has been variously described as -

(1) independent of biological factors (Kinsman 1969),

(2) dependent on the temperature shift of a chemical distribution coefficient between seawater and aragonite (Kinsman 1969),

(3) dependent only on phylogenetic physiological differences to shift the skeletal Sr:Ca ratio of the skeleton from that of seawater (Thompson & Livingston 1970),

(4) independent of temperature with no significant difference between content in deep and shallow waters (Livingston & Thompson 1971),

(5) relative to the calcium content of the skeleton (Sr:Ca ratio) and almost identical to the Sr:Ca of sea water (Livingston & Thompson 1971),

(6) dependent on species-specific controls exerted by coral metabolism and rate of skeletogenesis (Livingston & Thompson 1971),

(7) dependent on temperature, biological controls and growth rate (with growth rate influenced by temperature, with a negative correlation to water depth (Weber 1973),

(8) predominantly inorganically initiated, independent of growth rate and light intensity, and dependent on temperature (Houck *et al* 1977),

(9) temperature dependent with relation to the Sr:Ca ratio of the skeleton, with species effects possible (Schneider & Smith 1979).

(10) environmentally controlled, probably by temperature, but with a 'lag' between the environmental parameter and skeletal strontium content (McCulloch *et al* 1993).

6.2.3. Magnesium:

Associations between environmental conditions and skeletal magnesium content have been reported. Magnesium, however, has a relatively small ionic radius (0.072 nm) compared with calcium (0.1 nm) and will not easily substitute into the aragonite structure. Because of this incompatibility, the magnesium content of aragonite is usually very low (approximately 0.1%) and there is doubt as to where this element resides in the coral skeletal structure. Possibilities are -

(a) within the crystal structure,
(b) associated with the surfaces of the crystals,
(c) associated with the organic material, or
(d) contained in the high magnesian calcite remains of boring algae.

In calcite, the magnesium is structurally compatible and low magnesian calcite is defined as usually less than 4 Mol% (Graf 1960). High magnesian calcite, however, is typically biogenically precipitated and more than 8 Mol% $MgCO_3$ may be present, with the $MgCO_3$ content temperature dependent within a similar species and genus (Chave 1954). Therefore, the Ca:Mg ratio in carbonates will be largely dependent on the mineralogical form of the carbonate.

Therefore, as with strontium, correlations between magnesium content and environmental parameters have not been consistent, and skeletal magnesium content has been variously reported as -

(1) **Temperature dependent,** with an inverse "hyperbolic" relationship between the Ca:Mg ratio in calcium carbonate skeletons and the temperature of the water (Chillingar 1953; Chave 1954).

(2) **Partially controlled by the deposition rate of the calcium carbonate skeleton.** Chillingar (1962) suggested that the "hyperbolic" shape of the "Ca:Mg ratio versus temperature" curve was due to the rapid rate of precipitation of $CaCO_3$ at higher temperatures, enabling $CaCO_3$ to trap more $MgCO_3$. Experimental results of Kitano (1967) also suggested that the formation and incorporation of magnesium into calcium carbonates was assisted by the rate of deposition of the calcium carbonate skeleton.

(3) **pH dependent.** In controlled laboratory experiments Chillingar (1962) found that changes to the Ca:Mg ratio of the precipitates could also be attributed to varied pH levels. Tissue pH may alter as hydrogen ions come into direct contact with added organic material, or as hydroxide ions result from the complex formation of calcium and/or magnesium in the presence of added organic material (e.g. Kitano & Hood 1965; Chillingar 1962). Therefore, Chillingar suggested that organisms may attain high pH (>9.49) within their tissues and thus precipitate magnesium as brucite ($Mg(OH)_2$), which, in some respects, is structurally similar to calcite.

(4) **Proportional to the Ca:Mg ratio of sea water.** Chillingar (1956) suggested that it may be possible for invertebrates to assimilate more magnesium in environments having higher concentrations of magnesium. The experimental

work of Kitano (1967) also suggested that the formation and incorporation of magnesium into calcium carbonates was assisted by the concentration of magnesium ions in the medium where the carbonate was precipitated.

(5) **Dependent on organic compounds in the seawater.** Chave (1965) and Chave & Suess (1970) noted that naturally occurring organic compounds inhibited reactions between carbonate minerals and seawater. Kitano (1967) showed that under experimental conditions, the formation and incorporation of magnesium into calcium carbonates was assisted by the concentration of organic materials in the medium.

6.2.4 Potassium:

With an ionic radius of 0.138 nm, K^+ is compatible with the aragonite structure, but if it is to substitute within the lattice, then co-operative charge compensation must occur, possibly via OH^- or HCO_3^- for CO_3^{2-}.

6.2.5. Sodium:

It is also possible for Na^+ to replace Ca^{2+} in the lattice as they are of similar ion size (0.09 nm and 0.1 nm respectively), but again, charge compensation must be made for CO_3^{2-}, possibly via HCO_3^- or OH^-.

6.2.6 Iron

Iron (ionic radius 0.076 nm), as with magnesium, is usually considered more compatible with the structure of calcite, rather than that of aragonite. High concentrations of iron are found in ferromanganese stained pelagic corals and in near-shore corals containing much detritus. In clean corals, the low concentrations of iron suggest that the corals discriminate against iron with respect to calcium uptake from seawater (Livingston & Thompson 1971). Incorporation into the coral skeleton, therefore, is probably a secondary addition, associated with the deposition of terrestrial sediments into skeletal cavities.

6.3. ANALYSIS

6.3.1 Chemical Analysis

Methodology is given in Appendix A.

6.3.2 Statistical analysis:

Statistical methods used in this study were outlined in Chapter 5. The dependent variables in this section of the study are weight-percent calcium, strontium, magnesium, potassium, sodium and iron for the univariate analysis. Variables selected for multivariate analysis are those most frequently used as proxy environmental indicators (calcium, strontium and magnesium).

6.4. RESULTS

The results from geochemical analyses using Atomic Absorption Spectrometry are shown in Appendix J. MANOVA results are described in the text and the resulting CDA biplot is displayed in Figure 20. ANOVA results are presented in Appendix I and graphically displayed where appropriate within the text. Interpretation of the results will follow in section 6.5.

(a) Multivariate Analysis:

MANOVA detected a significant Pillai's Trace Statistic for the effect of location (F=112.9974; Dfn=18; Dfd=2394; P<0.001). The discrimination of locations is presented in Figure 20. Canonical axis 1 (Can 1) and canonical axis 2 (Can 2) accounted for 83.2% and 11.6% of the total multivariate variation respectively. The third canonical axis (Can 3) was found to have little discriminatory power.

The biplot shown in Figure 20 discriminates the multivariate centroid means of the inner-and inner/mid-shelf sample sets from Green Island, Brook Islands and Batt Reefs from all locations. The sample set from Green Island is primarily discriminated on the basis of higher levels of strontium and low levels of magnesium. Due to its small vector length, calcium in this analysis has little discriminatory power. The Brook Islands sample set is discriminated from the other locations by low levels of both strontium and magnesium. High levels of magnesium discriminates between Batt Reef and the other samples. Upolu, Thetford, Hastings and No Name Reef sample sets are not discriminated from each other (Figure 20).

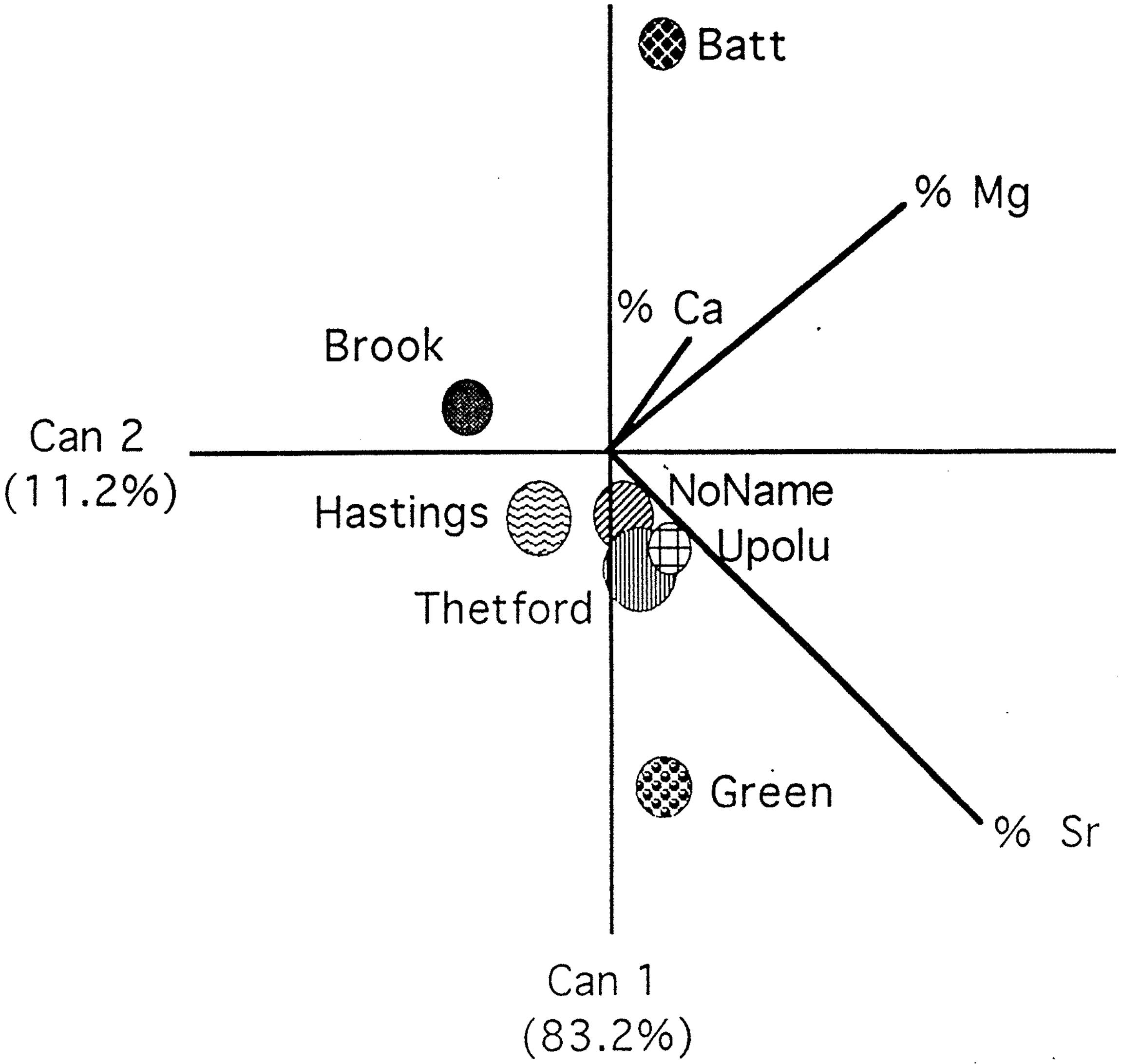

Figure 20: Biplot of multivariate centroid means with associated 95% confidence ellipsoids on the first two canonical axes exploring variation in chemical composition among locations for sample sets covering the time span n-1987.

(b) Univariate analysis:

ANOVA'S revealed statistically significant ($P<0.001$) differences among locations for all variables analysed.

(i) Calcium

Results of geochemical analysis are shown in Appendix J and summarised in Table 6.2. Univariate analysis of variance results are given in

Percentage calcium showed a statistically significant variation between locations (F=98.1495, P<0.001, Appendix I). All calcium means are 1 to 1.8 wt% below the theoretical value of pure $CaCO_3$ (40.0480 wt%). Comparison of means failed to detect a significant difference among the sample sets from Upolu, Brook Islands and Green Island Reefs, but detected a statistically significant difference between all other samples.

The highest calcium values were shown to be in the Batt Reef sample, followed by the sample sets from the mid- to outer-shelf locations of Thetford, Hastings Reefs (no statistically significant difference from each other). These two reefs show a statistically significant difference from the sample set from No Name Reef that is significantly different from the sample sets from Upolu, Green Island and Brook Islands Reefs. These three sample sets are not significantly different from each other.

Table 6.2: Summary statistics for calcium.

SAMPLING LOCATION	*Average Calcium in Each Sample Set (wt%)*	*Standard Deviation for Each Sample Set*	*Standard Error for Each Sample Set*	*Working Values*	*Number of Samples in Each Sample Set*
# No Name Reef	*38.4381*	*0.3180*	*0.0326*	*38.44 ± 0.32*	*95*
# Hastings Reef*	*38.6426*	*0.2871*	*0.0334*	*38.64 ± 0.29*	*74*
** Thetford Reef*	*38.8011*	*0.3728*	*0.0494*	*38.80 ± 0.37*	*57*
** Upolu Reef*	*38.4252*	*0.4277*	*0.0338*	*38.43 ± 0.43*	*160*
**@ Batt Reef*	*39.0488*	*0.3662*	*0.0283*	*39.05 ± 0.37*	*167*
**@ Green Island Reef*	*38.2776*	*0.4112*	*0.0390*	*38.28 ± 0.41*	*111*
@ Brook Islands Reef	*38.3289*	*0.3285*	*0.0284*	*38.33 ± 0.33*	*134*
Pure $CaCO_3$	*40.0480*			*40.05*	

 # Outer-shelf reefs
Mid/outer-shelf reefs*
** Mid-shelf reefs*
**@ Inner/mid-shelf reefs*
@ Inner-shelf reefs

NB - All calcium results are 1 - 1.8 wt% below the theoretical value of pure $CaCO_3$.

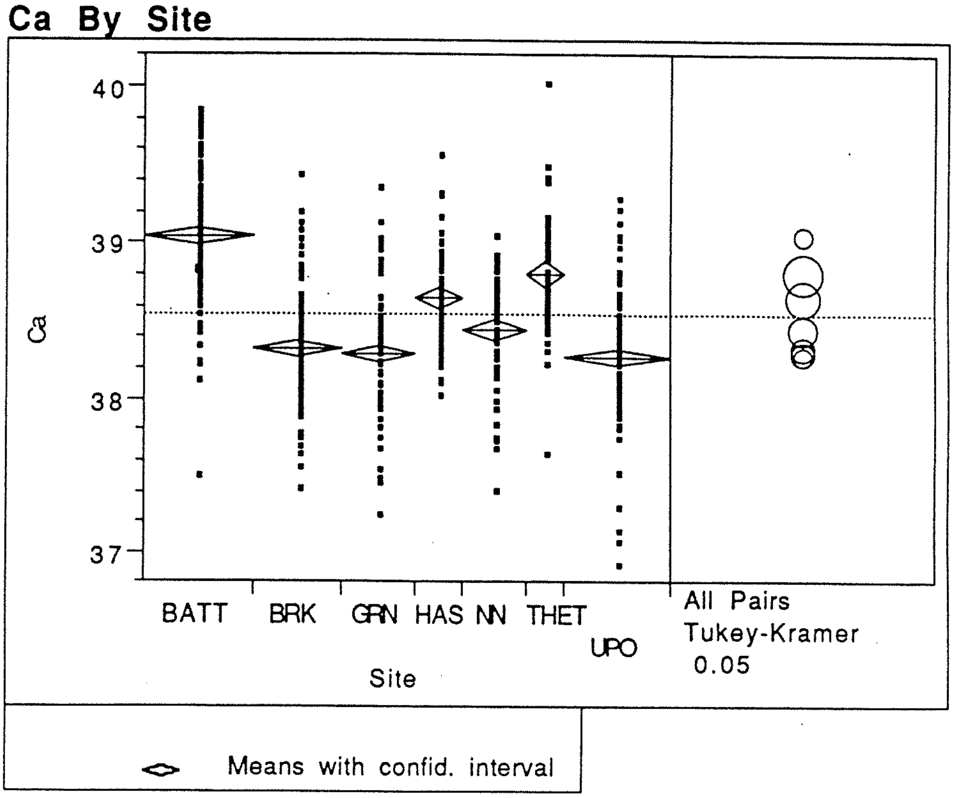

Figure 21: Graph of mean calcium concentration for each location over time (n-1987), ± 95% confidence intervals. Means comparisons presented were assessed using Tukey-Kramer HSD Test (α=0.05).

(ii) Strontium

Results of the geochemical analysis are shown in Appendix J. Summary statistics for strontium are given in Table 6.3. Weber (1973) collected an extensive strontium data base from Australia's Great Barrier Reef and from this data produced a strontium based thermometer (68 ppm strontium variation per 1°C temperature change). For comparative purposes, Table 6.3 includes the results from Weber's study of Great Barrier Reef corals (Weber 1973). Univariate analysis of variance results are given in Appendix I and displayed in Figure 22.

Averaged strontium concentrations are similar to those presented by Weber (1973). The considerably lower standard deviations of the present study reflect large sample size of this data set, and the use of a single coral species for chemical analysis (Table 6.3).

Table 6.3. Summary statistics for strontium, all reefs.

SAMPLING LOCATION	Average Strontium Content of Each Sample Set (wt%)	Standard Deviation for Each Sample Set	Standard Error for Each Sample Set	Working Values	Number of Samples in Each Sample Set
# No Name Reef	0.7627	0.0082	0.0008	0.7630 ± .008	95
#* Hastings Reef	0.7581	0.0079	0.0009	0.7580 ± .008	74
* Thetford Reef	0.7697	0.0117	0.0015	0.7700 ± .012	57
* Upolu Reef	0.7674	0.0066	0.0005	0.7674 ± .007	160
*@ Batt Reef	0.7314	0.0119	0.0009	0.7310 ± .012	167
*@ Green Island Reef	0.7861	0.0078	0.0007	0.7860 ± .008	111
@ Brook Islands Reef	0.7432	0.0158	0.0015	0.7430 ± .016	134
Data collected by Weber (1973) -					
Heron Island	0.7516	0.0247	0.0050		24
All localities	0.7372	0.0309	0.0024		164

 # Outer-shelf reefs
Mid/outer-shelf reefs*
** Mid-shelf reefs*
**@ Inner/mid-shelf reefs*
@ Inner-shelf reefs

Percentage strontium showed a statistically significant difference between locations (F=347.9876, α=0.001; Appendix I). Highest values were found in the sample set from Green Island, followed by the sample sets from Thetford, Upolu, No Name, Hastings, Brook Islands and Batt Reefs. Comparison of means failed to detect a statistically significant difference between the sample sets from Thetford and Upolu Reefs. Statistically, all other sample sets were significantly different from each other as well as to the Thetford and Upolu Reef samples. The inner- and inner/mid-shelf locations of Batt, Brook Islands and Green Island Reefs are isolated, both from each other, and from all other sample sets (Figure 22).

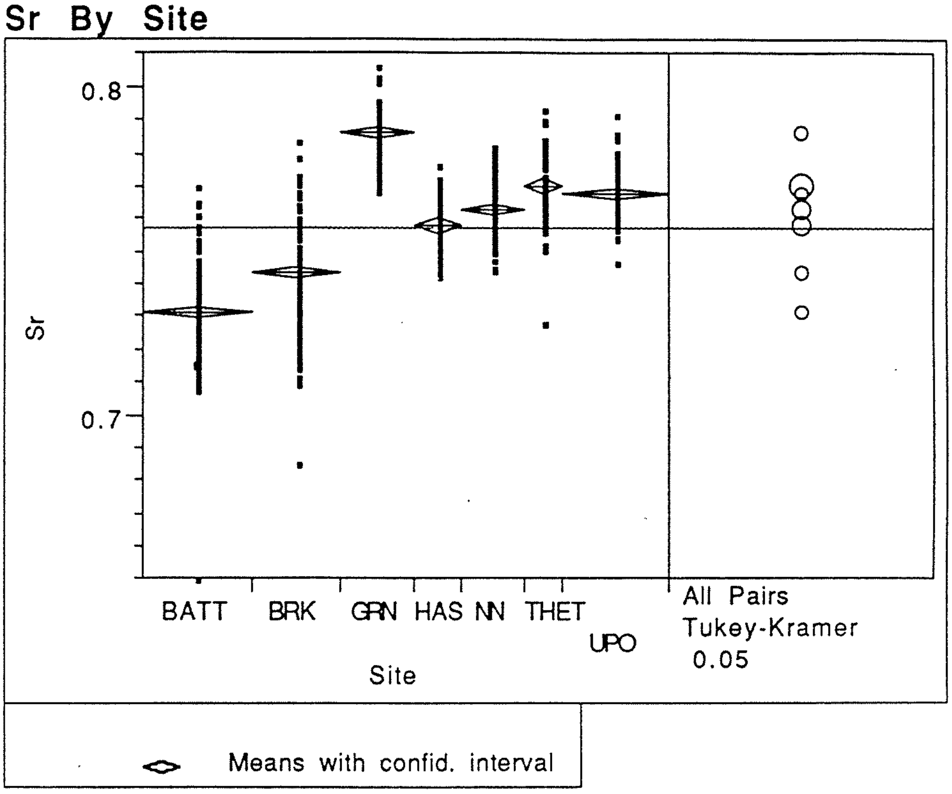

Figure 22: Graph of mean strontium concentration for each location over time (n-1987), ± 95% confidence intervals. Means comparisons presented were assessed using Tukey-Kramer HSD Test (α=0.05).

(iii) Magnesium

The results of the geochemical analysis are given in Appendix J and summarised in Table 6.4. Univariate analysis of variance results are shown in Appendix I and displayed graphically in Figure 23.

Table 6.4: Summary statistics for magnesium

SAMPLING LOCATION	*Average Magnesium in Each Sample Set (wt%)*	*Standard Deviation for Each Sample Set*	*Standard Error for Each Sample Set*	*Working Values*	*Number of Samples in Each Sample Set*
# No Name Reef	*0.1054*	*0.0049*	*0.0005*	*0.105 ± 0.005*	*95*
# Hastings Reef*	*0.0988*	*0.0045*	*0.0005*	*0.099 ± 0.005*	*74*
** Thetford Reef*	*0.0995*	*0.0028*	*0.0004*	*0.100 ± 0.003*	*57*
** Upolu Reef*	*0.1087*	*0.0035*	*0.0003*	*0.109 ± 0.004*	*160*
**@ Batt Reef*	*0.1250*	*0.0087*	*0.0007*	*0.125 ± 0.009*	*167*
**@ Green Island Reef*	*0.0957*	*0.0133*	*0.0013*	*0.096 ± 0.013*	*111*
@ Brook Islands Reef	*0.1044*	*0.0051*	*0.0004*	*0.104 ± 0.005*	*134*

 # Outer-shelf reefs
Mid/outer-shelf reefs*
** Mid-shelf reefs*
**@ Inner/mid-shelf reefs*
@ Inner-shelf reefs

Percentage magnesium varied significantly among locations (F=246.7229, α=0.001, Appendix I; Figure 23). Mean magnesium values were considerably higher in the sample set from Batt Reef, followed by the sample sets from Upolu, No Name, Brook Islands, Thetford, Hastings and Green Island Reefs. Comparison of means failed to detect a significant difference between sample sets from No Name and Brook Islands Reefs, or between Thetford and Hastings Reefs. There was a significant difference between the sample sets from Upolu and No Name Reefs, but not between the No Name and Brook Islands Reef samples. These sample sets were all significantly different from the sample sets from Thetford, Hastings, and Green Island Reefs, although comparison of means failed to detect a significant difference between the sample sets from Hastings and Thetford Reefs (Figure 23).

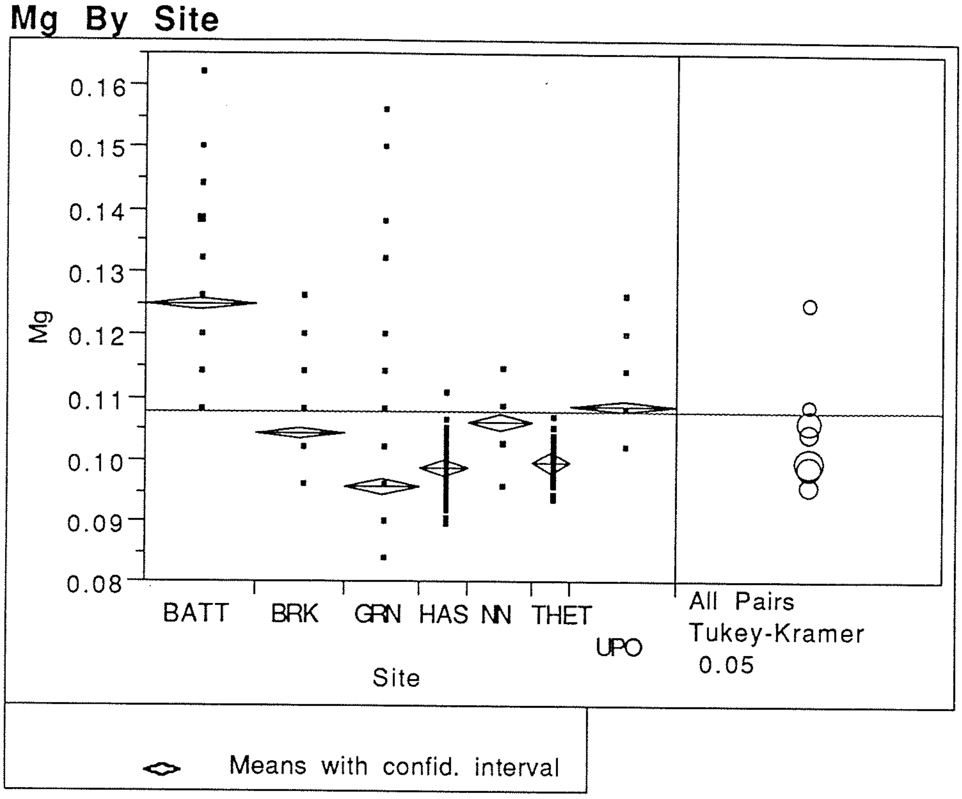

Figure 23: Graph of mean magnesium concentration for each location over time (n-1987), ± 95% confidence intervals. Means comparisons presented were assessed using Tukey-Kramer HSD Test (α=0.05).

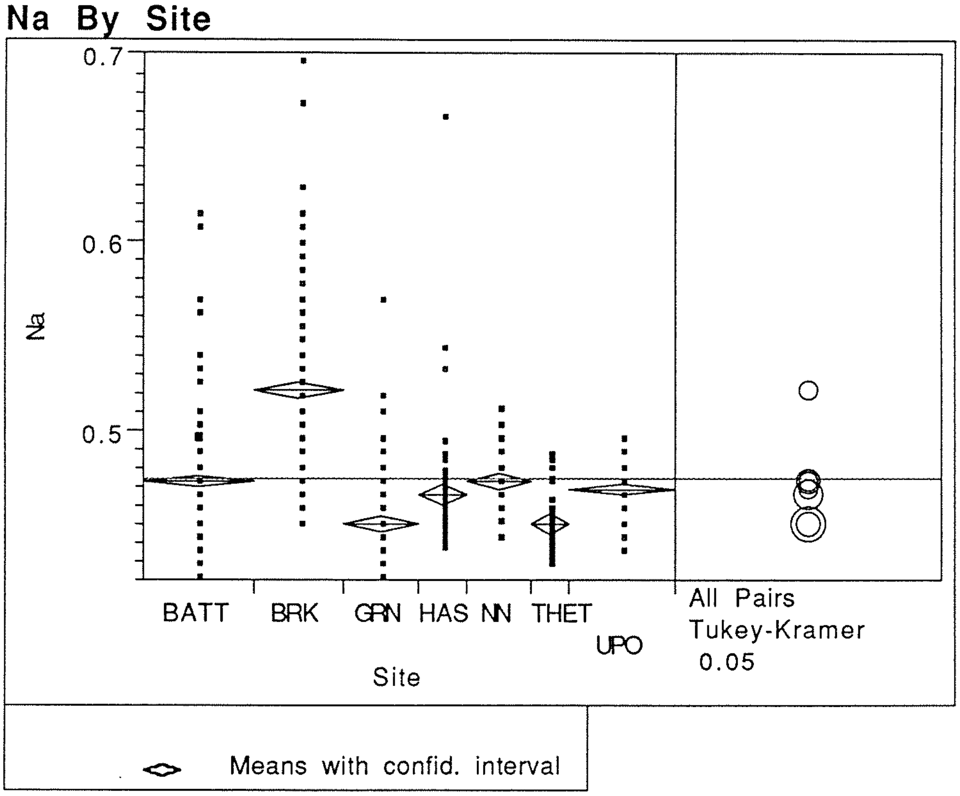

Figure 24: Graph of mean sodium concentration for each location over time (n-1987), ± 95% confidence intervals. Means comparisons presented were assessed using Tukey-Kramer HSD Test (α=0.05).

(iv) Sodium

Results of the geochemical analysis are given in Appendix J and summarised in Table 6.5. Univariate analysis of variance results are shown in Appendix I and displayed graphically in Figure 24.

Table 6.5: Summary statistics for sodium.

SAMPLING LOCATION	*Average Sodium in Each Sample Set (wt%)*	*Standard Deviation for Each Sample Set*	*Standard Error for Each Sample Set*	*Working Values*	*Number of Samples in Each Sample Set*
# No Name Reef	*0.4728*	*0.0136*	*0.0014*	*0.473 ± 0.14*	*95*
# Hastings Reef*	*0.4660*	*0.0298*	*0.0035*	*0.466 ± 0.03*	*74*
** Thetford Reef*	*0.4501*	*0.0132*	*0.0017*	*0.45 ± 0.01*	*57*
** Upolu Reef*	*0.4693*	*0.0112*	*0.0009*	*0.469 ± 0.01*	*160*
**@ Batt Reef*	*0.4736*	*0.0301*	*0.0023*	*0.474 ± 0.03*	*167*
**@ Green Island Reef*	*0.4508*	*0.0220*	*0.0021*	*0.451 ± 0.02*	*111*
@ Brook Islands Reef	*0.5208*	*0.0408*	*0.0035*	*0.52 ± 0.04*	*134*

 # Outer-shelf reefs
Mid/outer-shelf reefs*
** Mid-shelf reefs*
**@ Inner/mid-shelf reefs*
@ Inner-shelf reefs

Percentage sodium showed a statistically significant difference between locations (F=96.7051, α=0.001, Appendix I). Highest mean sodium values were found in the sample set from the Brook Islands. This sample set was shown to be significantly different from all other samples. Statistically, the sample sets from Batt, No Name and Upolu Reefs, were significantly different from the other samples, but comparison of means failed to detect a statistically significant difference between these three samples. A statistically significant difference could not be detected between the sample sets from Green Island and Thetford Reefs, although these two sample sets were significantly different from all other samples. The sample sets from Green Island and Thetford Reefs contained the lowest mean sodium values (Figure 24).

(v) Potassium

Results of the geochemical analysis are given in Appendix J and summarised in Table 6.6. Univariate analysis of variance results are shown in Appendix I and displayed graphically in Figure 25.

Percentage potassium showed a statistically significant difference between locations (F=91.7699, α=0.001, Appendix I). Highest and lowest potassium values were found in the sample sets from Green Island and Thetford Reefs respectively. Comparison of means suggested that the sample sets from Green Island, No Name and Upolu Reefs were significantly different, both from each other, and to all other samples. Comparison of means failed to detect a statistically significant difference between the sample sets from Batt and Hastings Reefs. No statistically significant difference was detected between sample sets from Brook and Thetford Reefs. However, these two groups of sample sets were significantly different from each other and from all other sample sets (Figure 25).

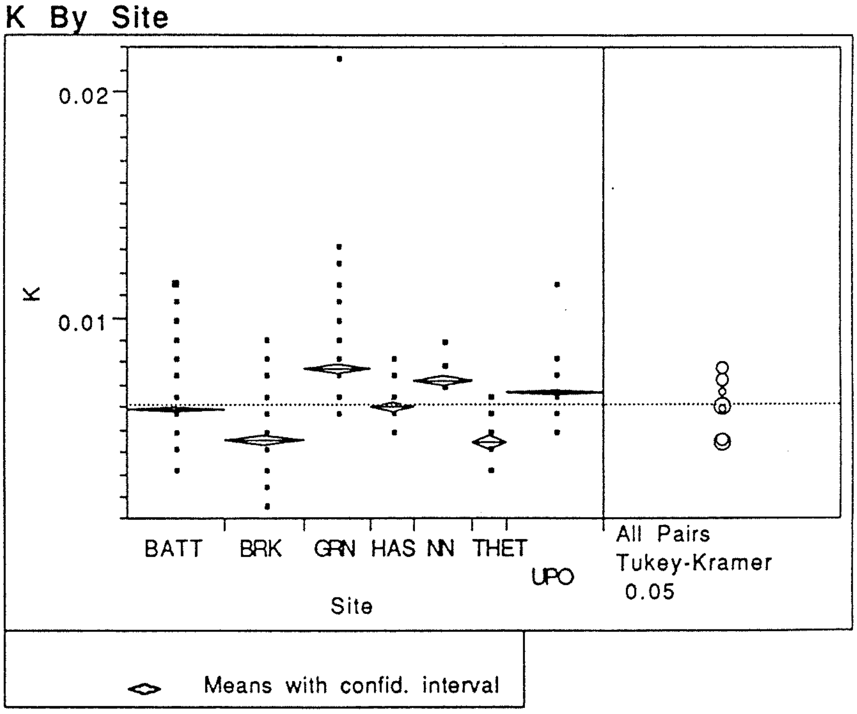

Figure 25: Graph of mean potassium concentration for each location over time (n-1987), ± 95% confidence intervals. Means comparisons presented were assessed using Tukey-Kramer HSD Test (α=0.05).

Table 6.6: Summary statistics for potassium.

SAMPLING LOCATION	Average Potassium for Each Sample Set (wt%)	Standard Deviation of Each Sample Set	Standard Error of Each Sample Set	Working Values	Number of Samples in Each Sample Set
# No Name Reef	0.0074	0.0006	0.0001	0.007 ± 0.001	95
* Hastings Reef	0.0060	0.0008	0.0001	0.006 ± 0.001	74
* Thetford Reef	0.0044	0.0006	0.0001	0.004 ± 0.001	57
* Upolu Reef	0.0067	0.0008	0.0001	0.007 ± 0.001	160
*@ Batt Reef	0.0059	0.0016	0.0001	0.006 ± 0.002	167
*@ Green Island Reef	0.0078	0.0021	0.0002	0.008 ± 0.002	111
@ Brook Islands Reef	0.0046	0.0015	0.0001	0.005 ± 0.002	134

 # Outer-shelf reefs
Mid/outer-shelf reefs*
** Mid-shelf reefs*
**@ Inner/mid-shelf reefs*
@ Inner-shelf reefs

(vi) Iron

Results of the geochemical analysis are shown in Appendix J and summarised in Table 6.7. Univariate analysis of variance results are given in Appendix I and displayed in Figure 26.

The use of AAS for iron detection was coarse and in many individual samples from No Name, Upolu and Brook Islands Reefs the value was 'rounded off'. The total data sets, however, are useful for inter-reefal comparisons, and for temporal comparisons within and between the sample sets, even though the levels of the concentrations are 'grouped' together.

Table 6.7: Summary statistics for iron:

SAMPLING LOCATION	*Average Iron in Each Sample Set (wt%)*	*Standard Deviation for Each Sample Set*	*Standard Error for Each Sample Set*	*Working Values*	*Number of Samples in Each Sample Set*
# No Name Reef	*0.0039*	*0.0000*	*0.0000*	*0.004 ± 0.00*	*95*
# Hastings Reef*	*0.0080*	*0.0018*	*0.0002*	*0.008 ± 0.002*	*74*
** Thetford Reef*	*0.0061*	*0.0024*	*0.0003*	*0.006 ± 0.003*	*57*
** Upolu Reef*	*0.0039*	*0.0003*	*0.0000*	*0.004 ± 0.00*	*160*
**@ Batt Reef*	*0.0083*	*0.0038*	*0.0003*	*0.008 ± 0.004*	*167*
**@ Green Island Reef*	*0.0058*	*0.0067*	*0.0006*	*0.006 ± 0.007*	*111*
@ Brook Islands Reef	*0.0039*	*0.0000*	*0.0000*	*0.004 ± 0.00*	*134*

 # Outer-shelf reefs
Mid/outer-shelf reefs*
** Mid-shelf reefs*
**@ Inner/mid-shelf reefs*
@ Inner-shelf reefs

Percentage iron varied significantly among sample sets (F=47.3956, α=0.001, Appendix I). Highest values were found in the sample set from Batt Reef, followed by the sample sets from Hastings, Thetford, Green Island, No Name, Upolu and Brook Islands Reefs. Comparison of means failed to detect a significant difference between the sample sets from Batt and Hastings Reef. These two sample sets were significantly different from the sample sets from Green Island and Thetford Reefs, and from the Brook, No Name and Upolu Reef samples. No significant difference could be detected between the sample sets from Green and Thetford Reefs, or between the Brook, No Name and Upolu Reef sample sets (Figure 26).

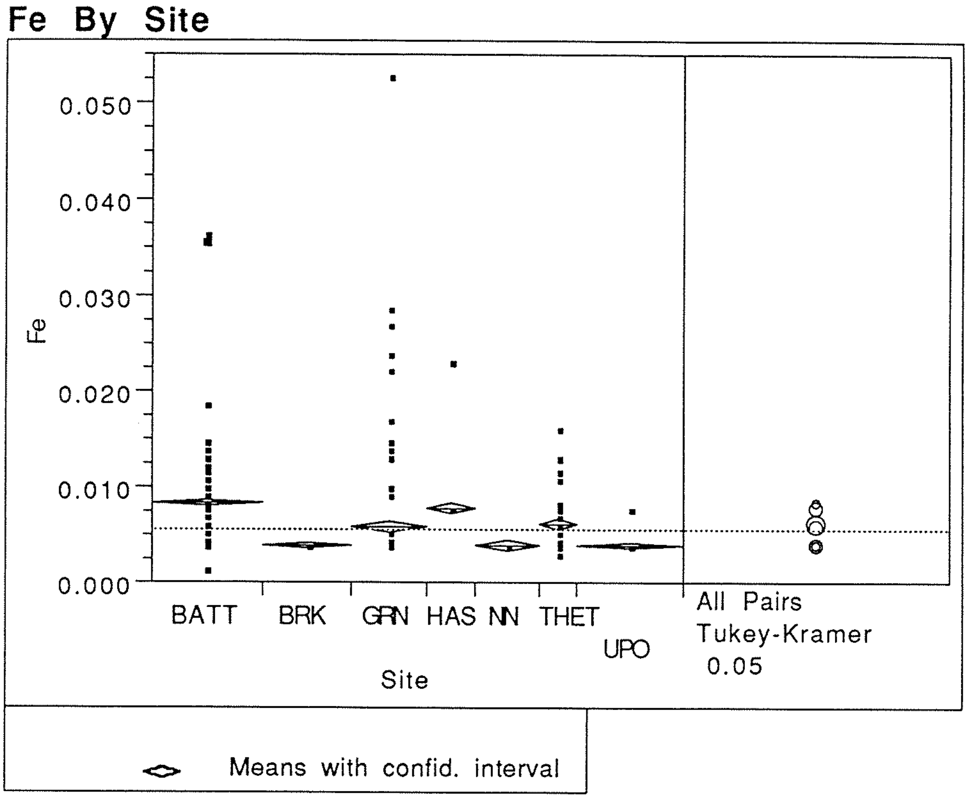

Figure 26: Graph of mean iron concentration for each location over time (n-1987), ± 95% confidence intervals. Means comparisons presented were assessed using Tukey-Kramer HSD Test ($\alpha = 0.05$).

(vii) Total values, all analysed elements:

The theoretical limit for calcium in pure $CaCO_3$ should be 40.0480 wt%. The incorporation of trace elements will cause the total weight percent of the cation contribution to the total to vary. Since the atomic weight of strontium is 87.62 compared to that of calcium at 40.08, the inclusion of strontium in the structure will have the effect of raising the total weight percent of cations present. The presence of magnesium in the structure, with an Atomic weight of 24.32, will have the tendency to lower this total. Since strontium occurs in greater abundance than magnesium, the maximum total is expected to be approximately 40.3 wt% for an aragonite containing around 0.7500 % strontium. No totals for any of the sample sets are significantly above this value (Table 6.8). The Batt Reef sample set (average value 40.3895%, std.dev. 0.3725%) is still within this range.

Table 6.8. Total values, all elements analysed.

TOTAL ELEMENTS ANALYSED		
SAMPLING SITE	Average Concentration Wt/%	Std.Dev Wt/%
# No Name Reef	39.7887	0.3187
#* Hastings Reef	39.9705	0.2877
* Thetford Reef	40.1337	0.3780
* Upolu Reef	39.6195	0.3626
*@ Batt Reef	40.3895	0.3725
*@ Green Island Reef	39.6304	0.4065
@ Brook Islands Reef	39.7049	0.3182
# Outer-shelf reefs #* Mid/outer-shelf reefs * Mid-shelf reefs *@ Inner/mid-shelf reefs @ Inner-shelf reefs		

6.5. DISCUSSION - REGIONAL PATTERNS

Data used in this inter-reefal study incorporated results of analyses from seven different locations and covered periods ranging from 1814-1987 (Batt Reef) to 1934-1987 (Thetford Reef), dependent on the age of the sampled colony (n-1987).

The CDA biplot used to interpret the inter-reefal relationships based on group membership of the variables calcium, strontium and magnesium (Figure 20), is similar to that shown in the micro-environmental (intra-reefal) study (Figure 16). In both biplots the sample sets from the inner- and inner/mid-shelf locations are clearly discriminated both from each other and from the mid- and outer-shelf samples. The lack of discrimination between the mid- and outer-shelf sample sets noted in the micro-environmental study is still present in this study. However, the moderate degree of overlap between the Hastings Reef 95% confidence ellipsoid and those from the other mid- and outer-shelf sample sets (No Name, Upolu and Thetford Reefs) suggests that this sample set is slightly different from the other. The reasons for this difference need to be explored.

Interpretation of the ANOVA results shows that for the three elements frequently used for the interpretation of environmental parameters (calcium, strontium, magnesium), only the sample set from Batt Reef was consistently and significantly different from all other samples. This was similar to that noted in the micro-environmental (intra-reefal) study reported in Chapter 5. The contribution of the various elements to each sample, including the undiscriminated mid- and outer-shelf samples, again varied with location. However, in this study the contribution of the different elements to the chemical composition of the skeleton was different from that noted in the micro-environmental study. For example -

(1) **Calcium:** In the micro-environmental study only the Batt Reef sample set was significantly different from the other locations. In this study calcium content falls into four groups (Figure 21), with each group significantly different from the others -

  (a) The Batt Reef sample set is again significantly different statistically from all other samples.

  (b) The sample sets from Hastings and Thetford Reefs were not included in the micro-environmental study (see 5.5.1). There is no statistically significant difference between these two sample sets although there is only a minor degree of overlap according to the location of the Tukey-Kramer 95% confidence circles. These two sample sets are statistically different from all other samples.

  (c) The No Name Reef sample set is statistically different from all other samples, with a minor degree of overlap in the Tukey-Kramer 95% confidence circles with the sample set from the Brook Islands.

  (d) There is no statistically significant difference between the sample sets from the inner-shelf Brook Islands, the inner/mid-shelf Green Island Reef, and the mid-shelf Upolu Reef. This group was statistically different from the three other groups.

  (e) There is no obvious cross-shelf division of calcium content with the highest and lowest values coming from the inner/mid and inner-shelf locations of Batt Reef (39.0488 wt%), and Green Island (38.2776 wt%) and Brook Islands (38.3289 wt%), respectively.

(2) **Strontium:** In the micro-environmental study strontium fell into three groups (Green Island; Batt Reef and Brook Islands; Upolu and No Name Reefs) (Figure 18). In this study -

(a) Strontium content is clearly separated throughout the study area -

  (i) Only the sample sets from Upolu and Thetford Reefs were unable to be separated by the Tukey-Kramer comparison of means test (Figure 22).

  (ii) Each of these sample sets is significantly different from all other sample sets.

  (iii) All other sample sets are significantly different from each other.

(b) There are no obvious trends in the strontium data -

  (i) Highest values are from the inner/mid-shelf Green Island sample set (0.7861 wt%).

  (ii) Lowest values are from the inner/mid-shelf Batt Reef (0.7314 wt%), and the inner-shelf Brook Islands (0.7432 wt%) sample sets.

(c) If the nearer-to-shore reefs are removed from the examination, there is an indication of a cross-shelf separation in the remaining sample sets -

  (i) The sample sets from the outer- and outer/mid-shelf locations (Hastings and No Name Reefs) contain the lowest average strontium values (0.7581 wt% and 0.7627 wt% respectively).

  (ii) The two mid-shelf sample sets (Thetford and Upolu Reefs) contain the highest average strontium values (0.7697 wt% and 0.7674 wt% respectively).

(d) The greatest spread of values around the mean is found in the inner/mid- and inner-shelf locations of Batt (σ=0.0119) and Brook Islands (σ=0.0158) Reefs. However, the spread of values for the other inner/mid-shelf sample set (Green Island Reef, σ=0.0078) is relatively tightly constrained.

(3) **Magnesium:** In the micro-environmental study magnesium fell into three groups (Batt Reef; Brook Islands, No Name and Upolu Reefs; Green Island Reef) (Figure 19). In this study magnesium concentration (Figure 23) also falls into three groups. These groups are similar to the micro-environmental study.

  (a) Highest average level is in the Batt Reef (0.1250 wt%) sample set and this sample set is significantly different from all other samples.

  (b) The sample set from Upolu Reef is significantly different from all other samples. However, average levels from this sample set (0.1087 wt%) are similar to the sample sets from the Brook Islands and No Name Reefs

(0.1044 and 0.1054 wt% respectively). These latter sample sets are not significantly different from each other.

(c) Although the sample set from Green Island Reef (0.0957 wt%) is significantly different from the other sample sets in this group (Thetford and Hastings Reefs; 0.0995 wt% and 0.0988 wt% respectively), the average value is closer to this group than to any other samples, and this group is separate from the other samples.

(d) There is no indication of cross-shelf differentiation in the results with the highest and lowest average values coming from the inner/mid-shelf locations of Batt Reef (0.1250 wt%) and Green Island Reef (0.0957 wt%) respectively. However, a greater spread of values is apparent in the inner/mid- and inner-shelf sample sets (Green Island σ=0.0133, Batt σ=0.0087, and Brook Islands Reefs σ=0.1044). By comparison, the mid- and outer-shelf sample sets display relatively minor variation in values (e.g. Thetford Reef σ=0.0028).

(e) The high levels of magnesium in the Batt Reef sample set are consistent with infilling into the numerous boring algal cavities in this sample (Milliman 1974b). In some instances XRD examination detected the presence of high magnesian calcite in the Batt Reef sample. Further examination using Scanning Electron Microscopy and associated Electron Microprobe Analysis found compositional evidence of high magnesian calcite infilling in remnant boring algal chambers in this sample.

6.6. DISCUSSION - ANTHROPOGENIC SIGNALS

Comparison of the two studies (micro-environmental and regional) shows that only the contribution of magnesium to the chemical composition of the skeleton at the different locations has retained the same geographical pattern. In the regional study, the relative contribution of each element to the total chemical composition of the sample sets is different to the results of the micro-environmental study. If it can be presumed that the coral skeleton responds to change in the chemistry of its environment, then this would suggest considerable environmental change occurred during the latter period of coral growth. Examination of outlier distances using Mahalanobis Distances from the multivariate mean, shows that the spread of values around the mean increased in the sample sets from Green Island, Upolu and Hastings Reefs during the latter years of growth. Barnes & Lough (1991) have pointed out that the calcium content of the *Porites* skeleton can vary considerably throughout the life of the colony. Indeed, the magnitude of the variability is greater in the early part of the sample set from Brook Islands Reef. However, the change in the magnitude of the fluctuations in the Green Island, Upolu and Hastings Reefs data sets coincides with major landuse change in the Barron River Catchment (Valentine 1988; Pulsford 1990) and is worthy of further examination.

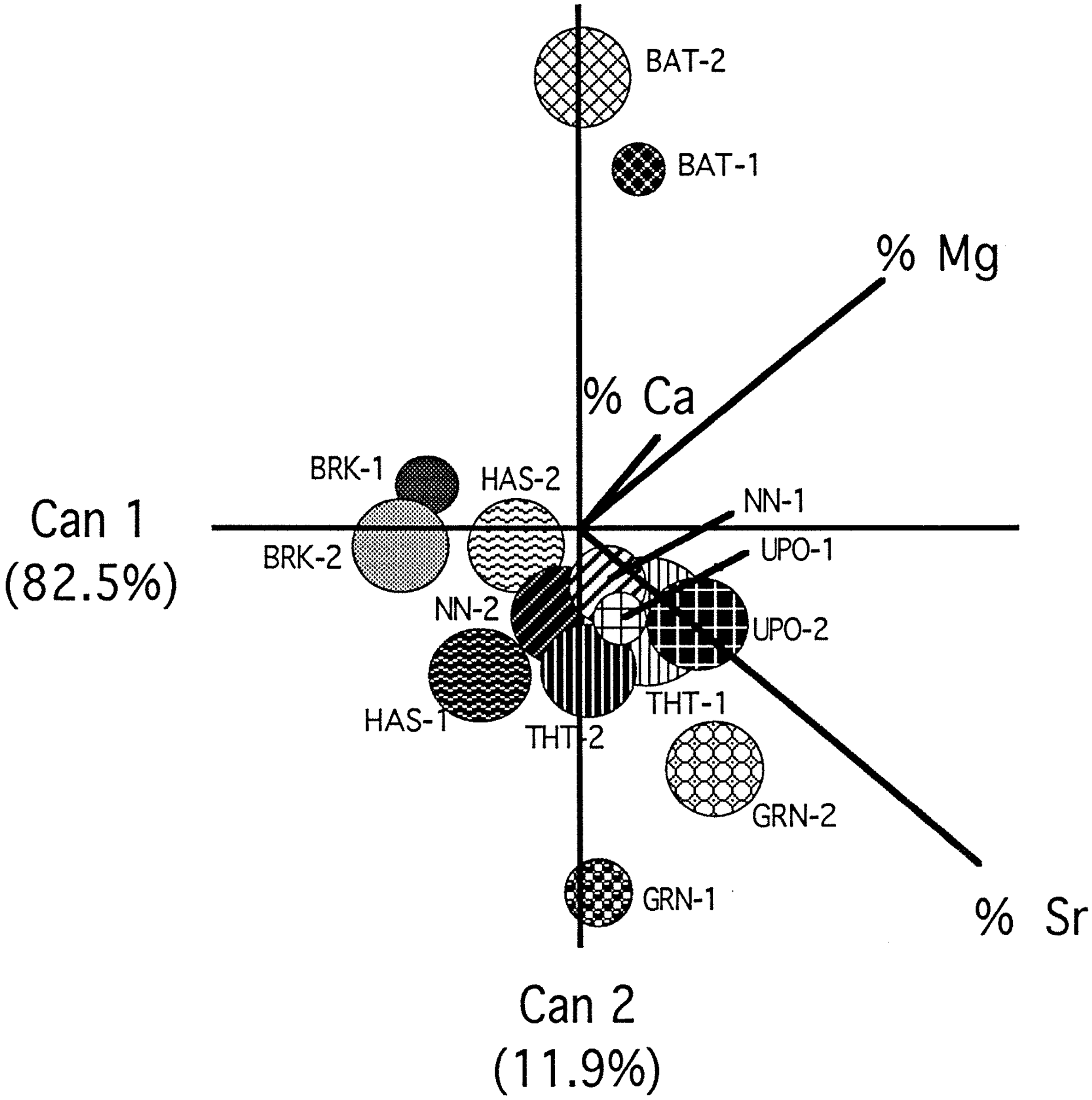

Figure 27: Biplot of multivariate centroid means with associated 95% confidence ellipsoids on the first two canonical axes exploring variation in chemical composition of calcium, strontium and magnesium between locations, for sample sets covering the two periods pre-1950 and post-1950.

To assess the significance of these observations, the data were examined using multivariate analysis pre- and post- the major period of landuse change suggested by Valentine (1988) and Pulsford (1990). The CDA biplot for the two periods pre- and post-1950 (Figure 27) shows that in all sample sets, the relative proportion of calcium, strontium and magnesium in the skeleton is different pre- and post-1950. However, because the multivariate 95% confidence ellipsoids around each centroid mean overlap, the difference is not significant in the No Name, Thetford and Upolu Reef samples. The pre- and post-1950 variation is significant in the inner/mid-shelf locations of Batt and Green Island Reefs and for the outer/mid-shelf sample set from Hastings Reef. There is an indication of temporal variation in the Brook Islands sample set based on lower levels of magnesium post-1950, but the difference is modest when compared to the sample sets from Hastings, Batt and Green Island Reefs. Figure 27 shows that these sample sets are discriminated by -

(1) Green Island - higher levels of magnesium post-1950.

(2) Batt Reef - lower levels of strontium post-1950.

(3) Hastings Reef - higher levels of magnesium post-1950.

Figure 27 suggests that the variation in the pre- and post-1950 sample sets was predominantly influenced by changes in the magnesium content of the sample sets. Magnesium content also increased post-1950 in the Batt Reef sample set although this increase is within the range of one standard deviation.

Magnesium has a relatively small ionic radius (0.072 nm) compared with calcium (0.10 nm) and will not easily substitute into the aragonite structure. Magnesium is more compatible with the structure of calcite, rather than aragonite (Chillingar 1953; Chave 1954; Chillingar 1962; Kitano 1967). Any significant addition to the relative proportion of this element in the coral skeleton is usually associated with boring algal activity or diagenetic alteration (Milliman 1974b). XRD analysis detected high magnesian calcite in the Batt Reef sample set, which is probably associated with boring algal activity, but there is only minor evidence of this in the Green Island and Hastings Reef sample sets. If the post-1950 variations in Figure 27 are related to changes in water quality associated with land management practices, then the addition of the trace elements potassium, sodium and iron to the multivariate analysis may show a similar variation in the relative abundance of these elements post-1950.

Iron, with an ionic radius of 0.076 nm, is also considered more compatible with the structure of calcite than aragonite. K^+ and Na^+ (ionic radii 0.138 nm and 0.09 nm respectively) are compatible with the aragonite structure, but co-operative charge compensation must occur if they are to substitute within the lattice. A number of researchers (e.g. Chillingar 1953; Chave 1954; Chillingar 1956; Mitchell 1961) have suggested that environmental and/or chemical associations related to variations in the seawater column may indirectly affect the concentration of these elements in the structure of the coral skeleton. The incorporation of iron into the coral skeleton is considered a secondary addition, associated with the deposition of terrestrial sediments into skeletal cavities (Livingston & Thompson 1971). This data was included in the analyses using CDA for the two periods pre- and post-1950.

Average values for calcium, strontium, magnesium, potassium, sodium and iron, plus/minus one standard deviation, for the two periods pre- and post-1950 are given in Table 6.9. The CDA biplot displayed in Figure 28 shows that in this analysis, potassium, sodium, magnesium, and iron have greater discriminating power than strontium and calcium. Calcium, because of the reduced size of the vector, has very little discriminatory power. This indicates that the spread of values around the multivariate mean is greater between reefs than within reefs for the elements potassium, sodium, magnesium, iron, and to a lesser extent, strontium.

The biplot again discriminates the multivariate centroid means of the inner- and inner/mid-shelf sample sets from Batt, Brook and Green Island Reefs from all other locations. The various sample sets are discriminated by -

(1) Green Island - high levels of strontium.

(2) Batt Reef - high levels of magnesium.

(3) Brook Islands - high levels of sodium.

(4) No Name Reef and Upolu Reef (not discriminated from each other) - high levels of potassium, and low levels of iron.

(5) Thetford Reef - lower levels of potassium and sodium, and reasonably high levels of strontium

The CDA biplot further discriminates between the pre- and post-1950 sub-sets from Green Island and Hastings Reef, with an indication of change in the sub-sets from Batt and Upolu Reefs, based on -

(1) Green Island - higher levels of magnesium, potassium and iron post-1950.

(2) Hastings Reef - higher levels of magnesium; lower levels of strontium post-1950.

(3) Batt Reef - indication of higher levels of magnesium; lower levels of strontium post-1950.

(4) Upolu Reef - indication of higher levels of magnesium post-1950.

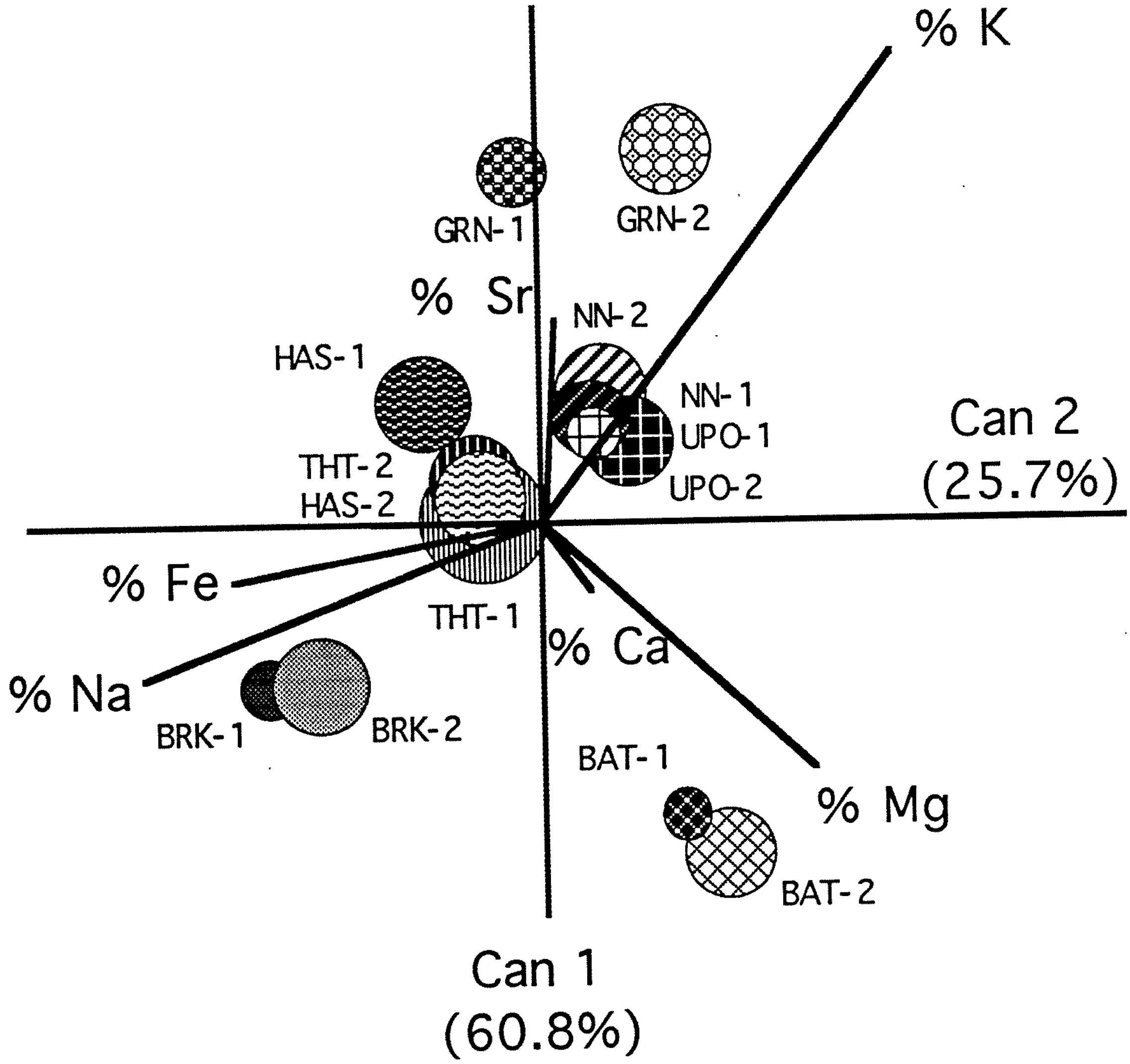

Figure 28: Biplot of multivariate centroid means with associated 95% confidence ellipsoids on the first two canonical axes. The biplot explores the variation in chemical composition of calcium, strontium, magnesium, potassium, sodium and iron between locations, for sample sets covering the two periods pre-1950 and post-1950.

Table 6.9. Average values for calcium, strontium, magnesium, potassium, sodium and iron, for the two periods pre- and post-1950.

Sampling Location	Calcium wt%		Strontium wt%		Magnesium wt%		Potassium wt%		Sodium wt%		Iron wt%	
	Pre-1950	Post-1950	Pre-1950	Post-1950	Pre-1950	Post-1950	Pre-1950	Post-1950	Pre-1950	Post-1950	Pre-1950	Post-1950
# No Name Reef	38.52 ±0.28	38.32 ±0.34	0.763 ±0.009	0.762 ±0.007	0.106 ±0.005	0.105 ±0.005	0.008 ±0.001	0.007 ±0.001	0.479 ±0.012	0.464 ±0.010	0.004 ±0.001	0.004 ±0.001
#* Hastings Reef	38.55 ±0.25	38.73 ±0.29	0.762 ±0.008	0.754 ±0.006	0.095 ±0.003	0.102 ±0.003	0.006 ±0.001	0.006 ±0.001	0.463 ±0.040	0.469 ±0.015	0.008 ±0.001	0.008 ±0.003
* Thetford Reef	38.95 ±0.41	38.72 ±0.33	0.770 ±0.011	0.770 ±0.012	0.102 ±0.002	0.099 ±0.003	0.005 ±0.001	0.004 ±0.001	0.461 ±0.015	0.445 ±0.008	0.006 ±0.003	0.006 ±0.002
* Upolu Reef	38.25 ±0.23	38.29 ±0.63	0.766 ±0.006	0.772 ±0.007	0.108 ±0.003	0.111 ±0.004	0.007 ±0.001	0.007 ±0.001	0.470 ±0.014	0.466 ±0.013	0.004 ±0.001	0.004 ±0.001
*@ Batt Reef	39.08 ±0.35	38.93 ±0.42	0.734 ±0.012	0.722 ±0.015	0.124 ±0.009	0.128 ±0.006	0.006 ±0.001	0.006 ±0.002	0.475 ±0.030	0.471 ±0.029	0.008 ±0.002	0.010 ±0.007
*@ Green Island Reef	38.24 ±0.39	38.306 ±0.44	0.787 ±0.007	0.785 ±0.009	0.092 ±0.004	0.103 ±0.020	0.007 ±0.001	0.009 ±0.003	0.452 ±0.024	0.448 ±0.018	0.004 ±0.001	0.010 ±0.110
@ Brook Islands Reef	38.31 ±0.33	38.40 ±0.31	0.727 ±0.106	0.745 ±0.018	0.106 ±0.005	0.101 ±0.004	0.005 ±0.001	0.003 ±0.001	0.536 ±0.037	0.482 ±0.019	0.004 ±0.001	0.004 ±0.001

 # Outer-shelf reefs
Mid/outer-shelf reefs*
** Mid-shelf reefs*
**@ Inner/mid-shelf reefs*
@ Inner-shelf reefs

6.7. POSSIBLE CAUSES OF CHANGES PRE- AND POST-1950

Comparison of Figures 27 and 28 suggests that variability in the chemical composition of the corals is a natural occurrence in the Great Barrier Reef Lagoon. However, the movement in the relative location of the centroid means in the CDA biplots suggests that change has taken place in the Green Island and Hastings Reefs sample sets post-1950.

Several parameters could influence these variations (e.g. change in the distribution coefficient of the various elements induced by changes in water temperature; coral growth rates; diagenetic alteration of the coral skeleton). The variations may be either naturally stimulated, or anthropogenically forced, and will be discussed below. For simplicity, the discussion will primarily divide the chemical composition of the skeleton into individual components, and will explore the various relationships within these components.

6.7.1. Calcium:

Barnes & Lough (1991) have shown that the calcium content of the coral skeleton fluctuates through time. However, examination of the Mahalanobis outliers shows that the fluctuation is greater towards the end of the Green Island and Upolu Reef sample sets (Figure 29).

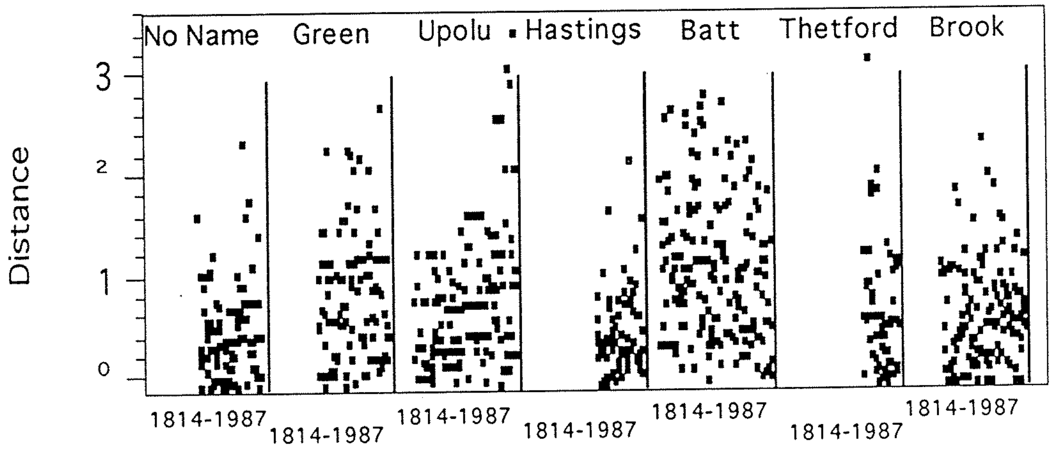

Figure 29: Estimation of calcium outlier distances using the Mahalanobis Distance of each point from the multivariate mean.

A possible reason for the variations in the data sets includes a temperature shift. If this is the case, then, due to changes in the distribution coefficients for these elements between seawater and aragonite (Kinsman 1969), cooperative compositional response by other elements, in particular strontium, could be expected (see below).

6.7.2. Strontium:

As mentioned in 6.6.1, Barnes & Lough (1991) have shown that temporal variations in calcium content are a natural occurrence in corals of the Great Barrier Reef. As outlined in Chapter 5, strontium has a similar ionic radius to calcium (0.118 nm and 0.10 nm respectively) and can readily substitute for calcium in the aragonite structure. Therefore, from a purely chemical consideration, any variation in calcium content should be reflected in a cooperative inverse compositional response by strontium.

Statistical analysis using Pearson's Product Moment Correlations (Appendix N) suggests that the only significant correlations between calcium and strontium in the present data set are a negative correlation in the sample set from Hastings Reef ($r=-0.2667$; $\alpha=0.05$), and a positive correlation for the sample set from Batt Reef ($r=0.3183$; $\alpha=0.05$). Thus, a simple process of cooperative substitution of strontium for calcium cannot be considered a sufficient explanation for the variations in the data set or all correlations should be negative and considerably more significant. Factors that may contribute to this discrepancy need to be considered.

(a) **Strontium/Temperature Relationships:**

The precipitation of aragonite in the laboratory has shown that strontium incorporation into the skeleton is temperature dependent with the concentration of the skeletal strontium negatively correlated to the temperature of the water (Kitano *et al* 1971; Houck *et al* 1977). If the variations in the two data sets (1883-1902 and n-1987) are attributable only to temperature variations of the surrounding waters, then it is reasonable to assume that variations would be uni-directional provided local interference could be eliminated as a possibility. As there are no localised influences that could significantly alter water temperature at any of the sampled areas (e.g. industrial discharge of heated or cooled water), this possibility can be discarded.

Further, if the incorporation of strontium into the aragonite skeleton is controlled by temperature alone, then the average strontium content of the sampled corals from each location should provide reasonable temperature estimates of the waters surrounding the corals at the time of growth. Based on Weber's equation (Weber 1973; see above, p.108), the temperature estimates constructed for the sampled locations[1] provide a reasonable estimate of average seawater temperature for the mid- and outer-shelf reefs. The estimates, however, are less reliable when derived from the strontium content of corals of the inner- and inner/mid-shelf. From their similarities in latitude, distance from shore, and water depth, with no industrial effluent in the vicinity, it is unlikely that two reefs (Green Island and Batt) would have such diverse water temperature readings as 23.4 °C and 32.0 °C. Temperature readings taken at Low Isles (approximately 15 km west of Batt Reef and 50 km north of Green Island) show that sea surface temperature averaged around 26°C. Temperatures ranged from 21.6°C in winter to 29.8°C in summer during the period January 1978 to July 1983 (CSIRO Hydrographic Data; measurements taken around midnight). Using this measured average, it is unlikely that the proxy strontium temperature estimates for Batt and Green Island Reefs could be correct.

It is also unlikely that the highly seasonal and temporally variable discharge of the Barron River could maintain low water temperatures (average 23.4°C) around Green Island Reef. It is further unlikely that deep ocean upwellings could cool the nearer-to-shore waters to a greater extent than waters at the edge of the Continental Shelf (e.g. Batt Reef compared to No Name Reef). Brook Islands Reef, approximately 300 km south of the study area, also produced dubious proxy-temperature estimates (29.6°C ± 2.3°C). Thus, if the sample sets from Green Island, Brook Islands and Batt Reefs represent inner- and inner/mid-shelf corals, the results suggest that temperature alone cannot explain strontium variations at all locations. Therefore, use of the strontium content of the coral skeleton becomes an inadequate method of hindcasting water temperatures in near-shore locations (Table 6.10).

Strontium is lower in high magnesian calcites than in aragonite. Therefore, the presence of the high magnesian calcite from boring algal activity in the Batt Reef

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[1] Temperature estimates were constructed using the average strontium content of the No Name Reef sample as a base, and the known average water temperature from Yonge Reef (Yonge Reef is an outer shelf reef approximately 20 km north of No Name Reef; Weber 1973).

sample would lower the strontium content (Milliman 1967, 1974b) and thus increase the temperature estimate. However, these explanations are not applicable to the Green Island and Brook Islands sample sets. This topic is discussed more fully in section 6.6.2d - *Diagenetic alteration and strontium content.*

Table 6.10: Proxy seawater temperatures estimated using (a) Weber's (1973) calculations - 68 ppm strontium variation per degree C variation (based on 7627 ppm strontium at No Name Reef = a known sea surface temperature of 26.7°C at Yonge Reef, approximately 20 km north of No Name Reef), and (b) Schneider & Smith's (1982) equation - Sr:Ca x 10^{-3} = 10.94 - 0.070T(°C).

Sampling Site	*Avg. Skeletal Sr %*	*Avg. Skeletal Ca %*	*Avg. Sr:Ca Ratio*	*(a) Sr Concentration Estimated Temperature (°C) (Weber 1973)*	*(b) Sr:Ca Ratio Estimated Temperature (°C) (Schneider & Smith 1982)*	*Difference (a) - (b) (°C)*
# No Name Reef (n = 95)	*0.7627 (± 0.0082)*	*38.4381*	*0.0198 (± 0.0003)*	*26.7*	*26.6*	*0.1*
# Hastings Reef (n = 74)*	*0.7581 (± 0.0079)*	*38.6426*	*0.0196 (± 0.0003*	*27.5*	*28.1*	*-0.6*
** Thetford Reef (n = 57)*	*0.7697 (± 0.0117)*	*38.8011*	*0.0198 (± 0.0003)*	*25.7*	*26.6*	*-0.9*
** Upolu Reef (n = 160)*	*0.7674 (± 0.0066)*	*38.4252*	*0.0200 (± 0.0003)*	*26.0*	*25.2*	*0.8*
**@ Batt Reef (n = 167)*	*0.7314 (± 0.0119)*	*39.0488*	*0.0187 (± 0.0003)*	*32.0*	*33.9*	*-1.9*
**@ Green Island Reef (n = 111)*	*0.7861 (± 0.0078)*	*38.2776*	*0.0205 (± 0.0003)*	*23.4*	*22.1*	*1.3*
@ Brook Islands Reef (n = 134)	*0.7432 (± 0.0158)*	*38.3289*	*0.0194 (± 0.0005)*	*29.6*	*29.6*	*0*

 # Outer-shelf reefs
Mid/outer-shelf reefs*
** Mid-shelf reefs*
**@ Inner/mid-shelf reefs*
@ Inner-shelf reefs

(b) Strontium/Calcium Temperature Relationships:

While Weber's (1973) calculation proved an inadequate method of estimating the temperature of the inner-shelf waters of the study area, Weber's calculations relied solely on the strontium content of the coral skeleton. The ratio of strontium to calcium in coral aragonite has been shown to produce a more reliable estimate of seawater temperature at the time of precipitation, providing the seawater ratio of these two elements remains stable (Houck *et al* 1977). As the Sr:Ca ratio of seawater is generally regarded as constant under natural, well-mixed, open ocean conditions, variations in the Sr:Ca ratio of the water have generally been discounted as a reason against the use of skeletal Sr:Ca ratios as proxy temperature indicators in natural systems. Field collections by Smith *et al* (1979) and further studies by Schneider & Smith (1982), subsequently validated the relationship between temperature and the Sr:Ca ratio of the coral skeleton.

Sr:Ca ratios were constructed for each sampled location and temperature estimates calculated according to Schneider & Smith's (1982) equation (Sr:Ca x 10^{-3} = 10.94 - 0.070T(°C). The results are shown in Table 6.10 (p.129). While these estimates provide additional evidence of the coral's ability to retain historical recors of seawater temperature in their skeletal chemical composition, reliability of the estimates is again restricted to locations further from the mainland (Upolu, Thetford, Hastings and No Name Reef corals).

It should also be noted that the temperature estimates obtained using both strontium and Sr:Ca ratios differ, with the magnitude of the difference (irrespective of the sign) increasing as proximity to major river systems decreases (e.g. +0.8°C at Upolu Reef; -0.9°C at Thetford Reef; +1.3°C at Green Island; -1.9°C at Batt Reef). The reasons for this difference are not clear, but are possibly related to the kinetics and mechanisms of precipitation and trace element uptake. Nevertheless, the results from this section of the study suggest that some variable, or variables, as yet undefined, affects the activities of the competing elements, including strontium and calcium, in the near-shore water column. These changes in the relative activities of the ions are then reflected in the predictions made from the use of relatively simple, elemental geothermometers. Therefore, the results from these analyses need to be considered when paleoclimatic conditions are being estimated.

Many explanations for the cause of the discrepancies can be explored, but those that should be considered include -

(1) A species effect in the sampled corals -

It is possible, but unlikely, that sample selection favoured a particular genetic population in the inner- and inner/mid-shelf corals. *Porites* species are notoriously difficult to identify (Veron, Australian Institute of Marine Science, pers.com.). Therefore, genetic population differences could be responsible for the offsets from the strontium and Sr:Ca vs temperature calibrations (Schneider & Smith 1982). However, other studies around the world have also reported similar nonconformity (e.g. see Schneider & Smith 1982).

(2) Relative changes in the Sr:Ca ratio in freshwater runoff -

It is unlikely that changes in the Sr:Ca ratio of inflowing river waters would be sufficient, once dispersed, to influence the seawater composition in the manner suggested by the proxy record. However, this is a possibility that was not examined in this study and further research is needed into the Sr:Ca ratio of shallow, near-shore waters.

(3) Changes in relative speciation between calcium and strontium in the marine environment due to -

(a) biological and biochemical influences,
(b) nutrient levels,
(c) organic inputs.

Muir (1984) also noted discrepancies in the Sr/temperature relationship from near-shore corals and concluded that the proxy strontium thermometer was efficient only in the absence of external influences. Muir considered that the periodic influx of water masses from rivers into inner-shelf waters affected coral growth kinetics and the subsequent uptake of strontium. Human activity on the coastline was considered the probable source of these additives (Muir 1984). Muir included all polyphosphates, organo-phosphates and other man-made organics as possible sources of contaminants. Phosphate and organics have been associated with proximity to river runoff. Phosphate, in one or other of its many forms, could interact with the strontium in solution and thus chemically interfere with the incorporation into the coral skeleton.

An additional source of phosphate to the marine environment could conceivably come from the use of agricultural fertilisers. However, the Green Island sample predates the period of major European influence, and while fluctuations occur, there is no evidence of major change in the average Sr:Ca ratio during the last 40 years, the period when major land clearance and the use of superphosphate increased significantly in the Barron River Catchment (Pulsford 1990). Therefore, it is unlikely that the inaccuracy of the inner- and inner/mid-shelf proxy Sr:Ca temperature record is due to an anthropogenic effect.

(4) Strontium/skeletal growth rate relationships -

This will be discussed fully below.

(5) Diagenetic alteration -
This, also, will be discussed below.

(c) Strontium/Skeletal Growth Rate Relationships:

Growth rate, or linear extension of the coral skeleton, has been shown to exert an influence on the incorporation of strontium into the coral skeleton, with faster growth rate associated with lowered levels of strontium in the skeleton for any given species or genus of coral (Weber 1973). Aragonite is inversely soluble with temperature in an inorganic system (de Kanel & Morse 1978), so at given levels of Ca^{2+} and HCO_3 activity, the supersaturation with respect to $CaCO_3$ would be greater at high temperatures. Therefore, if there is a constancy of composition, nucleation and growth processes should be more rapid at higher temperatures. Thus, Weber's suggestion has a theoretical basis. The lower strontium content would be the result of suppression of the distribution coefficient of Sr^{2+} relative to Ca^{2+} in seawater. This could be due merely to an increase in temperature, and is likely to affect the lighter Ca^{2+} ion to a greater extent than the heavier Sr^{2+} ion via some form of thermal fractionation process.

To examine this possibility, three separate periods (1920-29, 1930-39 and 1980-87) from six of the sampling locations were compared for the relationship between skeletal strontium and rate of linear extension of the coral skeleton. Selection of time periods was restricted to periods when dating could rely on X-radiography to define the beginning and end of the light and dark density bands. Dates were then assigned to three identifiable periods within each sample set with a reasonable degree of accuracy. No material was available from the Thetford Reef sample set pre-1930, and this data was eliminated from the analysis. Results are displayed in Figure 30 and Table 6.11.

Except for sample sets from Batt and Hastings Reefs, the results suggest an inverse relationship between average skeletal extension and average skeletal strontium. However, statistical examination (Table 6.11) showed no significant correlation between skeletal strontium content and skeletal extension ($r=-0.2693$, $n=18$, $\alpha=0.05$) for the three periods at each site. At Batt Reef the water temperatures estimated using strontium are considered inaccurate and later it will be shown that the strontium values at this site have suffered diagenetic alteration. Thus, it was considered logical to remove this sample set from the analysis. When this was done a strong inverse correlation was detected (r=-0.8361, n=15, α=0.01). At this scale of analysis, strontium incorporation into the coral skeleton is correlated with growth.

Table 6.11: Average skeletal strontium content and skeletal growth rate for the periods 1920-29, 1930-39 and 1980-87.

Reef	*Period*	*Avg. Sr %*	*Average growth rate (mm/yr)*
# No Name Reef	*1920-29*	*.7563*	*11.8*
	1930-39	*.7709*	*10.6*
	1980-87	*.7665*	*11.3*
# Hastings Reef*	*1920-29*	*.7652*	*14.5*
	1930-39	*.7611*	*13.6*
	1980-87	*.7541*	*14.6*
** Upolu Reef*	*1920-29*	*.7650*	*13.6*
	1930-39	*.7664*	*14.7*
	1980-87	*.7732*	*12.6*
**@ Batt Reef*	*1920-29*	*.7306*	*14.1*
	1930-39	*.7241*	*10.1*
	1980-87	*.7209*	*8.8*
**@ Green Island Reef*	*1920-29*	*.7859*	*14.8*
	1930-39	*.7888*	*14.7*
	1980-87	*.7881*	*15.8*
@ Brook Islands Reef	*1920-29*	*.7431*	*20.0*
	1930-39	*.7488*	*19.1*
	1980-87	*.7364*	*20.1*

 # Outer-shelf reefs
Mid/outer-shelf reefs*
** Mid-shelf reefs*
**@ Inner/mid-shelf reefs*
@ Inner-shelf reefs

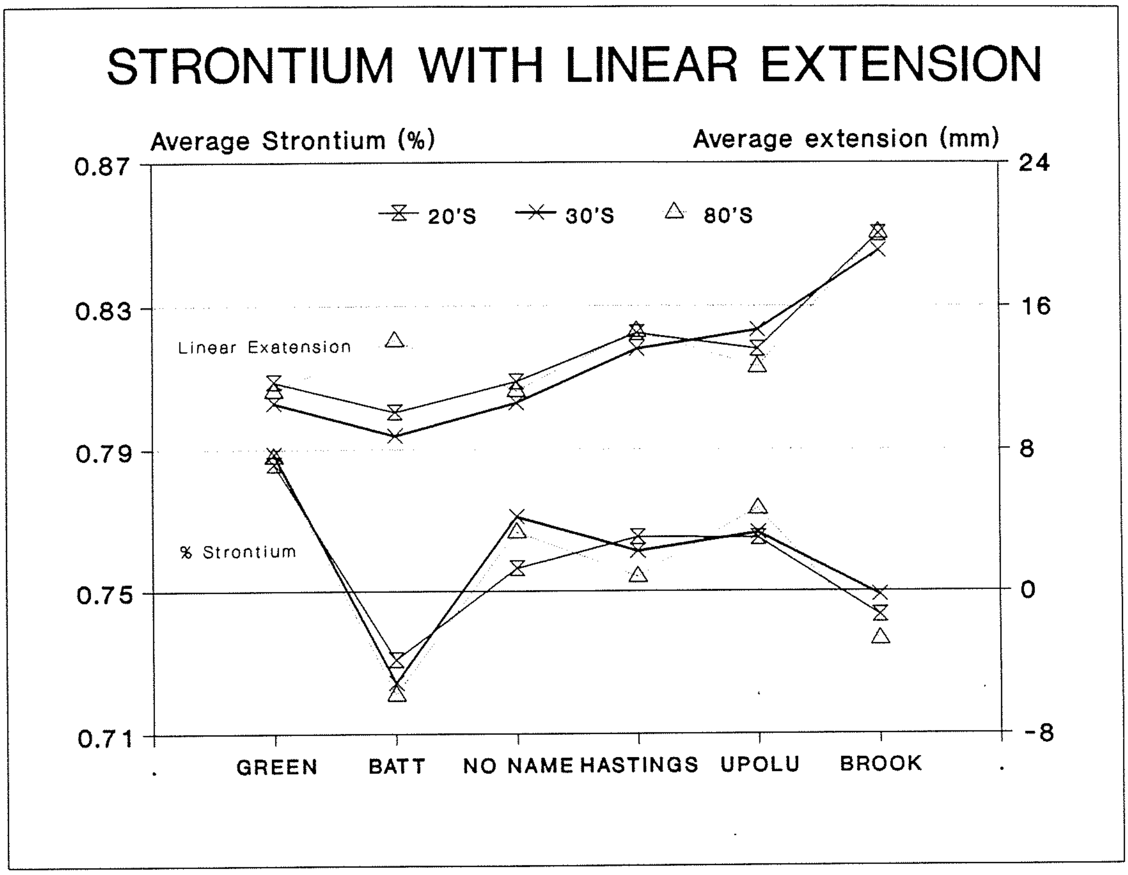

Figure 30: Average linear extension with average strontium content from selected decades. Thetford Reef has been eliminated from this data set because of insufficient material.

The data set from Green Island was then evaluated on an annual scale. Time and financial constraints limited this section of the study to a single sample set. The Green Island sample set was chosen for several reasons -

(a) The poor proxy temperature estimates from this sample set suggested that additional factors were influencing the uptake of strontium into the coral skeleton.

(b) Annual assessment using X-radiography (Knutson *et al* 1972) was reasonable through a long section of the sample set (1930-1987).

(c) This sample set has a relatively high rate of linear extension (approximately 15 mm a year compared with 13.6 mm and 11.0 mm in the Upolu and Batt Reef samples).

(d) Green Island Reef has a known environmental history with a record of tourism and occupation since circa 1920 should such an assessment be needed.

While the examination of average skeletal extension and average strontium content over a number of decades suggests that skeletal strontium and growth follow similar patterns, at an annual scale the results are less convincing. Statistical analysis using cross correlations detected a positive correlation ($r=0.2913$, $n=55$, $\alpha=0.05$) when skeletal extension preceded strontium content by one year. This lag may be an artefact of the sampling procedure. McCulloch *et al* (1993) have shown that strontium peaks sharply over a very short interval during the coral year. In this case, the sampling procedure used in this study could easily incorporate the peak into the wrong time period.

In addition, graphic examination of the two data sets over time suggests that the relationship is irrational, with periods of reasonable correspondence interspersed with periods when no correlation is present (Figure 31). Again, this could be related to the sharpness and location of the strontium peak in the annual sample (McCulloch *et al* 1993). However, it could be a true record of the relationship. This then suggests an additional parameter, or the combination or interplay of several parameters, is influencing the two data sets.

This combination, or interplay, of factors could include temperature and growth. For example, Houck *et al* (1977) showed that in their studies *Porites* colonies displayed a sharp growth optimum between 26°C and 27°C, after which linear growth dropped sharply. Temperatures for coastal waters in the Cairns section of the Great Barrier Reef Marine Park range from a low 21°C to a high 30°C (Low Isles data; extracted from CSIRO Hydrographic records). It is unlikely that the growth rates of inner- and inner/mid-shelf corals can be sustained at optimum conditions for any extended period. Thus, dependence probably oscillates almost constantly between growth and temperature domination. It was shown in section 6.7.2.(a&b) that the relationship between skeletal strontium and temperature was reasonably stable with distance from shore. Therefore, while growth rate of the coral skeleton may be associated with the uptake of strontium into the coral skeleton, partitioning of the various elements into the coral skeleton is clearly being influenced by additional factors. Undoubtedly these include temperature.

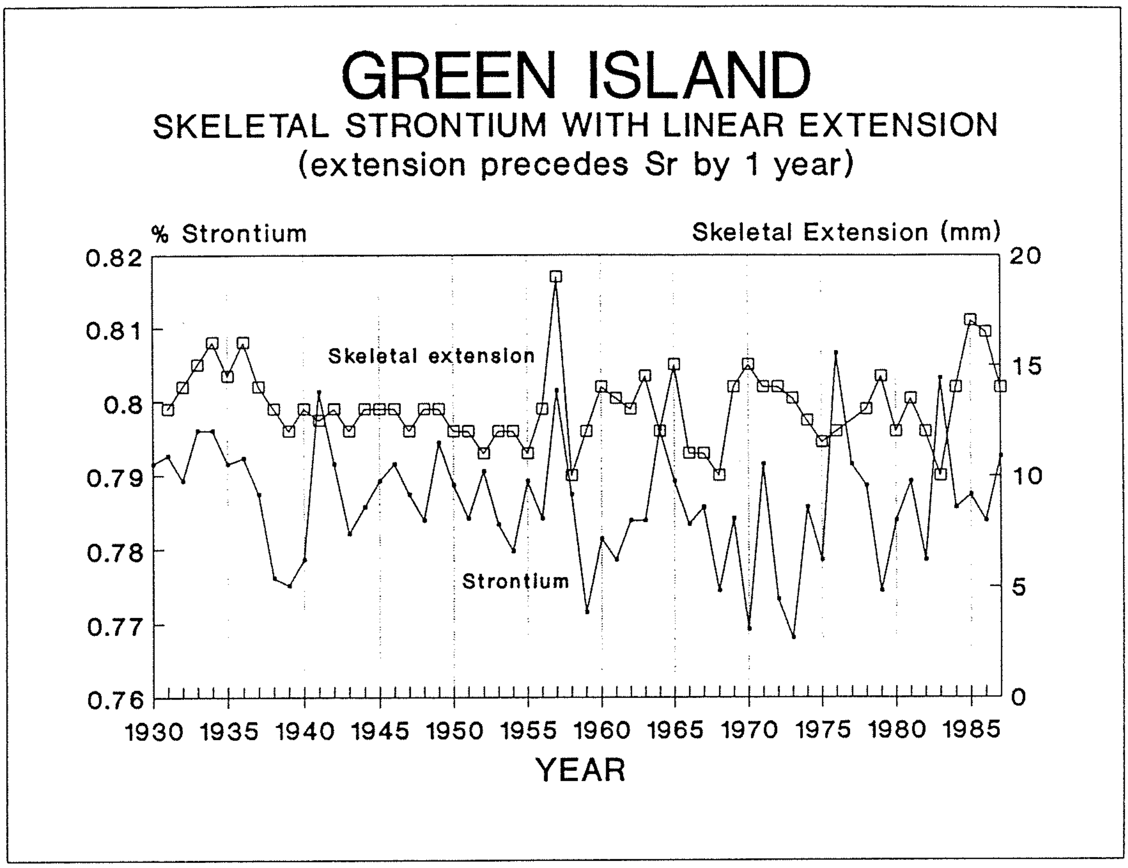

Figure 31: Annual strontium content of the sample set from Green Island Reef plotted against annual rates of linear extension.

(d) **Diagenetic alteration and strontium content:**

Parameters that could significantly influence the strontium content of skeletal aragonite include modification and early diagenetic alteration. The presence of a high magnesian calcite phase in aragonite is known to give lower strontium values due to the general structural incompatibility of strontium with the calcite structure. Therefore, secondary infilling of boring algal cavities with high magnesian calcite could influence the strontium content of the skeleton. This possibility was examined by X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM). Where applicable a qualitative chemical assessment was made using the Electron

Microprobe attached to the SEM. This examination focussed on the inner- and inner/mid-shelf sample sets (Batt, Green Island and Brook Islands Reefs) where the strontium inferred temperature records are suggested, above, to be anomalous.

(i) Batt Reef:

This sample set contained many hiatuses and evidence of boring algal remains. While considerable care was given to the removal of any calcareous contaminants during laboratory preparation, XRD analysis detected some evidence of high magnesian calcite. Hence, introduced or diagenetically altered material may be responsible for the particularly low strontium values and the anomalously high temperature estimates in this sample. Fine lines were identified throughout this sample set when examined using the SEM. Qualitative analyses with the microprobe attached to the SEM indicated the 'lines' contained high levels of magnesium, together with calcium. These observations are consistent with the suggestion that the fine lines are remnant algal borings infilled with high magnesian calcite.

(ii) Green Island:

This sample set contained only minor evidence of infilling into algal cavities during the latter growth stage. A partial interruption to the growth of the colony was evident around 1974. Care was given to the removal of this material during the sampling process. XRD and microprobe analysis detected only minor evidence of possible high magnesian calcite around the growth interruption. AAS analysis detected erratic, high levels of magnesium in the sample set from the 1960's onwards.

(iii) Brook Islands:

This sample set contained (a) no evidence of diagenetic change, (b) no evidence of boring algal activity, and (c) consistent growth patterns, but anomalous strontium and strontium inferred temperature records.

The process of diagenetic alteration, or the introduction of algal high magnesian calcite, cannot alone explain the discrepancies in the coral inferred temperature record because these processes were not observed in the sample set from the Brook Islands. Strontium content is particularly low in both the Batt Reef and

Brook Islands samples. Major evidence of diagenetic alteration and algal infilling is only evident in the sample set from Batt Reef. The results suggest that either the uptake of strontium into the coral skeleton is being controlled by different parameters at the inner- and inner/mid-shelf locations, or the chemical composition of the surrounding waters is different at each location.

(e) Summary of factors contributing to strontium discrepancies:

If calcium carbonate precipitation is partially controlled by the presence in the water column of chemical species that interact to affect either the activity of the CO_3^{2-} component of $CaCO_3$ (for example $[SrHCO_3]^+$ ion pairs) or the Ca^{2+} component (for example $[CaPO_4]^-$ ion pairs), then it would be expected that precipitation would increase or decrease as a response to the presence, and/or concentration, of these additional species. If this is the case, the results suggest that the corals have been exposed to some influence that can change the calcium carbonate ratio of the skeleton.

From differences in the crystallochemical ionic radii (Sr^{2+} = 0.118 nm; Ca^{2+} = 0.10 nm; Henderson 1982) the incorporation of strontium instead of calcium into the aragonite structure should lead to a very small increase in unit cell size. It was initially expected that this variation would be beyond the limit of instrumental resolution. However, to test this prediction, the core from Green Island was examined using X-ray Diffractometry. The results of deviations from the anticipated location of the XRD (111) aragonite reflection (see Appendix A) were then assessed with the strontium record from the same sample. Results are shown in Appendix K. Product-Moment correlations of the log normalised values show a positive correlation ($r=0.2127$, $n=112$, $\alpha=0.05$) when the XRD (111) aragonite reflection anomalies precede strontium values by one year. If the chemical composition of the skeleton is controlled by the composition of the seawater as well as by internal depositional media (Pilkey & Goodell 1963), then a relationship between crystallographic parameters and chemical composition could be anticipated. From the results presented above, several environmental factors may influence the precipitation of the aragonitic skeleton. This will be discussed further in Chapter 8.

6.7.3 Magnesium:

Examination of the CDA biplot (Figure 27, p.121) showed that the magnesium content in the Green Island sample set varied significantly pre- and post-1950. Further examination using univariate analysis of individual decades, suggested that the magnesium content in this sample set increased during the 1920's and again during the 1960's and 1980's with a considerable increase during the 1970's (Figure 32, p.141). Magnesium values during the latter three decades are erratic.

Associations between environmental conditions and skeletal magnesium have been fully discussed in Chapter 5.2.3, and include -

(1) temperature (Chillingar 1953; Chave 1954) - (Chapter 5.2.3 - 1),

(2) the deposition rate of the calcium carbonate skeleton (Chave 1965; Kitano 1967; Chave & Suess 1970) - (Chapter 5.2.3 - 2),

(3) pH dependence (e.g. Kitano & Hood 1965; Chillingar 1962) - (Chapter 5.2.3 - 3),

(4) the Ca:Mg ratio of sea water (Chillingar 1956; Kitano 1967) - (Chapter 5.2.3 - 4),

(5) dependence on organic compounds in the seawater (Chave 1965; Kitano 1967; Chave & Suess 1970) - (Chapter 5.2.3 - 5)

No change in seawater temperature could be detected pre- and post-1950 in the strontium, and Sr:Ca proxy temperature estimates and the deposition rate of the calcium carbonate skeleton increased only marginally post-1950 (Table 6.11). The Ca:Mg ratio of the surrounding seawater and the pH level of the coral tissue were not examined during this study.

Chave (1965), Kitano & Hood (1965) and Chave & Suess (1970) have suggested that organic compounds inhibit reactions between carbonate minerals and seawater. In the study area an increase in the level of organics can occur -

(1) **From algal blooms** - Algal blooms are a natural occurrence in coral reef waters. However, it has been argued that the strength and periodicity of these blooms (e.g. *Trichodesmium* or *Oscillatoria*) has increased in Great Barrier Reef waters during the last 50 years (e.g. see Bell & Gabric 1990a, 1990b, 1991)

(2) **From mainland runoff** - Mainland runoff has a direct and an indirect effect on the level of organics added to the marine waters of the study area -

(a) land clearance alters catchment hydrology and runoff patterns, making additional quantities of natural organics (e.g. soil humics and fulvics) available to the marine system.

(b) finer plant litter caused by mechanical harvesting is easily transported to ocean waters during the high energy rainfall events of North Queensland's wet season.

(3) **From increased nutrient supply** - In the study area there are two possible sources of additional nutrient supplies (a) from sewage, and (b) from agricultural runoff. Increased organics are a natural by-product of an increase in nutrient supply. Smith *et al* (1981), considered that the major role of sewage discharge into Kaneohe Bay (Oahu) was nutritional, providing a perturbation at the base of the foodweb that subsequently increased biomass and productivity. It is logical that nutrient enriched runoff would have a similar nutritional effect. The scale of the effect will be controlled by the concentration of the nutrient, the periodicity of the discharge, the geographical scale of the discharge, and residence time in the area of influence.

The elevated magnesium values in the Green Island sample set coincide with increased tourism (and, therefore, anthropogenic activity, including increased sewage) at Green Island. During this period, tourist visits increased from an estimated 28,000 visitors in 1957/58, to 82,000 in 1966, and 400,000 in 1988/89 (Baxter 1990). However, the two periods of elevated magnesium values (1920's and 1960's) also overlap known periods of agricultural and urban expansion on the adjacent mainland (Pulsford 1991). Data on fertiliser use in the area are unreliable before the 1950's. However, the second period of elevated magnesium content is consistent with Pulsford's (1991) description of major increases in fertiliser usage on the mainland from the mid-1950's onwards. In addition, enhanced magnesium levels during this period coincide with the appearance of severe skeletal discolouration and confused growth patterns during a period when rainfall was above average for several years.

Chillingar (1956a) noted that the Ca:Mg ratio of some calcite secreting organisms was proportional to the Ca:Mg ratio of the sea water in the experimental aquarium, but did not quantify the relationship. He also suggested that other invertebrates may also assimilate more magnesium in environments having a higher concentration of magnesium. It is known that considerable quantities of calcium/magnesium (dolomite) are used on the cane fields of North Queensland. However, it is unlikely that sufficient calcium and magnesium could be added via runoff to appreciably alter the Ca:Mg ratio of the sea water medium. It is possible that the increased levels of magnesium in the post-1950's portion of the Green Island sample set are due to secondary enhancement from increased levels of organics (either in the water column or in the tissue of the coral sample). It is also possible that the increased levels of organics are due to increased nutrients in the water column. Where the magnesium is located in the aragonitic skeleton is presently unknown and it is possible that the additional magnesium in the Green Island sample set is associated with the organic composition of the skeleton.

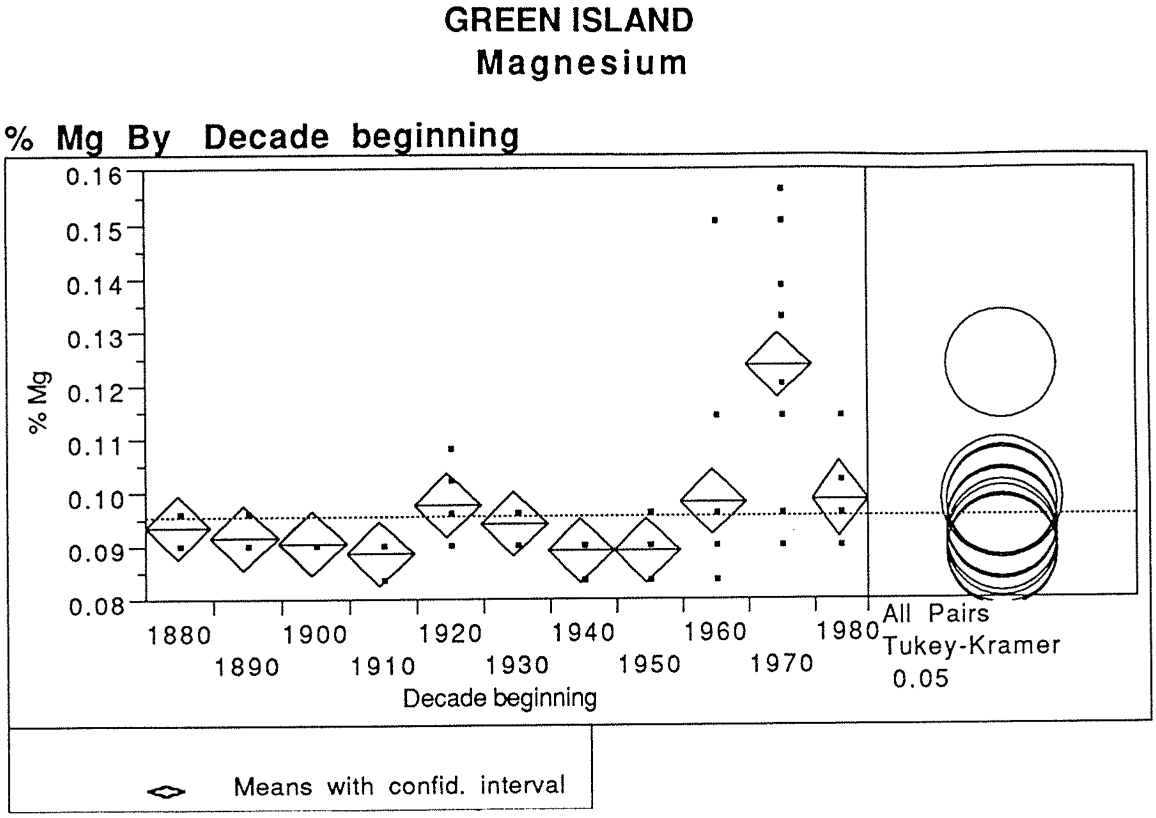

Figure 32: Graph of mean Green Island magnesium concentration for each decade ± 95% confidence intervals. Means comparisons presented were assessed using Tukey-Kramer HSD Test (α=0.05). N.B. It should be noted that values often overlap. n=10 for each decade except the 1980's where n=8.

6.7.4. Potassium:

Examination of the CDA biplot presented in Figure 28 shows that the potassium content of the Green Island sample set increased post-1950. Further examination using univariate analysis of individual decades, shows that the potassium content of the Green Island sample set increased slightly during the 1920's and 1930's (from an average 0.0066 wt% to 0.0081 wt% in the 1920's and 1930's). There was a further increase during the 1960's, 1970's and 1980's (0.0091, 0.0110, and 0.0097 wt% respectively) (Figure 33). These are approximately the same periods when magnesium content of the Green Island sample set also increased.

Potassium is a trace element present in seawater with a concentration of approximately 380 ppm . The ionic radius of K^+ (0.138 nm) makes it compatible with the metal atom position in aragonite, but before substitution can take place within the crystal structure, co-operative charge compensation must occur. Under normal circumstances the extent of substitution of potassium into the aragonite structure is limited and much of the potassium usually exists as a surface adsorbed phase (Fyfe 1964). If a significant increase in potassium does occur, either within the structure or adsorbed on to the surface, then changes in crystal growth processes, driven by changes in the solution chemistry of the system, are likely to have occurred. These may be inorganically or biologically related. The elevated levels of potassium occur at the same period when magnesium is elevated. Therefore, an association may exist with boring algal activity, infilling into algal cavities, or diagenetic alteration of small surfaces of the skeleton. However, the sample set with the most evidence of these factors, the Batt Reef sample, showed no indication of similar elevation of potassium values. If the magnesium in the Green Island sample set results from an increase in organics, either within the skeleton, or in the seawater surrounding the growing coral, then it is possible that both the chemical composition and structure of the Green Island sample set has been sufficiently perturbed to favour the incorporation of additional levels of potassium into the coral skeleton. It is also possible that the potassium has entered the perturbed skeleton attached to other material. If potassium is incorporated within the structure, rather than within the tissue, the results would suggest that the inclusion is secondary and has occurred only after primary damage has already occurred to the coral skeleton.

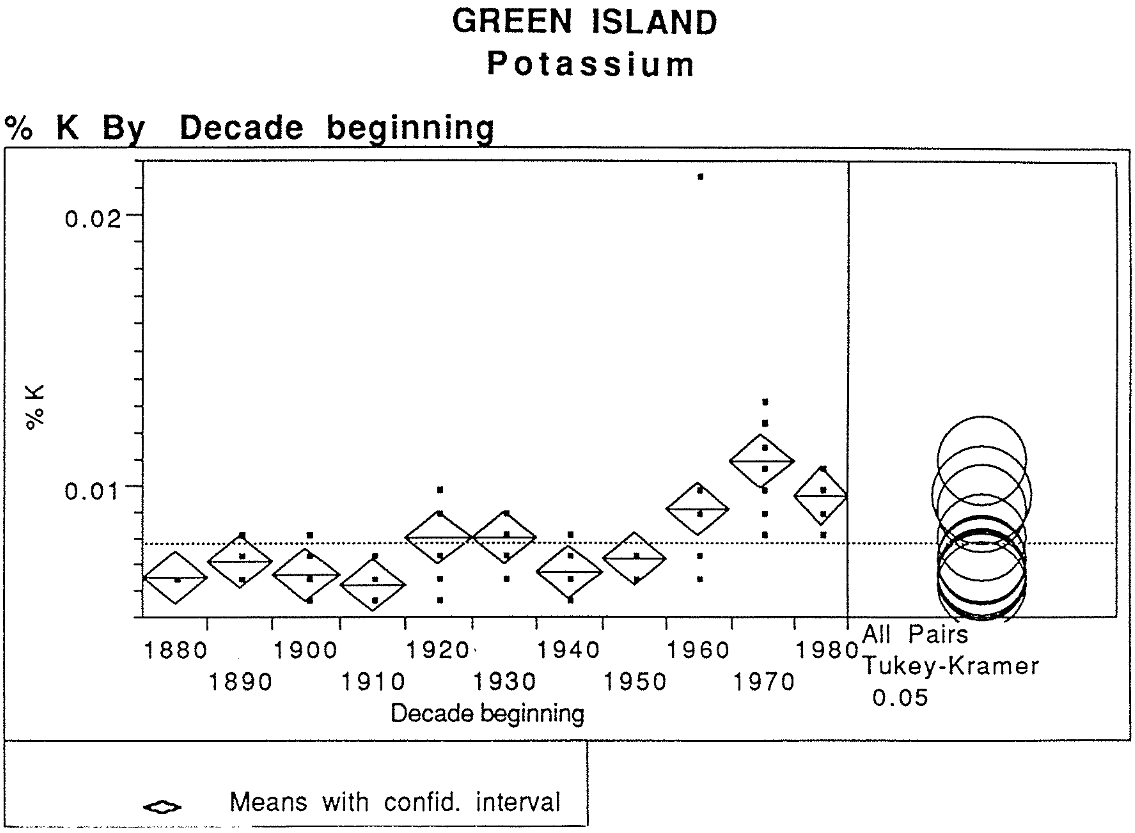

Figure 33: Graph of mean Green Island potassium concentration for each decade ± 95% confidence intervals. Means comparisons presented were assessed using Tukey-Kramer HSD Test ($\alpha=0.05$). N.B. It should be noted that values often overlap. n=10 for each decade except the 1980's where n=8.

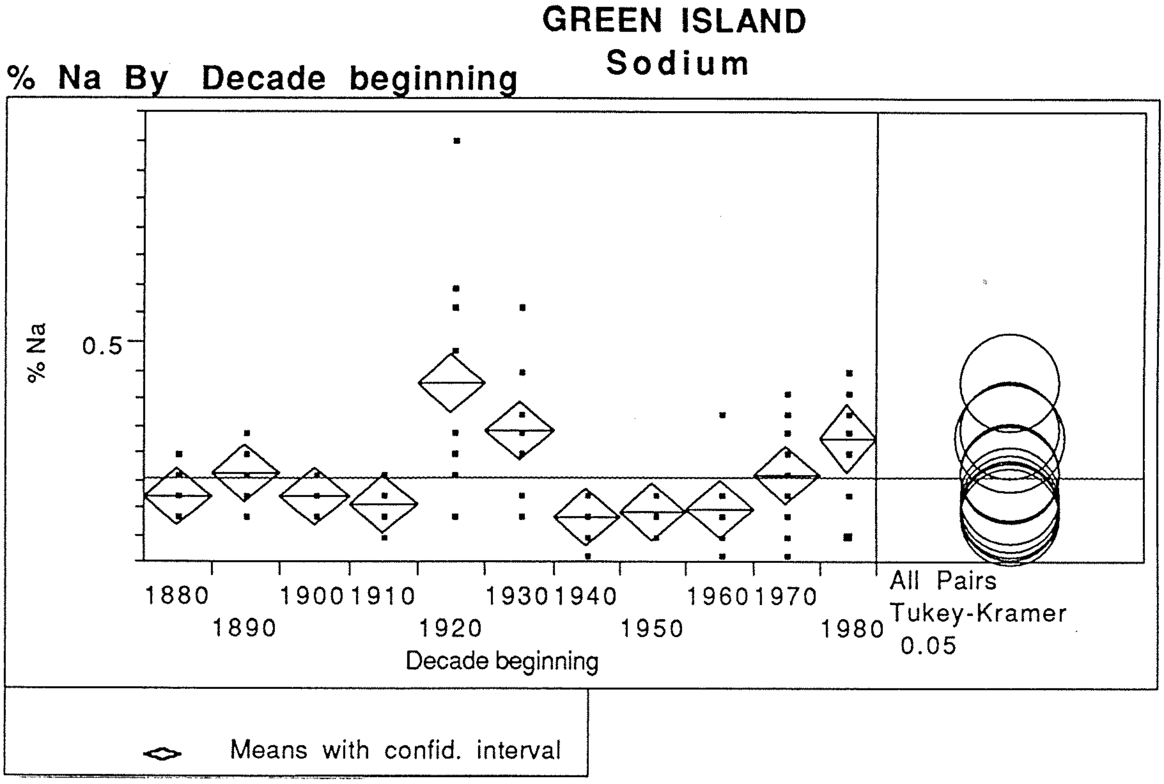

Figure 34: Graph of mean Green Island sodium concentration for each decade ± 95% confidence intervals. Means comparisons presented were assessed using Tukey-Kramer HSD Test ($\alpha=0.05$). N.B. It should be noted that values often overlap. n=10 for each decade except the 1980's where n=8.

6.7.5. Sodium:

Sodium in the Green Island sample set (and the neighbouring Thetford Reef sample) is considerably below concentrations measured at all other reefs (Figure 24). The decadal concentration, however, rose during the 1920's and 1930's (from an average concentration of 0.4448 wt% to 0.4852 and 0.4674 wt% respectively) and again during the 1970's and 1980's (0.4518 and 0.4646 wt% respectively) (Figure 34). However, the spread of values around the mean decreased considerably after the 1940's in the Green Island sample set (Figure 34).

Although the physiological role of sodium on corals is not yet clear, the ion is a necessary factor in optimum respiration and membrane stability in other organisms (Mitchell 1961). If this applies equally to the coral organism, then the changes in the levels of sodium would suggest that the optimum development of the Green Island coral organism has been affected.

6.7.6. Iron:

Iron values in the sample set from Green Island Reef increased from an average 0.0040 wt% to 0.0123 wt% and 0.0154 wt% in the 1960's and 1970's respectively (Figure 35 and Appendix I). Before the 1960's, concentrations in the Green Island sample set (0.0039 wt%) were similar to those in the nearby Upolu Reef sample set (0.0040 wt%) (Figure 36). Iron in the No Name and Brook Islands Reef sample sets remained relatively unaltered throughout the growth of each colony. The Hastings Reef sample set also displays relatively stable iron concentrations, with evidence of minor perturbation during the 1950's.

The results are consistent with the natural affinity of iron to the intrusion of boring algae, either as part of the high magnesian calcite structure of the boring organism, or as iron oxyhydroxide clays, etc., retained in the cavities left by the boring algae. Evidence of boring algal activity was only minor in the sample set from Green Island Reef. The partial hiatus in the coral skeleton during the mid-1970's, and the discolouration of the core from the 1960's onwards, however, suggests the possibility of both retention in algal cavities and an association with the high magnesian calcite structure of the hiatus. However, there is no evidence of boring algal activity in the sample set from Upolu Reef during the period of increased iron content.

Iron, in particular, could conceivably be held within the organic matrix. Because of the empty 3 d electron orbitals, iron shows a strong tendency to form covalent bonds and to complex with organic molecules (Yariv & Cross 1979). Chillingar (1953) and Chave (1954) noted the ability of calcium carbonate material to precipitate additional magnesium and potassium in the presence of elevated levels of organic matter. In the Green Island sample, both the magnesium and the iron, plus the potassium and the sodium, are perturbed during the same period. If the iron is held in the organic matrix of the coral skeleton, then it could be argued that this is also the location of the magnesium. It could then also be argued that -

(a) some unknown interference is responsible for increased tissue formation in the coral skeleton,

(b) increased organic matter in the water column results in greater complex formation via covalent bonding involving iron and magnesium, thus allowing their retention.

(c) some unknown influence is stimulating the production of symbiotic algae in the coral tissue thus fostering increased incorporation of iron and magnesium, and possibly potassium and sodium, within the tissue.

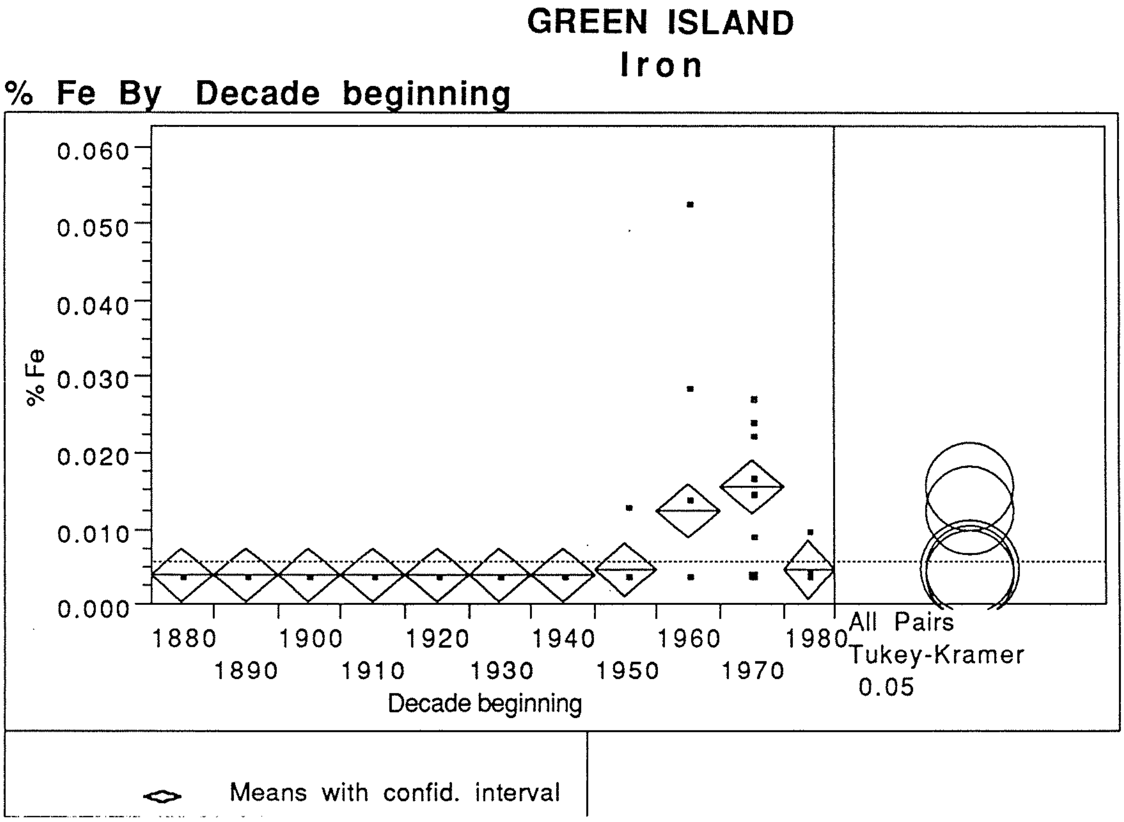

Figure 35: Graph of mean Green Island iron concentration for each decade ± 95% confidence intervals. Means comparisons presented were assessed using Tukey-Kramer HSD Test (α=0.05). N.B. It should be noted that values often overlap. n=10 for each decade except the 1980's where n=8.

6.8. CHEMICAL/MORPHOLOGICAL RELATIONSHIPS AND HUMAN DISTURBANCE:

6.8.1. Introduction

In Chapter 3 it was shown that large quantities of phosphate entered the ocean during periods of heavy river discharge. It was suggested that reef flats in the plume of this discharge acted as phosphate reservoirs, with subsequent utilisation and redistribution by biological, physical and chemical activity. In Chapter 4 it was shown that nutrient supplementation suppressed the production of calcium carbonate material in the experimental *A.formosa* corals. This suppression had a visual representation that could be viewed, and the variation estimated, using a Scanning Electron Microscope. In this present Chapter it has been shown that the chemical composition of the sample set from Green Island Reef in particular, has undergone considerable change post-1950. While the levels of phosphate enhancement exposures for the experimental corals were considerably higher than could realistically be anticipated in the natural environment, considerable skeletal alteration was visible at the lower level of enhancement. Thus, it was considered appropriate to examine the internal morphology of the Green Island sample set for any indications of skeletal change that could be interpreted as consistent with elevated levels of phosphate in the surrounding water. Sample preparation and the appropriate SEM analyses used in this examination are outlined in Appendix A.

Minor changes in the chemical composition of skeletal material are suggested to be related to crystal growth rate (Pilkey & Goodell 1963). Powder X-ray diffractometry (XRD) is a method for the recognition of crystalline substances based upon their crystal structure and inter-atomic distances. The XRD pattern of aragonite is well documented (Joint Committee of Powder Diffraction Standards, Pattern No.5-0453) and examination of this pattern shows that the major reflections occur between 20-51° 2θ for CuKα radiation. In pure chemical systems the patterns from XRD analysis are almost perfectly reproducible. However, in impure, natural systems, small positional and intensity deviations occur. These small deviations are related to many factors including crystallite size, chemical impurities, their ability to incorporate into the structure, and their affects upon the growth of the crystalline phase. Any perturbations in the sea-water column affecting the activities of the competing chemical species should be reflected in the composition of the aragonite skeleton. Therefore, any changes in seawater controlling the chemical partitioning into the coral skeleton, may also exert an influence on the precipitating aragonite crystal, and this influence might be detectable using XRD.

Analysis of the major (111), (021) and (012) reflections of aragonite indicated shifts up to 0.2° 2θ when referenced to the Joint Committee of Powder Diffraction Standards, Pattern No.5-0453. For CuKα, the aragonite (111) reflection is located at 26.24° 2θ for the NBS standard aragonite referenced in the JCPDS file, and this was chosen as the monitor of crystallographic perturbation. For this study, any shift to lower angles (i.e. higher d-spacing) was termed 'negative deviation' and any shift to the higher angles (i.e. smaller d-spacing) termed 'positive deviation'. To examine whether the alteration in the post-1950 chemical composition of the Green Island sample set was accompanied by subtle changes in the crystallography of the skeleton, the sample set was examined using XRD according to the methodology outlined in Appendix A.

6.8.2. Spatial mapping of the Green Island sample.

The calcium carbonate void distribution was mapped using the Image Analysis package on a Scanning Electron Microscope (SEM). This spatial mapping of the internal morphology of the Green Island sample set shows that fluctuations in skeletal porosity are a natural phenomenon throughout the life of the coral. However, the magnitude of the porosity increased dramatically post-1950 (Figure 36). These changes are similar to those noted in the phosphate supplemented *A.formosa* corals (Chapter 4).

Periods of rapid growth could conceivably account for increased porosity of the coral skeleton and indeed Chapter 4 noted a relationship between linear extension of the experimental *A.formosa* corals and skeletal porosity. In this study, the internal porosity of the skeleton correlates poorly with linear extension ($r=0.1518$, $n=47$), but strongly with the use of agricultural fertilisers on the nearby mainland ($r=0.6902$, $n=31$, $\alpha=0.05$), and with the magnesium concentration of the sample set ($r=0.4575$; $n=86$; $\alpha=0.05$). Further, the trend lines in Figure 37 show that -

(a) as the use of total fertiliser increased between 1951 and 1971, the porosity of the skeleton increased, and

(b) with the decrease in total fertiliser use on the mainland after 1971, skeletal porosity also declined.

This is important because it could be argued that any relationship between skeletal porosity and nutrient enhancement could come from increased sewage discharge at Green Island. However, while the use of total fertiliser on the mainland decreased after 1971, tourism at Green Island continued to increase. In addition, the use of agricultural fertilisers on the mainland also correlates strongly with the increased magnesium content of the Green Island sample set ($r=0.6078$; $n=36$; $\alpha=0.05$).

There is evidence to suggest that increased levels of organics in seawater can inhibit calcium carbonate precipitation (Chave 1965; Kitano & Hood 1965; Chave & Suess 1970). Elevated organic content is a by-product of enhanced levels of nutrients, principally through increased biomass production, for example by phytoplankton blooms (Smith *et al* 1981). By inference these, together with the results presented above and in Chapters 3 and 4, suggest that there may be a link between the use of fertiliser on the mainland, unknown but presumed increased levels of organics in the seawater, skeletal magnesium, and porosity of the coral skeleton.

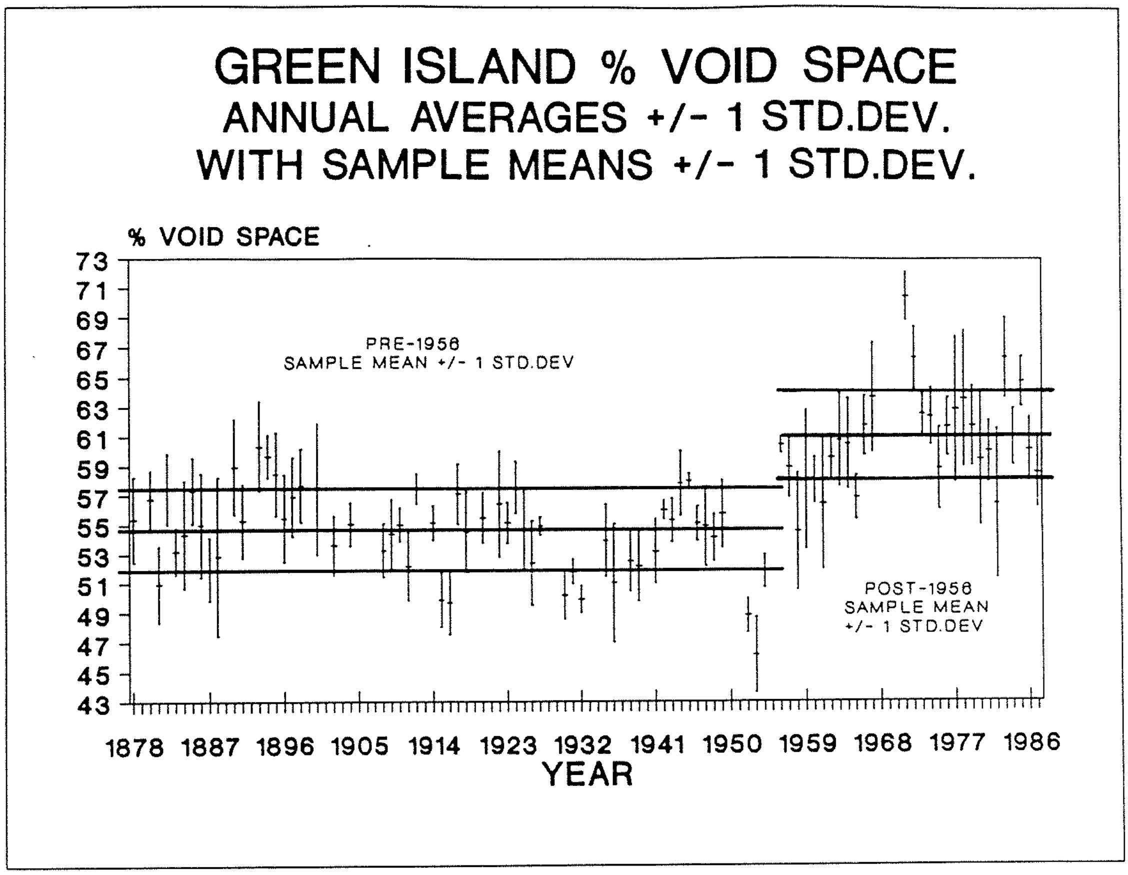

Figure 36: Skeletal porosity of the Green Island sample set.

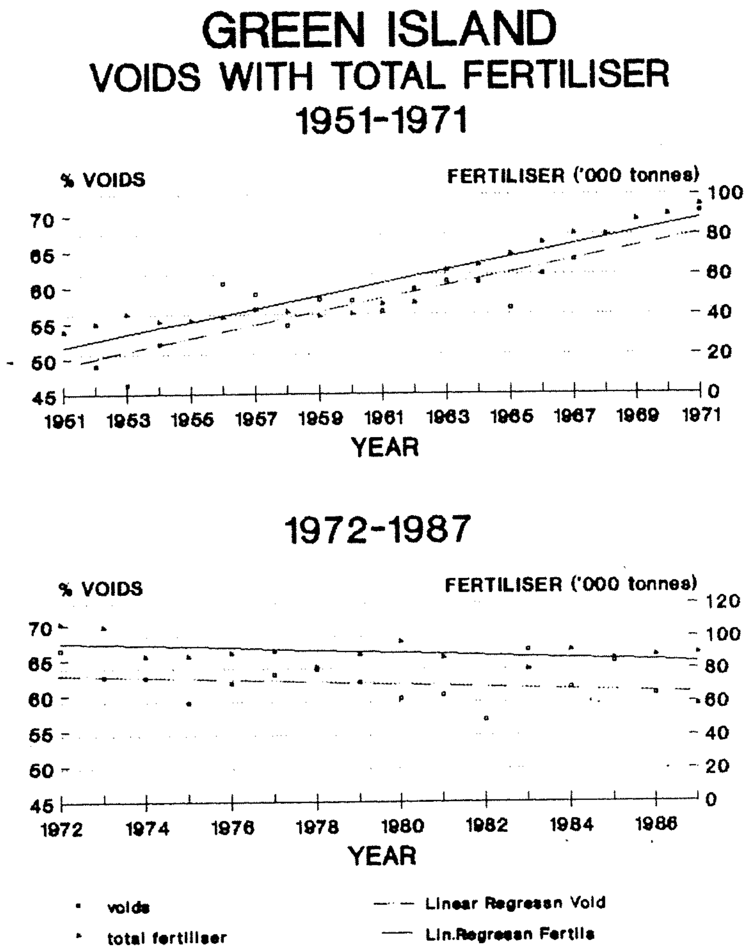

Figure 37: Trend lines indicating the association between skeletal porosity in the Green Island sample set and the use of total fertiliser on the nearby mainland.

6.8.3. Crystallographic variation of the Green Island sample.

XRD examination located small isolated peaks in the Green Island sample set between 29 and 30 degrees 2θ on the XRD trace during the years 1882, 1890, 1900-1903, 1921, 1931, 1955, 1959, 1962, 1966-68, 1970-75, 1982 and 1986. These features are consistent with the presence of high magnesian calcite, but of insufficient magnitude to justify the significant chemical and morphological change noted from the mid-1960's onwards.

Examination of the shifts in the theoretical location of the XRD (111) aragonite peak reflection (Figure 38) show that deviations from the anticipated location are a natural phenomenon throughout the life of the coral colony. However, the trend line in Figure 38 shows that there is an increase in the magnitude and occurrence of the negative shift from the theoretical location of the aragonite (111) reflection from around -0.02° 2θ in the early growth years to approximately -0.06° 2θ during the latter period. There is also a very strong negative deviation beginning around 1956 that coincides with the increase in skeletal porosity displayed in Figure 36. Further, during the period between 1966 and 1982, when magnesium content of the sample set was particularly high, magnesium content correlated strongly, but negatively, with the XRD anomaly, with the XRD anomaly preceding magnesium content by one year ($r=-0.7332$, $n=17$, $\alpha=0.05$). This negative correlation is not evident before the period when magnesium content became elevated. Therefore, if magnesium was substituting into crystal structure, since the ionic radius of magnesium (0.072 nm) is considerably smaller than that of calcium (0.10 nm), the 'd' spacing should decrease - i.e. the correlation should be positive. Since this lattice substitution should give rise to a positive shift, this evidence may imply that magnesium is not present as a substituent phase, but is present in other ways, possibly as an adsorbed phase on external and internal surfaces. This would also explain the correlation between magnesium and potassium, which is also considered to be an adsorbed phase.

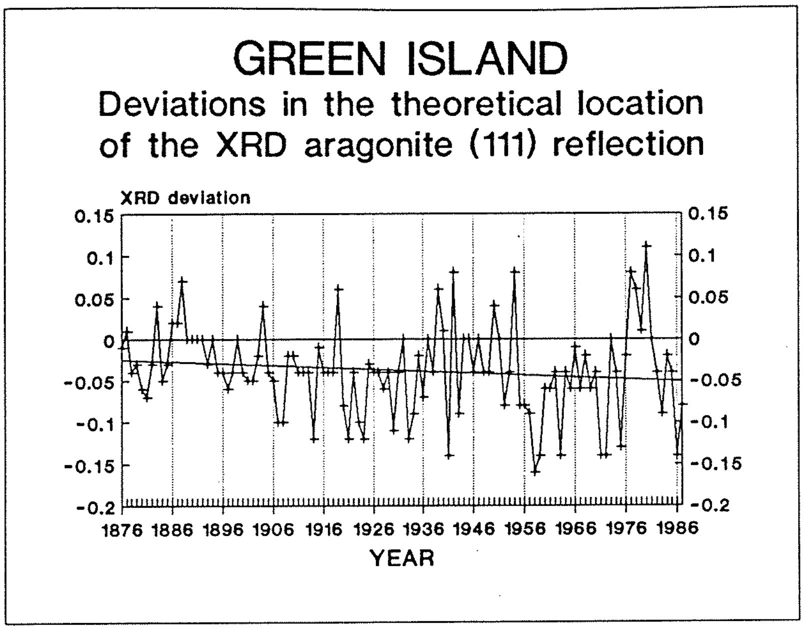

Figure 38: Examination of the shifts in the anticipated XRD (111) aragonite peak reflection for the Green Island sample

6.8.4. *Statement of the overall conclusion from a study of chemical/morphological relationships and human disturbance in the study area*

The results from the examination of the chemical/morphological relationships of the Green Island sample set suggest that the intrusion of high magnesian calcite into the sample set accounted for only a small proportion of the chemical and morphological anomalies present in the skeleton. It is concluded that an additional influence prior to the intrusion of magnesium into the skeleton, fostered skeletal porosity, interrupted calcium carbonate deposition, promoted crystallographic disturbance, and predisposed the organism to the inclusion of large amounts of impurities.

6.9 GEOCHEMICAL RECORDS RETAINED BY MASSIVE CORALS: REGIONAL VARIABILITY AND HUMAN IMPACT - CONCLUSIONS

6.9.1. Discussion and conclusions

This study examined the possibility that the chemical properties of the coral skeleton reflected variations in water quality and that these properties were useful in the interpretation of palaeoenvironmental conditions. Within this concept, the study also examined the possibility that these properties could also be used in the interpretation of signals that may have an anthropogenic influence.

Statistical analysis of the chemical data from the different sample sets showed that the inner- and inner/mid-shelf sample sets were significantly different from each other and from all other sample sets. This difference was based on high levels of strontium in the Green Island sample set, high levels of magnesium in the Batt Reef sample set, and low levels of both strontium and magnesium in the Brook Islands sample set. Multivariate analysis could not distinguish any significant difference in the mid- to outer-shelf sample sets.

Comparison of the results of the univariate analysis detected a change in the relative contribution of the individual elements to the total chemical composition of the coral skeleton between this study and that of the micro-environmental study (Chapter 5). Examination of the outliers in the data sets indicated that most outliers occurred in the younger section of the skeleton (from approximately 1950 onwards). It was hypothesised that the anomalies could be due to a change in water quality post-1950. CDA biplots for the two periods pre- and post-1950 showed that the calcium, strontium and magnesium composition of all sample sets varied slightly during the two periods. However, this variation was only significant for the sample sets from Hastings, Batt and Green Island Reefs. The two periods for these three sample sets were discriminated by higher levels of magnesium in the post-1950 Green Island and Hastings Reefs sub-sets, and by lower levels of strontium in the post-1950 Batt Reef sub-set.

Several researchers have suggested that environmental variations of the water column may indirectly affect the concentration of potassium, sodium and iron in skeletal material (e.g. Chillingar 1953; Chave 1954; Chillingar 1956; Mitchell 1961; Livingston & Thompson 1971). The inclusion of potassium, sodium and iron in the multivariate analysis further discriminated the sample sets of the inner- and inner/mid shelf reefs (Batt, Green Island and Brook Islands), from each other and from all other sample sets. This analysis also showed that the sample sets from Green Island and Hastings Reef had undergone considerable change post-1950. This change is caused by higher levels of magnesium, potassium and iron post-1950 in the Green Island Reef sample set, and higher levels of magnesium and lower levels of strontium in the post-1950 Hastings Reef sample set.

In the Green Island sample set, the increase in skeletal magnesium was accompanied by an increase in skeletal porosity. Both variables were strongly correlated with the use of agricultural fertiliser on the mainland. During this period the levels of potassium, sodium and iron in the skeleton were also elevated. It is highly unlikely that the application of calcium/magnesium (dolomite) to the North Queensland cane fields has sufficient influence on the chemical composition of nearby marine waters to bias the chemical composition of skeletal carbonates. It is more likely that the association is secondary and related to an increase in organics, either direct from the mainland, or from the stimulation of biomass production following the addition of nutrients to the marine waters. This argument is supported by Kitano & Hood's (1965) experimental work where it was shown that an increase in the concentration of organic material in solution led to a decrease in the rate of calcium carbonate formation. In addition, during the period between 1966 and 1982, when magnesium content of the sample set was particularly high, the magnesium content of the sample set correlated strongly, but negatively, with a shift away from the theoretical location of the XRD (111) aragonite reflection (XRD anomaly), with the XRD anomaly preceding magnesium content by one year ($r=-0.733$, $n=17$, $\alpha=0.05$). Further, the XRD analysis showed a significant negative deviation beginning around 1956 that coincides with the increase in skeletal porosity. This shows that some degree of crystallographic disturbance has taken place in the Green Island sample set. The nature of this structural disturbance is not yet known.

The argument connecting changes in skeletal magnesium and other properties of the Green Island sample set is tentative, but is hard to ignore if the experimental research of Chave (1965), Kitano & Hood (1965) and Chave & Suess (1970) can be extended past the laboratory. If this is the case, then it is tempting to hypothesise that either -

(1) additional amounts of organic material have been incorporated into the skeleton, thereby stimulating skeletal extension. These, either individually or together, are capable of altering the calcium to trace element ratio, increasing porosity and subsequently weakening the skeleton by reducing the relative volume of skeletal fabric, or

(2) elevated levels of organics in the water column have interfered with the optimum precipitation of the aragonite crystal subsequently altering the calcium to trace element ratio, stimulates skeletal extension, increases porosity, and weakens the skeleton by reducing the relative volume of skeletal fabric.

However, where magnesium resides in the coral skeleton is presently unknown. Therefore, the environmental controls responsible for its distribution in the coral skeleton cannot be adequately determined. Until all roles in the process of skeletogenesis are understood, the quantitative usefulness of this element as an environmental indicator will be limited. However, the results from the XRD analysis show that the association between skeletal magnesium and the XRD anomaly is negative for the period when magnesium content of the Green Island sample set is particularly elevated (1966-1982). If magnesium was substituting into the crystal structure, since the ionic radius of magnesium (0.072 nm) is considerably smaller than that of calcium (0.10 nm), the 'd' spacing should decrease - i.e. the correlation should be positive. This implies that magnesium is not present as a substituent phase, but is present as an adsorbed phase on external and internal surfaces.

Although the magnesium content of the Green Island sample set increased dramatically post-1950, the strontium and Sr:Ca record retained by the skeleton remained relatively constant through the life of the colony. Reconstruction of past seawater temperatures using the strontium and Sr:Ca records in the various sample sets, clearly shows that the proxy coral record produces reasonably accurate estimates in a clean, well mixed, open ocean system. Estimates made from near-shore coral samples, however, are inconsistent, both with each other and with measured seawater temperature data. It could be argued that this breakdown in the inshore samples is caused by -

(a) a genetic effect. However, the inconsistent temperature estimates are found in the three inner- to inner/mid-shelf sample sets,

(b) anthropogenic interference. However, the inconsist temperature estimates are present in skeletal material that pre-dates the period of major European influence,

(c) diagenetic alteration. But, the erroneous estimates are also applicable to the Brook Islands sample set where no evidence of diagenetic change could be detected.

Therefore, it is unlikely that any of these arguments are feasible. It is more likely that the inaccurate estimates are caused by the large temperature fluctuations in the shallow tropical waters. In these waters it would be difficult to maintain the narrow temperature window critical to optimum skeletal growth for any extended period (Houck *et al* 1977).

A correlation between skeletal growth and strontium content of the coral skeleton was also shown ($r=-0.8361$, $n=15$, $\alpha=0.01$), when the values were averaged over a particular period (in this case, decade). Examination of the annual variability in the Green Island data set suggested a positive correlation ($r=0.2913$. $n=55$, $\alpha=0.05$) when skeletal extension preceded strontium content of the skeleton by one year. This lag effect could be caused by the location and abruptness of the strontium peak within the annual strontium variability (McCullough *et al* 1993) in which case it could easily be incorrectly included in an adjacent annual density couplet during the sampling process. However, it could also be a true indicator of the relationship. If so, an additional parameter must be associated with the two data sets. However, the correlation coefficient in the analysis was low, and when the two data sets were graphed, the relationship was shown to be inconsistent. Again, in shallow tropical waters it would be difficult to maintain optimum skeletal production within the very narrow temperature window necessary for ideal growth conditions. Still, the data shows periods where a reasonable correlation is present between the two data sets and other periods where no correlation is apparent. This inconsistency is not easily explained by oscillation between control parameters, unless an additional parameter is exerting a control on both the biotic and abiotic variables.

From the results presented throughout this Chapter it is concluded that both the chemical and morphological properties of the coral skeleton are useful for the interpretation of a number of palaeoenvironmental conditions. Interpretation of trace element composition related to minor changes in environmental conditions is limited only by the coarseness of the analytical techniques. The sensitivity of the corals to environmental variations noted in this study, and in Chapter 5, suggested that improvements in analytical precision will greatly improve the interpretative power of a wide range of trace and ultra-trace elements present in the coral skeleton.

The results also show that considerable change has taken place in the chemical composition and morphological structure of the Green Island sample set post-1950. From the correlations with agricultural fertilisers it is concluded that this is probably an anthropogenic influence. One result of this influence is considered related to either the direct or indirect effects of nutrient enhancement in the waters around the reef. This has led to considerable weakening of the coral skeleton. Skeletal weakening will lead to a greater susceptibility to routine destruction by wave action, a major cause of coral reef destruction in areas prone to cyclonic activity. This is particularly relevant in an area where larval recruitment is also likely to be hindered by the elevation of nutrient levels (Tomascik 1991). It is of greater concern in view of the findings of Zann (1993) that link anthropogenic influences (possibly related to elevated levels of nutrients) to *Acanthaster planci* infestations.

CHAPTER 7

GEOCHEMICAL RECORDS RETAINED BY MASSIVE CORALS

(C)

MACRO-ENVIRONMENTAL (GLOBAL) ASSESSMENT OF THE GEOCHEMISTRY OF THE CORAL SKELETON: AN UNDERLYING GLOBAL INFLUENCE IN THE ENVIRONMENTAL RECORD?

7.1 INTRODUCTION

The results presented in Chapter 6 showed that correlation between skeletal strontium and water temperature is best in corals from clean open-ocean situations. This suggests that the inaccurate strontium based temperature estimates from the near-shore coral samples were obtained from coral skeletons precipitated under less than optimum conditions. Further, this implies that either large-scale temperature fluctuations in shallow near-shore waters prevent optimum precipitation of the coral skeleton (Houck *et al* 1977), or that the input of terrestrial components plays a role in influencing the organic precipitation of calcium carbonate in near-shore corals. The delivery of terrestrially derived material into the ocean is primarily a function of river discharge, itself a function of climatic influences. In the Cairns area, this is closely associated with ENSO activity (McBride & Nicholls 1983; Nicholls 1984a,b,c; Allan 1988; Allan & Pariwono 1990; Allen *et al* 1990).

It was hypothesised that the major influence on the strontium content of the outer-shelf corals was water temperature associated with the Southern Oscillation Index (SOI), and that this global climatic signal was perturbed in the nearer to shore corals. It was further hypothesised that if the cause of the ambiguous strontium based temperature estimates of the inner- and inner/mid-shelf corals was associated with terrestrial discharge, then this association should also have a climatic signal.

In Chapter 6.6.2e an association was also noted between the strontium content of the sampled corals and deviations from the theoretical location of the aragonite XRD (111) reflection peak as referenced by the Joint Committee of Powder Diffraction Standards, Pattern No.5-0453. The direction of the shift was not uniform, suggesting that the precipitating nuclei was being irregularly affected. Because the shifts occurred throughout the life of the coral, it was presumed the discrepancies were not purely anthropogenic, although an association with other skeletal parameters post-1950 was argued. It was hypothesised that the dominant influence could be similar to the suspected climatic influence on the strontium content of the Green Island and No Name Reef samples. As such, this could also be related to parameters associated with the Southern Oscillation.

Previous research has established the value of strontium and Sr:Ca ratios as indicators of sea surface temperatures. However, there is no indication in the literature that small variations in the crystallographic structure of aragonite could exhibit an environmental signal. Nevertheless, this section of the study will focus on skeletal strontium and the anomalies in the position of the aragonite XRD (111) reflection and their potential to provide paleoclimatic information. This information is particularly pertinent as this may be interpreted in terms of ENSO activity in the Cairns region of Australia's Great Barrier Reef.

The El Niño Southern Oscillation, or ENSO, is the major factor influencing large-scale oceanic temperature variations in the western equatorial Pacific (Rasmusson & Wallis 1983; Fu *et al* 1986; Nicholls 1987; Schonher & Nicholson 1989). This chapter, therefore, examines the possibility of a more global influence on the chemical composition and morphological structure of coral skeletons in North Queensland, particularly as this relates to ENSO events, and upon which local signals are superimposed.

7.2. DATA AND ANALYSIS

7.2.1. Climatic data

Climatic records were obtained from the Townsville Bureau of Meteorology for the Southern Oscillation Index (SOI) and Mean Sea Level Pressure (MSLP) at Darwin and Townsville. The El Niño Southern Oscillation (ENSO) is a family of oceanographic and meteorological events closely linked to the "seesaw" action of the South Pacific subtropical high (measured at Tahiti) and the Indonesian equatorial low (measured at Darwin, Australia) (Quinn *et al* 1978; Ramage 1986; Quinn 1991). The SOI is the most accepted numeric indicator of ENSO activity and represents the difference between these two pressure readings (Quinn *et al* 1978; Quinn 1991). Missing data in the SOI was caused by missing Tahiti MSLP information. For statistical purposes, MSLP at Darwin was substituted for the SOI when it was felt that use of the complete Darwin data set aided interpretation. This decision was justified by the significant negative correlation between the SOI and Darwin MSLP ($r=-0.8861$, $n=96$, $=0.001$). Therefore, a positive correlation with Darwin MSLP implies a negative correlation with the SOI at approximately the same significance level.

Location and strength of the pressure system over Darwin determines the timing and geographical distribution of the Monsoonal Trough, a band of low pressure systems stretching across the top of Australia. Location of this trough controls rainfall duration and intensity in the Cairns region (McBride & Nicholls 1983; Nicholls 1984a,b,c; Allan 1988). During the active phase of the ENSO cycle the trough remains close to the Equator, concentrated in the Indonesian/Darwin region. During the passive phase of the ENSO cycle, the trough drifts eastward towards the east coast of North Queensland and the Great Barrier Reef, and southwards to approximately 19°S (Townsville) (e.g. Quinn *et al.* 1978; Rasmusson & Carpenter, 1982; Rasmusson & Wallace 1983). Quinn (1991) allocated a "severity" index to ENSO activity, which included the SOI, but incorporated other climatic signals as well. Where appropriate, Quinn's allocation is used in this section of the study.

Although 400 km south of the study site, Townsville is the only centre next to the Great Barrier Reef where reliable MSLP data are available (Figure 1). While pressure is generally higher, and fluctuations greater, at Townsville than at Darwin (Figure 39), the significant positive correlation between the two sets of data ($r=0.8236$, $n=37$, $\alpha=0.001$), suggests that the same pressure cell controls Sea Level Pressure in the two areas (Figure 39).

7.2.2. Statistical analysis

The samples used in this part of the study were from No Name Reef (control site, outer-shelf), and Green Island Reef (inner-shelf). The independent variables in the study were the SOI, MSLP at Darwin, Barron River discharge, and Kuranda rainfall. The dependent variables were weight-percent calcium, strontium, and magnesium, and XRD anomalies.

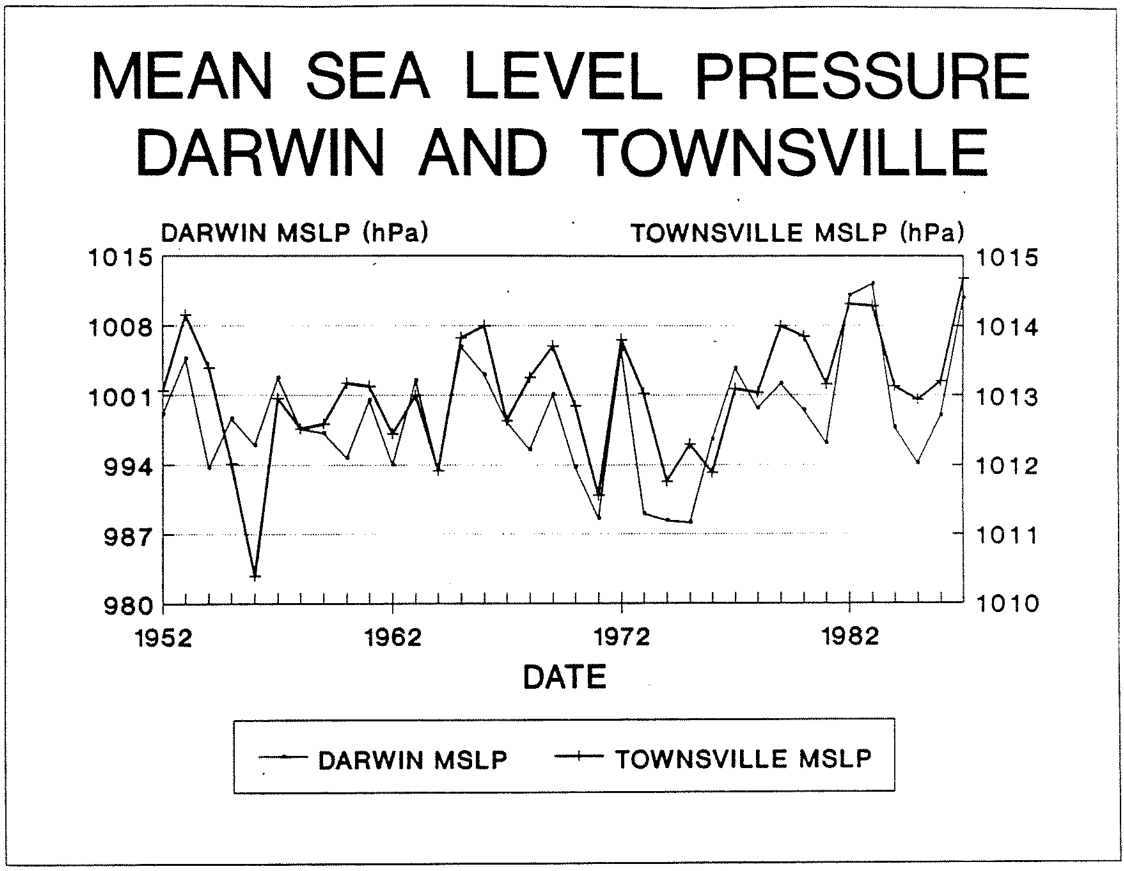

***Figure 39:** Mean Sea Level Pressure read at Darwin and Townsville ($r=0.8236$, $n=37$, $\alpha=0.001$)*

Interpreting the results requires an understanding of the relationship between seasonal coral growth and the "floating" location of proxy environmental indicators within the coral year (McCulloch *et al* 1993; Dunbar & Cole 1993), coral dating techniques, and the irregularity of length, occurrence and intensity of the passive and active phases of the ENSO cycle (Quinn *et al* 1987; Druffel & Griffin 1993) -

1. ENSO events are the representation of a series of interacting weather and climatic variabilities closely associated with, but not necessarily directly correlated to, the SOI. Therefore a very high SOI is usually, but not always, an indicator of a very strong ENSO event.

2. Duration of an ENSO event is typically from six months to two years and can stretch across several years. The beginning and end can be vague and indiscrete.

3. Annual averages for the Southern Oscillation and Mean Sea Level Pressure extend from December to November with the yearly average indicated by the year in which the January falls.

4. The precise interval during which the dense bands form in the coral may vary by several months and uncertainties of 1 to 2 years per century are considered reasonable (Dunbar & Cole 1993).

5. Annual bands were selected from the coral core samples at the beginning of the period inferred to be summer according to the location of the high density band. Shifts between density bands are not always well defined and the chosen point of dissection between the coral years could cause further discrepancies.

6. There is considerable dispute surrounding the mechanism by which density banding arises, and the location of the change from low to high density bands may not always coincide with the start of the summer wet season.

7. The North Queensland summer wet season can start anywhere between November and May, but is usually January/February.

8. Recent work by McCulloch *et al* (1993) has shown that the chemical content of the coral skeleton varies significantly throughout the year. In particular, strontium content of the skeleton rises and falls sharply over a very short period. The location of this peak within an annual time frame is irregular, pronounced, and may be restricted to less than one month.

To reduce these complications, a smoothing curve has been applied to graphs to aid interpretation when considered necessary. The smoothing function is a component of the Harvard Graphics Statistical Package. It does not connect the annual data points, but passes a smooth, curved line of best fit through the graphing area. This marries neighbouring data points while still allowing individual values to be shown.

The statistical techniques most commonly used to elucidate the nature of global teleconnections associated with ENSO events are (1) simple linear correlations (both simultaneous and lagged), and (2) a composite approach, often restricted to simple graphical interpretation. The lagged approach used by Wright (1977) and Newell *et al* (1982) displays the spatial nature of the teleconnections, but has produced enormous, complicated sets of results consisting of relationships at various lags for each season. In the composite approach a set of years is selected according to some criterion, and the mean values of various fields over these years are calculated (e.g. van Loon & Madden 1981; Rasmusson & Carpenter 1982). The composite approach does not assume that the relationships between the different variables and the SOI are linear. This approach is considered appropriate if the Southern Oscillation can be regarded as a sequence of discrete events separated by periods within which the variations are of less interest (Wright *et al* 1985). Researchers who have reported correlation discrepancies in fields of variables have noted that such variables can take on one representation during periods of ENSO activity and another during the passive phase of the ENSO cycle (e.g. Cane 1983; van Loon 1984; van Loon & Shea 1985; Druffel & Griffin 1993). Such discrepancies are best displayed using the composite approach.

To explore any lag (or precedence) effects, biotic data (chemical and morphological) were cross correlated with abiotic data (SOI, MSLP, river discharge and rainfall) using a Statistix 2 computer package. Periodicity was also explored by conducting auto-correlations on the data sets using a Statistix 2 computer package.

Moving averages at the frequency suggested by the cross correlations were conducted within the computer software package 'Harvard Graphics'. As indicated by Dunbar & Cole (1993), this method of examination is not particularly rigorous, but provides a useful assessment of any long term trends in the data set that may otherwise be hidden by high frequency variability.

7.3. RESULTS

Using Pearson's Product Moment Correlations, when values preceded climatic variables by two years, strontium values from the No Name Reef sample correlated positively with both the Darwin MSLP austral winter average ($r=0.206$, $n=96$, $\alpha=0.05$) and the annual average ($r=0.215$, $n=96$, $\alpha=0.05$; Table 7.1) (implying a negative correlation with the appropriate SOI variables). However, when values preceded climatic variables by two years, the strontium values from the Green Island sample correlated negatively with the Darwin MSLP austral winter ($r=-0.238$, $n=106$, $\alpha=0.05$) and spring ($r=-0.190$, $n=106$, $\alpha=0.05$), and the annual average ($r=-0.221$, n=106, α=0.05; i.e. positive correlation with the appropriate SOI variables), and positively with rainfall (r=+0.215, n=92, α=0.05) in the hills above Cairns (Kuranda) and discharge from the Barron River (r=+0.310, n=41, α=0.05).

Preliminary exploration of the data using auto-correlations suggested the presence of an approximate 10-year periodicity in the SOI, Darwin MSLP and the two data sets of the XRD anomalies (Green Island and No Name Reef).

Table 7.1: Cross correlations of various parameters associated with indices of the Southern Oscillation (Darwin MSLP) and the strontium content of samples from No Name and Green Island Reefs.

VARIABLES UNDER EXAMINATION	*PEARSON'S PRODUCT MOMENT CORRELATION COEFFICIENT*	*PERIOD OF PRECEDENCE*	*N*	*SIGNIFICANCE LEVEL*
NO NAME REEF				
WINTER MSLP (DARWIN) AND Sr	*+0.206*	*+2 YEARS*	*96*	*95%*
ANNUAL MSLP (DARWIN AND Sr	*+0.215*	*+2 YEARS*	*96*	*95%*
GREEN ISLAND REEF				
WINTER MSLP (DARWIN) AND Sr	*-0.238*	*+2 YEARS*	*106*	*95%*
SPRING MSLP (DARWIN) AND Sr	*-0.190*	*+2 YEARS*	*106*	*95%*
ANNUAL MSLP (DARWIN AND Sr	*-0.221*	*+2 YEARS*	*106*	*95%*
KURANDA RAINFALL AND Sr	*+0.215*	*+2 YEARS*	*92*	*95%*
BARRON RIVER DISCHARGE	*+0.310*	*+2 YEARS*	*41*	*95%*

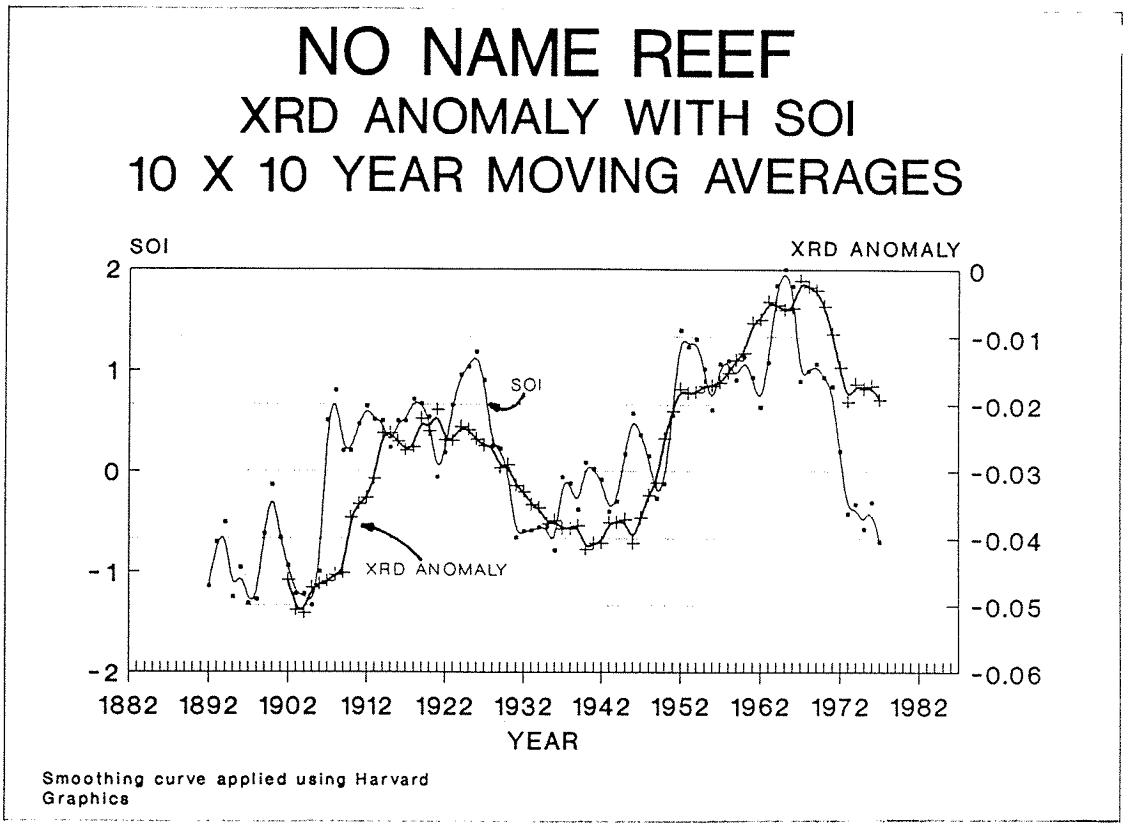

Figure 40: Examination using 10x10 year moving averages suggests a positive coherence[1] between the SOI and XRD anomalies at No Name Reef.

10x10 year moving averages applied to the data within the Harvard Graphics statistical package suggests a positive coherence[1], between XRD (111) anomalies in the No Name Reef sample and the Southern Oscillation Index (Figure 40).

On an annual time-scale, statistical analysis failed to detect a significant correlation between the theoretical location of the XRD aragonite (111) reflection and the Darwin MSLP. However, a negative correlation was found between variations in the theoretical location of the XRD aragonite (111) reflection and the Darwin MSLP spring average ($r=-0.2294$, $n=96$, $\alpha=0.05$; i.e. a positive correlation with the spring SOI).

The term "coherence" has gained acceptance in the paleoclimatic/sclerochronological literature in instances when statistical analysis fails to detect a significant correlation between the data sets, but obvious patterns of association are apparent (e.g. Shen *et al* 1987; Druffel & Griffin 1993).

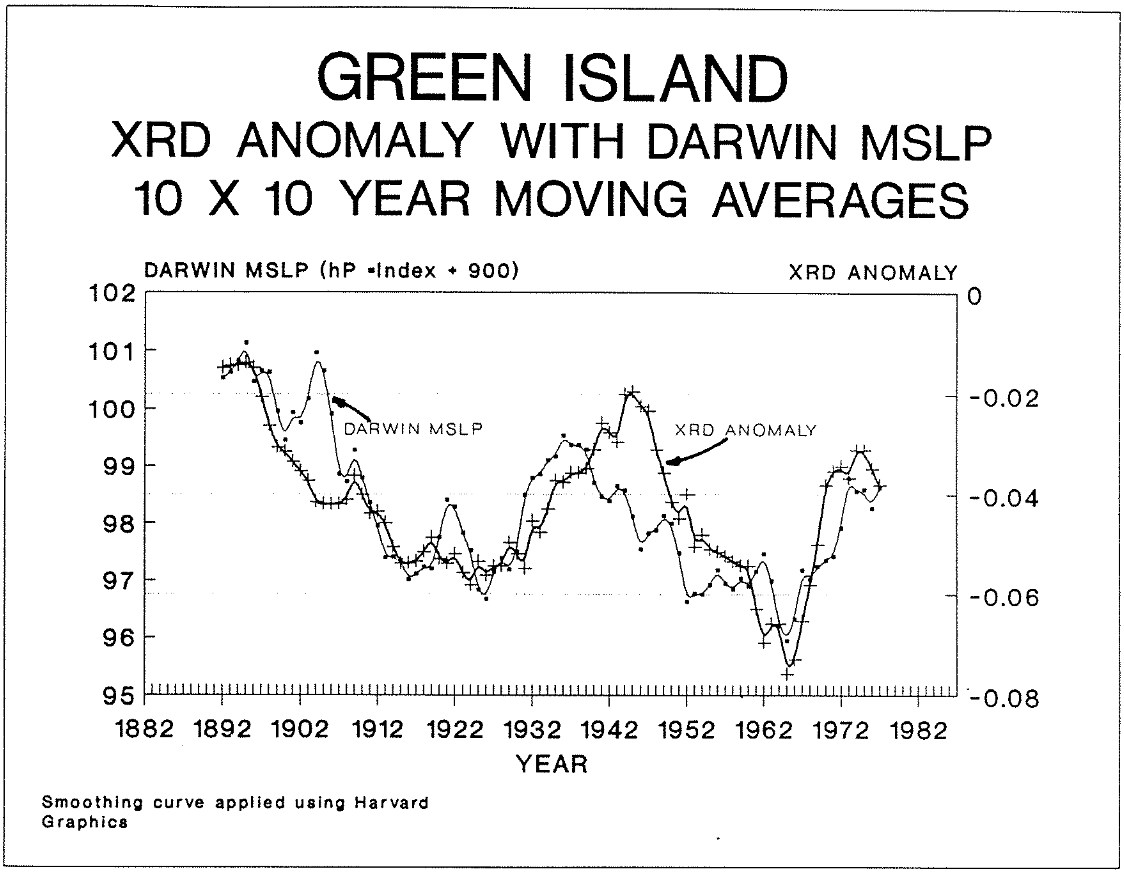

Figure 41: Examination using 10 x 10 year moving averages for the Green Island XRD (111) anomalies and Darwin MSLP, indicates a positive correspondence.

Examination of the Green Island Reef data using 10x10 year moving averages suggests a positive coherence between Darwin Mean Sea Level Pressure and the movement of the XRD (111) aragonite reflection from the theoretical location (Figure 41). It is important to note that in this data set, the association between the XRD (111) anomalies and the SOI is negative. The Green Island aragonite XRD (111) anomalies are correlated positively with only one half of the numeric indicator of the Southern Oscillation, MSLP measured at Darwin (the association between the SOI and Darwin MSLP is outlined in Section 7.2.1).

On an annual time scale, Pearson's Product Moment correlations failed to detect a significant correlation between the XRD (111) aragonite anomaly and annual values for Darwin MSLP. However, a positive correlation ($r=0.3732$, $n=36$, $\alpha=0.05$) was detected between Townsville MSLP and the XRD anomaly when the XRD anomaly preceded Townsville MSLP by one year.

7.4. *DISCUSSION*

7.4.1. *Comparisons between strontium content and the Southern Oscillation:*

Houck *et al* (1977) have shown that the uptake of strontium is controlled by both temperature and the growth rate of the skeleton, with optimum skeletal deposition taking place within a narrow temperature window (around 27°C at their location). In near-shore waters it is unlikely that optimum temperature can be sustained for very long. In Chapter 6 it was shown that the use of strontium as a paleoenvironmental temperature indicator was unreliable in the corals from the near-shore locations. In northeast Australia, the single most significant factor controlling climate and weather (and hence water temperature) is the location of the monsoon trough. The intensity and movement of this trough are closely linked to Darwin MSLP.

The lag in the correlations between the strontium content of the samples and parameters associated with the SOI is consistent with lagged results noted by other research (e.g. Wright 1984, 1985; Wright *et al* 1985; Nicholls 1984a,b,c,d, 1987; Allan 1988, 1991; Allan & Pariwono 1990; Allan *et al* 1991). Using an adaptation of Canonical Correlation Analysis, Nicholls (1987) reported a strong relationship between the Southern Oscillation and air temperatures at Willis Island with the Willis Island data field leading the Southern Oscillation variable by several months[2]. In this present study, lags were also persistent in the results from all examinations, often extending to two years. There are several reasons why this lag period is both acceptable and pertinent to the interpretation of the coral inferred climatic record -

(1) Dissection of the coral core into annual components was determined by the change in density within the coral skeleton. The dissection line was presumed to be October. This may not coincide with the critical "floating" period when strontium content of the skeleton is at a maximum (see McCulloch 1993), in which case an additional lag will be introduced into the data set.

(2) The eastern Pacific is considered the "center of action" (Dunbar & Cole 1993) for most ENSO related sea surface temperature anomalies. Therefore, west Pacific sea surface temperatures will not immediately 'fit' the pattern of anomalies noted in the eastern Pacific association with the ENSO phenomenon (Nicholls 1987; Druffel & Griffin 1993). Further, in the western

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[2] Although limited water temperature data have been collected from some sites in the northern section of the Great Barrier Reef lagoon (CSIRO Division of Oceanography), the data cover only limited time periods, usually less than 6 years. Wright, 1984, had previously shown that relationships between air temperature and the Southern Oscillation are similar to relationships between sea surface temperature and the Southern Oscillation in this region)

central Pacific, climatic variables (precipitation; sea surface temperature anomaly patterns) have been shown to precede the El Niño warming in the east Pacific and associated changes in the Southern Oscillation by approximately one year (Rasmusson & Wallis 1983; Fu *et al* 1986; Nicholls 1987; Schonher & Nicholson 1989).

Within this context, two important points emerge -

(1) The correlations between strontium content of the samples and parameters associated with the ENSO phenomenon (Table 7.1) consistently display a 2-year lag, and

(2) The correlations between the SOI (the most accepted numeric indicator of the ENSO phenomenon) and strontium content of the outer-shelf sample set are reversed for the inner-shelf sample set and are, in fact, correlations with one half of the index, MSLP read at Darwin.

However, while the correlations between the strontium content of the coral skeleton and parameters associated with the ENSO phenomenon in North Queensland are significant at the 95% confidence level (Table 7.1), only a small proportion of the relationship is explained by the correlations. This suggests that other factors must also be influencing strontium incorporation into the coral skeleton. Nevertheless, the links between skeletal strontium and abiotic data associated with the SOI are strengthened by the consistency of the correlations and the persistence of the 2-year lag. The results imply that as skeletal strontium of the outer-shelf corals goes up (and presumably temperature goes down), within two years the SOI may go down (MSLP up). When the skeletal strontium of the inner-shelf corals goes up (and presumably temperature goes up), within two years MSLP at Darwin will go down, and rainfall and river discharge will increase. This is an important point. Weather patterns along the North Queensland coast are controlled by the location of the monsoonal trough. This is determined by the depth and location of the atmospheric pressure cell measured at Darwin (see Section 7.2.1. above, and Chapter 2.2.3). ENSO activity is associated with a warming of the waters in the Coral Sea (Nicholls 1987).

The most logical reason for -

(a) the lack of correlation between skeletal strontium of the inner-shelf sample sets and the SOI, and

(b) the inaccuracies in the reconstructed temperature estimates from the Green Island sample set, would be undetected analytical errors in the strontium data set. It is possible that the analytical results from Green Island could be consistently incorrect. However, this would not explain why the strontium results from only the inner- and inner/mid-shelf samples (Batt, Brook Islands, and Green Island Reefs) produced unreliable temperature estimates, when all analyses were conducted in a similar manner. Further, such an explanation does not account for the persistent correlation between strontium in the Green Island sample set and parameters associated with Darwin MSLP, even though the reconstructed temperature estimates were shown in Chapter 6 to be inaccurate.

Clearly, the reconstruction of paleoclimatic signals using strontium is complex. Either the incorporation of strontium into the coral skeleton is not purely temperature dependent (and Houck *et al* 1977, have proved that optimum skeletal deposition takes place within a very narrow temperature window) or physical conditions (including sea surface temperatures) across the Continental Shelf are controlled by different parameters. These parameters may be related to the ENSO phenomenon, but driven by additional and/or individual forces.

7.4.2. Comparison of the aragonite XRD (111) reflection anomalies and the SOI

Auto-correlations suggested the presence of a 10-year periodicity in the XRD and climatic data sets. The anomalies located by traces of the XRD (111) aragonite reflection and parameters associated with ENSO (SOI and Darwin MSLP) follow consistent patterns when examined using 10 x 10 year moving averages. As noted in the strontium data set, the pattern of the XRD anomalies from the No Name Reef sample is consistent with the pattern for the SOI. The pattern from the Green Island sample data is consistent with the pattern for Darwin MSLP. Druffel & Griffin (1993) found an impediment in the SOI around 1925 that they attributed to a change in the nature of ENSO activity. This period coincides with the first change in amplitude in the cycles shown in Figures 40 and 41. The beginning of an apparent new cycle around the 1960's, however, corresponds to the suggestion of decadal, rather than century, time scale changes in the nature of ENSO (Druffel & Griffin 1993).

While a pattern of cyclic association is present between the biotic (Green Island and No Name Reef XRD anomalies) and abiotic (Darwin MSLP and the SOI) data sets, at the level of the annual time scale the association is complex. Correlations, although statistically significant, account for only a minor portion of the relationship. Pearson's Product Moment correlations failed to detect a significant correlation between the annual XRD (111) aragonite anomalies from both sample sets (No Name and Green Island Reefs) and annual values for Darwin MSLP. A negative correlation was found between variations in the XRD anomalies from the No Name Reef sample and the Darwin MSLP spring average ($r=-0.2294$, $n=96$, $\alpha=0.05$; implying a positive correlation with the spring SOI). A positive correlation ($r=+0.3732$, $n=36$, $\alpha=0.05$) was detected between the XRD anomalies from the Green Island sample and annual values for Townsville MSLP when the XRD anomaly preceded Townsville MSLP by one year. Visual assessment and interpretation of the graphed data suggest an inconsistent relationship similar to that reported in the strontium/SOI comparison (7.4.1.). Periods of strong negative correlation are interspersed with periods when no correlation is apparent (Figures 42 and 43).

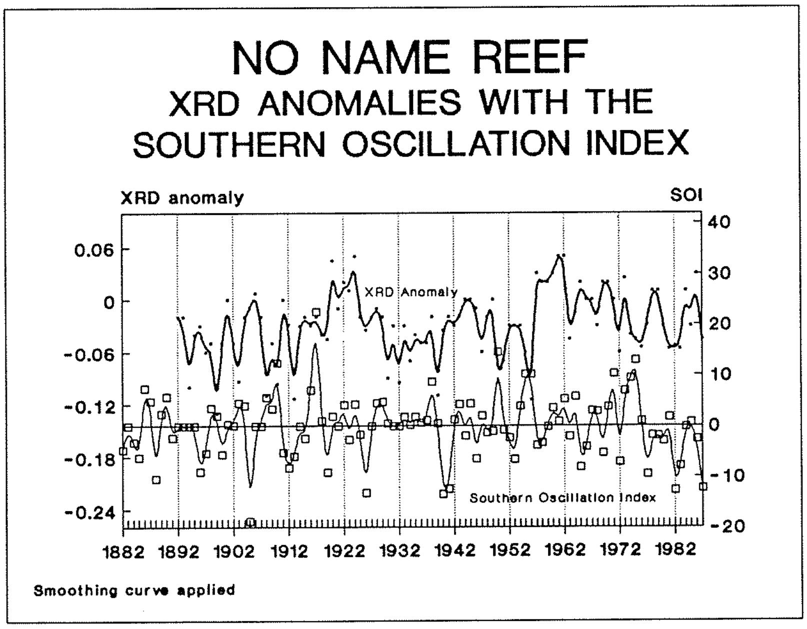

Figure 42: Annual variations between the Index of the Southern Oscillation and deviations in the location of the Aragonite (111) reflection in the No Name Reef sample.

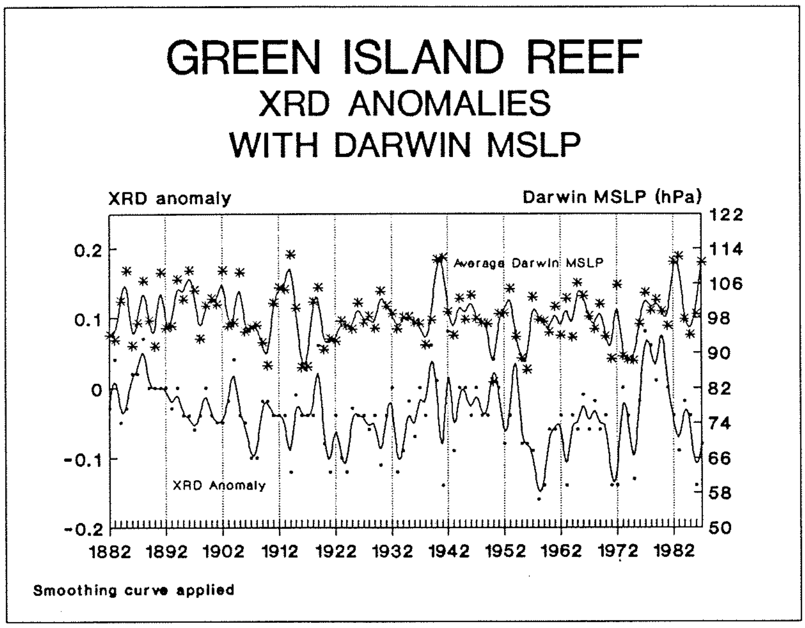

Figure 43: Annual variations of Mean Sea Level Pressure at Darwin, and deviations in the location of the Aragonite (111) XRD reflection in the Green Island sample.

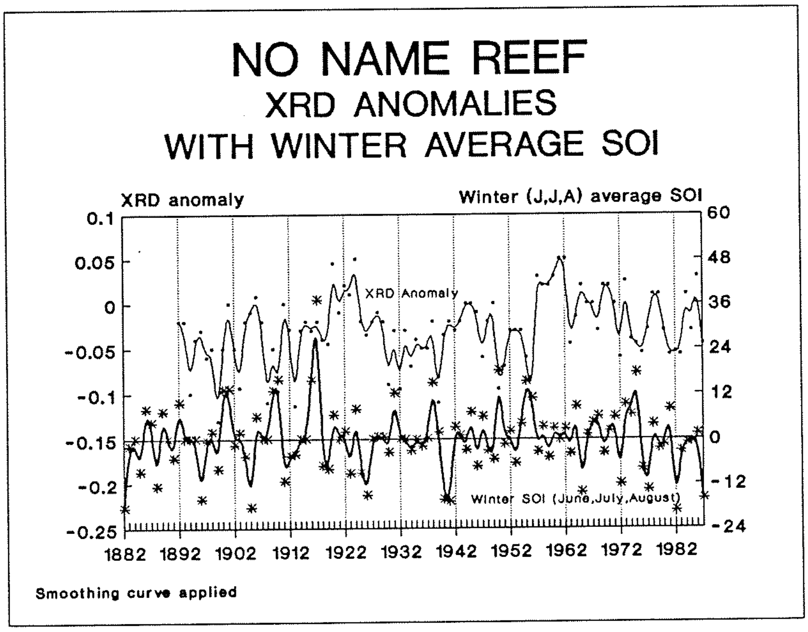

Figure 44: Variations between the June/July/August (winter) average SOI and annual deviations in the location of the Aragonite (111) reflection in the No Name Reef sample.

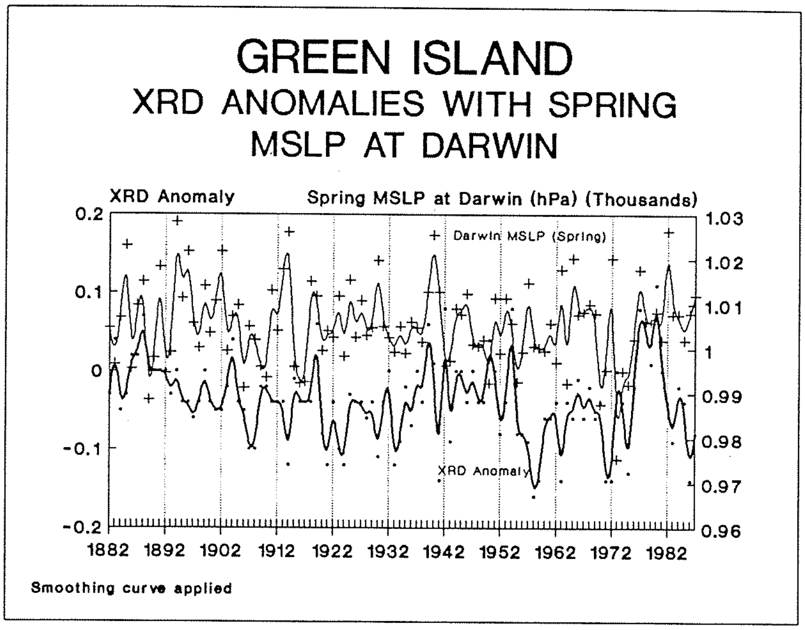

Figure 45: Variations between the September/October/November (spring) average Darwin MSLP and annual deviations in the location of the Aragonite (111) reflection in the Green Island Reef sample.

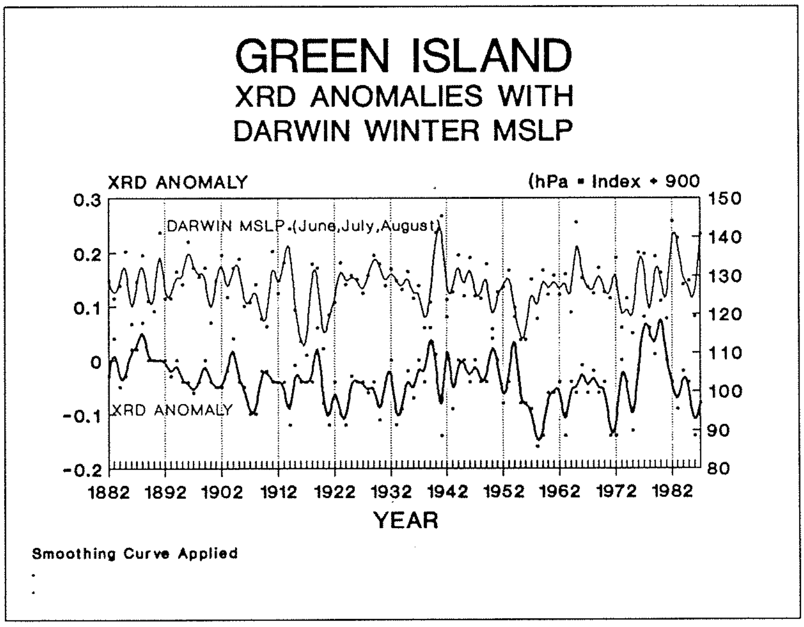

Figure 46: Variations between the June/July/August (winter) average Darwin MSLP and annual deviations in the location of the Aragonite (111) reflection in the Green Island Reef sample.

This lack of consistency in data correlation has previously been noted (e.g. Cane 1983; van Loon 1984; van Loon & Shea 1985; Druffel & Griffin 1993). Cane (1983) commented that fields of variables often take on two different representations during the active and passive phases of the ENSO cycle. These observations are compatible with the view that the Southern Oscillation is a sequence of discrete events (Wright *et al* 1985). Close examination of the data in this study shows that most periods of obvious negative correlation (1929/30; 1939/41; 1952/53; 1972/73; 1982/83; 1987) correspond to periods of ENSO activity with a tendency towards a weakening of the relationship during the passive phase of the ENSO cycle (Figures 42 and 43). In the two data sets under review (No Name and Green Island Reefs) the tendency towards negative correlation during the active ENSO phase is enhanced when the record of the XRD anomalies is assessed with the preceding winter (June, July, August) SOI for the No Name Reef sample (Figure 44) and the previous winter (June, July, August) and spring (September, October, November) Darwin MSLP data for the Green Island sample (Figures 45 & 46). This association with fields of variables from the previous winter or spring has been noted by other researchers (e.g. van Loon & Madden 1981; van Loon & Rogers 1981; Yarnal 1985; Wright *et al* 1985; Nicholls 1987) and is a common indicator of ENSO relationships with various fields of data (Druffel & Griffin 1993; Dunbar & Cole 1993), in particular sea surface temperature.

7.5 SUMMARY AND CONCLUSIONS

The agreement in the long-term data sets between climatic indicators (SOI and MSLP) and the relative XRD anomalies, together with the negative associations during periods of ENSO activity, suggest that the sample from the No Name Reef location is influenced by large scale circulation patterns associated with the Southern Oscillation. On the other hand, the agreement suggests that the sample from Green Island Reef is also influenced by large scale circulation patterns associated with the Southern Oscillation, but that this influence is controlled by the dominant pressure cell located over the North Australian land mass, interpreted as MSLP at Darwin.

The precise cause of the crystallographic disturbance in the corals is presently not known. Clearly, however, the anomalous behaviour of the aragonite XRD (111) peak location is closely associated with the same parameters that drive the Southern Oscillation. It is possible the common link is temperature or salinity. However, these alone, or together, cannot explain the contrasts in the two data sets. It was shown in Chapter 5 that temperature estimates based on strontium, or Sr:Ca ratios, were unreliable in near-shore environments. By elevating the levels of nutrients in the water column, Belda *et al* (1993) induced crystallographic changes in the skeletons of the giant clam *Tridacna gigas.* Shen *et.al* (1987) attributed a strong coherence between trace element composition and ENSO events in corals from the Galapagos Islands to variations in nutrients in upwelling waters. On the outer shelf of the Great Barrier Reef the major source of nutrient supply is from upwelling events (Andrews & Gentien 1982; Andrews & Pickard 1990). Nutrient delivery to near-shore reefs is predominantly land-derived (Hopley 1982). It is possible, therefore, that the cause of the disturbance is related to nutrients and that the reason for the contrasting data sets is some form of nutrient speciation.

The patterns of coherence, and the differences in the associations, could also be due to changes in the large-scale horizontal mixing of different water masses. A change in horizontal mixing that would alter the chemical composition of the waters of the outer- and inner-shelf involves the variable transport of waters associated with both the South Equatorial Current and the East Australian Current. Vertical mixing from upwelling occurs along the continental shelf. Shen *et al* (1987) have shown that the addition of nutrients during ENSO events is associated with upwelling. However, it is unlikely that this would reach into the inner-shelf waters around Green Island. Further, if this was the case, then the response to ENSO events should be similar at both locations. Pickard (1977) has shown that horizontal mixing processes dominate the study area. Water associated with the South Equatorial Current flows westwards into the Coral Sea, bifurcating at around 18°S and maintaining a predominantly southerly flow along the outer-shelf south of this latitude through most of the year. The East Australian Current originates in the West Central South Pacific, flows westwards across the Continental Shelf and travels northwards along the Australian coast pushed by the predominant southeasterly trade winds (Pickard 1977).

Druffel & Griffin (1993) showed that salinity, temperature, and sea-level observations of the 1982/83 ENSO event suggested that the centre of the South Pacific subtropical gyre shifted south from the usual 0°-10°S to 10°-20°S during this period. According to these authors this would bring low Δ^{14}C surface waters from the South Equatorial Current into the Coral Sea during periods of ENSO. This could provide for end member mixing resulting in an overall lower $\Delta^{14}C$ value than during non-ENSO years. A change in isotopic composition does not necessarily imply a compositional chemical change. It can be presumed, however, that different water masses will have differences in elemental composition, even if these are only subtle, and thus small, differences in, for example, salinity. Shen *et al* (1987) have shown that corals respond sensitively to very small changes in their environment, such that it is possible to detect minor nutrient variations of two different water masses. The possibility that the corals of the outer- and inner-shelf are recording subtle changes in the elemental composition of different water masses, the migration of which is aligned to the ENSO cycle, needs to be explored.

One reason for the anomalies in the coral data sets could be extraneous material or detritus included in the coral skeleton (e.g. see MacIntyre & Smith 1974), as no detailed cleaning of the coral skeleton was conducted. However, if this is the reason, then the clearly established relationship with ENSO activity and the inexplicable contrast between inner- and outer-shelf, needs to be explained.

The results presented above lead to the conclusion that conditions that affect the chemical composition and morphological structure of the coral are inextricably linked to global climatic parameters. This is critical to a reef within range of terrestrial runoff and further suggests that any additions or variations to the fluvial system will be transported to the near-shore reef along with the normal river load.

CHAPTER 8

IMPLICATIONS OF THE RESEARCH FINDINGS AND SUGGESTIONS FOR FUTURE RESEARCH.

8.1 SUMMARY AND OVERVIEW OF THE RESEARCH

Over the last few decades a considerable amount of interest has been shown in the effects of man on the Earth's resources. Some of this attention has focussed on coral reefs and Australia's Great Barrier Reef has received a substantial share of this attention. Considered a relatively pristine reef system, perceived changes have often attracted a "knee-jerk" reaction from the public and popular press. Lack of baseline data has hampered management decisions and created a situation where considerable information has to be collected before the need for ameliorative action can be assessed.

One concern that has been central to many debates, from an association with *Acanthaster planci* outbreaks to the degradation of reef systems, has been the possibility that the nutrient levels of the waters surrounding coral reefs have been elevated. Nutrient enriched agricultural runoff has usually been considered the primary source of this enhancement. Without baseline data, research must resort to comparative, experimental, or short-term historical records to gather information on whether the alterations are indeed anthropogenically induced, or simply a part of the natural cycle of reef ecology. When long-term knowledge on the natural variability of the system is lacking, interpretations of ecosystem dynamics are often ambiguous and as such invite argument.

Many researchers believe the chemistry of long-lived corals could provide information suitable for the reconstruction of environmental conditions operating at the time of skeletal formation. Sclerochronology is seen as a potential source of paleoenvironmental information for such diverse issues as sea surface temperature, salinity rainfall, nutrient availability, river runoff, anthropogenic impact and large scale oceanic circulation patterns (e.g. see Swart 1983; Isdale 1984; Shen *et al* 1987;

Lea *et al* 1989; McConnaughey 1989; Cole & Fairbanks 1990; D'Elia *et al* 1991; Druffel & Griffin 1993). This thesis explored the potential for chemical and morphological variation in *Porites* to provide information on environmental change, particularly as this related to the use of phosphate on the mainland. The study was based around the Cairns section of Australia's Great Barrier Reef. The research concentrated on the more abundant chemicals in the coral skeleton (calcium, strontium, magnesium, potassium, sodium and iron) and extended the study to include morphological characteristics such as skeletal porosity and crystallography.

An association was shown between land management practices of the Barron/Mossman River catchments and phosphate concentration of the adjacent rivers. The quantity of phosphate delivered to the ocean from the land was suggested to be the result of both concentration and the amount of water moving down the river. Both were shown to depend on rainfall, but with an upper limit imposed by complex solubility criteria. Thus, the phosphate levels in the rivers were considered dependent upon the amount available for transfer. Very large quantities of phosphate in solution were shown to be transported through the river systems with most of the load delivered during flood events. A direct correlation between marine phosphate levels and stream phosphate concentrations could not be found. However, a seasonal link between elevated levels of phosphate in marine waters and the use of agricultural fertilisers on the mainland was suggested. A correlation was indicated when marine sampling took place close to the time of river sampling.

A series of perturbations was noted in the post-1950 chemical composition and morphological structure of the Green Island *Porites* sample. The perturbations in the skeletal porosity of the sample were similar to the results of the phosphate supplementation programme on *Acropora formosa* corals (Chapter 4) . The Green Island perturbations correlated with the use of fertiliser on the nearby mainland. Before the 1950's the pattern of chemical and morphological variation of the Green Island sample was consistent with patterns displayed by other inner- and inner/mid-shelf samples.

There was a statistically significant difference in the chemical composition of the inner- and inner/mid-shelf samples (Batt, Green Island and Brook Island Reefs). These samples were shown to be different, both from each other and from all other sample sets. No statistical difference could be found in the chemical composition of the samples from the mid- and outer-shelf locations (No Name, Hastings, Thetford, Upolu Reefs).

Reconstructed strontium- and Sr:Ca-based temperature estimates were reliable for the mid- and outer-shelf samples, but inaccurate for the inner- and inner/mid-shelf samples.

A global climatic signal was shown in the coral samples from No Name and Green Island Reefs, and it was suggested that this signal contained evidence of the active and passive phases of El Niño Southern Oscillation (ENSO) activity. It was also shown that the sample from No Name Reef displayed a strong coherence with the Southern Oscillation Index (SOI). Coherence varied in the Green Island sample set to an association with Mean Sea Level Pressure (MSLP) measured at Darwin. This association strengthened when compared with MSLP measured at Townsville.

While no unambiguous conclusions linking variations in the coral skeleton to land management practices could be made, the combined results strongly suggest that the samples from the inner- and inner/mid-shelf locations are closely aligned to events on the mainland. This has implications for management based decisions and considerable research is necessary in many areas.

This section of the study will not reiterate details of the results (these can be found within the body of the study), but will use the overview of the research to examine the implications of the investigation.

8.2 IMPLICATIONS OF THE RESEARCH FINDINGS AND SUGGESTIONS FOR FUTURE RESEARCH.

Incorporation of chemical tracers into the skeleton of long-lived corals makes sclerochronology particularly suited to the historical examination of tropical ocean/atmosphere variability. In some cases the results are equivalent in quality and resolution to those derived from instrumental data (Dunbar & Cole 1993). The study presented above suggests that each coral colony originates with its own set of 'fingerprints' (see Chapters 5 and 6), with variations in both the chemistry and morphology of the skeleton a natural adaptation to a particular set of circumstances. In theory, therefore, the record of environmental conditions laid down in the skeleton of modern corals should be limited only by the age of the colony, with the possibility of extending the process of reconstruction to fossil corals once the effects of diagenetic change on the environmental record are known. Ironically, however, the sensitivity of the corals to record change in the surrounding water also makes interpretation of any proxy environmental signal particularly difficult. Two examples of the complex nature of chemical tracers noted in the present study were -

(1) the variation in the reconstruction of temperature estimates from samples taken from various cross-shelf locations (Chapter 6). It was shown that the reconstruction of strontium and Sr:Ca based temperature estimates provided a reasonable estimate of water temperature in clean systems, but that this method broke down in near-shore waters. Analytical error and genetic variation were ruled out as possible explanations because all inner- and inner/mid-shelf samples (Batt, Green Island and Brook Islands Reefs) returned anomalous results. Anthropogenic interference was also ruled out because the proxy temperature estimates did not vary dramatically through time, and

(2) the relationship between the Southern Oscillation Index (SOI) and the strontium content and XRD anomalies of the outer-shelf No Name Reef sample, and the reversal of this relationship in the inner-shelf Green Island sample to a coherence with only one-half of the SOI, Mean Sea Level Pressure (MSLP) read at Darwin.

Research into the interpretation of the relationship between environmental parameters and the chemical composition of the coral skeleton is further hampered by the coarseness of the less expensive analytical techniques (e.g. Atomic Absorption Spectrometry), and by the cost and inaccessibility of the more precise instrumentation (e.g. Thermal Ionisation Mass Spectrometry, TIMS). The value of sclerochronology to the reconstruction of paleoenvironmental and paleoclimatic records, and the need for access to higher precision instrumentation was also recognised by participants of the "*Coral Paleoclimatic Reconstruction Workshop*" (Dunbar & Cole 1993).

One area that has received very little attention is the development of a tracer signal suitable for examining nutrient variations in the sclerochronological record. Observations made during this research suggest that the relative proportion of calcium in the skeleton may be affected by elevated levels of phosphate. Inability to demonstrate this statistically was probably due to the coarseness of the analytical technique (Atomic Absorption Spectrometry) and the proportion of calcium in the skeleton relative to the other elements. Thermal Ionisation Mass Spectrometry will produce higher precision results, and examination of minor concentration variability (e.g. parts per billion) may prove interesting.

This study has also shown that it is possible to induce skeletal variations in the coral skeleton by elevating the levels of nutrients in the surrounding water column (Chapter 4). This suggests that the technique could prove useful as an indicator of elevated levels of nutrients. However, the levels used in this study were considerably higher than would normally be encountered in seawater (2.0, 4.0 and 8.0 μM PO_4), and were held constant for an extended period. To produce a reliable indicator using this method, considerably more needs to be known about the reaction of the coral to (a) lower levels of enhancement, and (b) the spasmodic introduction of higher concentrations. The ENCORE programme is presently investigating many nutrient related issues *in situ* at One Tree Reef, but circumstances require that the One Tree Reef study must use the same nutrient concentrations reported in Chapter 4. It was shown in Chapter 4 that considerable alteration to the coral skeleton had already taken place at the lowest level of phosphate supplementation (2.0 μM PO_4). In Chapter 3 it was shown that phosphate levels in the waters around coral reefs can occasionally reach concentrations greater than 2.0 μM PO_4. Therefore, further research needs to examine the effects of episodic injections of phosphate into the system. This should include lower levels of phosphate (e.g. 0.5, 0.8 and 1.0 μM PO_4), both over extended periods, and interspersed with injections of higher concentrations.

The work of Kinsey & Domm (1974) and Kinsey & Davies (1979) noted that calcification processes were suppressed for a considerable period after the nutrient enrichment programme was discontinued. The authors suggested this was probably due to nutrient retention by the sediments. Smith *et al* (1979) also noted similar effects at Kaneohe Bay. Other researchers have suggested that a 'memory' or 'lagged' effect may operate on the coral skeleton. If such a condition is present, a cumulative effect on the skeleton could be anticipated. Research, therefore, needs to be extended to examine the effects of spasmodic enhancement.

Further, it is unrealistic to expect that anthropogenically enhanced nutrient levels will be restricted to a single nutrient. Belda *et al* (1993) have demonstrated the additional effects of N and N+P on the shell of the giant clam *Tridacna gigas*. Belda *et al's* studies need to be extended to a variety of corals.

In addition, it was shown in Chapter 3 that stream nutrient concentration increased rapidly following rainfall. It was also shown that considerable quantities of phosphate could be delivered into the marine environment. Most of the annual soluble phosphate load was transported during flood events (approximately 90% in the March/April 1988/89 wet season). The majority of this load was carried during a single flood event in April 1989. During this flood the dissolved load transported through Lake Placid was estimated to be equivalent to 57 tonnes of phosphate when calculated as PO_4^{3-}. This value was then recalculated to be equivalent to either 2850 tonnes of superphosphate based on Cosser's (1987) and Douglas' (1987) estimate of a 5:1 ratio of adsorbed to soluble phosphate in the river load, or 710 tonnes of superphosphate based on Brodie & Mitchell's (1992) more conservative estimate of a 1:5 ratio of adsorbed to soluble phosphate in the river load during flood events. The latter estimate provides a more realistic calculation of the total amount of phosphate transported through the river system (compared to the estimated use of fertiliser in the catchment). However, the variation in the ratio of dissolved to particulate material, and the consequent increase in the dispersal pattern of the nutrient load, suggests that the potential for delivery of phosphate enriched waters further into the vicinity of coral reefs needs to be reassessed. The results suggest that reefs within reach of the flood plume will be exposed to the rapid influx of considerably greater quantities of phosphate during flood events than was previously considered likely, and implies that the distribution of soluble phosphate through marine waters will be restricted only by the force, direction, duration and phosphate content of the river plume.

It was also shown in Chapter 3 that the reef flat sediments of Low Isles acted as a phosphate reservoir. Although proximity to the coast and the extensive mangrove system of Low Isles may make this an atypical reef flat, the results suggest that the phosphate retention properties of terrestrial sediments on reefs needs further research. Based on Brodie & Mitchell's (1992) work, it was suggested that a flood plume can transport phosphate in solution considerable distances through the marine environment. The results from this study suggest that Green Island corals have been exposed to environmental perturbations, over and above normal environmental variations, during the last forty years. That the system adjusts to the altered status is apparent by the continued response of the corals to global environmental influences such as those associated with the Southern Oscillation. What is not known is how much adaptation is tolerable, or whether the coral-inferred record is representative of an ecosystem under stress.

There is sufficient evidence from several other sources to suggest the Green Island Reef is under considerable stress. This study suggests that environmental perturbation began in the late 1950's. The first recorded major outbreak of *Acanthaster planci* at Green Island occurred in the 1960's. Recent research by Zann (Great Barrier Reef Marine Park Authority) implicated *A.planci* infestations with both anthropogenic influences and ENSO events. The results from this study suggest the stress on Green Island reef is related to the use of agricultural fertilisers on the nearby mainland, but this suggestion is made with caution. Green Island has become increasingly popular as a tourist destination. However, while tourism has continued to increase, the use of agricultural fertiliser and the extent of skeletal disconformity both decreased during the 1980's. If the sclerochronological interpretation is correct, and the Green Island Reef is under stress, then it is necessary to establish whether the stress is chronic or acute, and how this stress is manifested in the overall concept of the Green Island environment.

This research also indicates post-1950 variation in the Hastings Reef sample set, and possibly also in the Upolu Reef sample set. While the sample set from Hastings Reef is higher in magnesium and lower in strontium post-1950, the results from the Upolu Reef sample set were harder to interpret. In this sample set the average content of the different elements remained relatively stable, but the magnitude of the variance around the calcium mean increased post-1950. Hastings and Upolu Reefs are distant from the mouth of the Barron River. River waters would only reach these areas during peak floods. This is particularly true of Hastings Reef and has been confirmed by examination of the fluorescent bands retained by the coral skeleton where strong fluorescence can only be seen during times of peak discharge. Inner- and inner/mid-shelf reefs (e.g. Green Island Reef) develop in association with mainland runoff (Hopley 1982), and could be expected to be relatively tolerant of such influences. Therefore, any perturbations able to influence the chemical composition and morphological structure of the skeleton to the extent suggested by the Green Island proxy record, would need to be both extreme and persistent. In contrast, coral reefs not normally associated with major fluctuations in ambient conditions would be more susceptible to environmental change. Under such circumstances, a relatively minor disturbance could be sufficient to register as a major perturbation in the chemistry and morphology of corals from mid-shelf and offshore areas such as Upolu and Hastings Reefs. If this is the case, then the tolerance of mid- and outer-shelf corals to environmental change needs to be established. To a certain degree this is already being attended to by Australia's *ENCORE* programme. However, constraints imposed on the *ENCORE* programme prohibit it from examining the response of reef systems to the spasmodic pulse of elevated levels of nutrients.

Following the results of the experimental component of this research, the role of internal depositional tissues in the calcification process is presently being conducted in a parallel study by Cuff and Yellowlees at James Cook University of North Queensland. However, because corals are notoriously difficult to grow for extended periods in experimental aquaria, this work has been done on the giant clam *Tridacna gigas*. Whatever the difficulties, the research should be extended to include a variety of corals.

This study has suggested that there is an anthropogenic signal in the sclerochronological record over the last forty years. The anomalies in the record may be related to an increase in the level of organics following the additions of enhanced levels of nutrients via mainland runoff. Carbonate cements have not been studied during this programme, but the logical extension of these results is that any increased loading of soluble phosphate also has the potential to interfere with optimal cementation processes. If the arguments put forward by Berner *et al* (1978) can be extended to include optimal precipitation of both aragonitic skeletal material and reef cementation processes, then the results from the present study suggest that the basic structure of reef formation requires examination.

The results from the study also inferred the presence of a global climatic signal in the chemistry and morphology of the samples from Green Island and No Name Reefs. Autocorrelations of various data sets suggested the presence of an approximate 10-year periodicity in the data. The use of 10 x 10 year moving averages to filter out high frequency annual variability showed a strong coherence between the SOI and deviations from the theoretical location of the XRD (111) aragonite reflection from No Name Reef. This changed in the Green Island sample to a strong coherence with MSLP measured at Darwin. A similar inner/outer-shelf discrepancy was noted in the relationship between climatic variables and the strontium data set. Strontium content of the outer-shelf No Name Reef sample correlated negatively with the SOI with a two-year lag. The Green Island sample correlated negatively with (a) MSLP at Darwin, (b) Barron River discharge, and (c) Kuranda rainfall, also with a two-year lag. Examination of the annual data noted that relationships within data sets were inconsistent. Periods of strong negative correlation were interspersed with periods when little or no correlation existed, with the periods of strong negative correlation coinciding with the active phase of the ENSO cycle. This inconsistency has been noted by other researchers (e.g. Cane 1983; Druffel & Griffin 1993).

Acknowledging the known associations between sea surface temperature and (a) the incorporation of strontium into the coral skeleton and (b) parameters associated with the SOI, the correlation between strontium content and climatic data is not surprising. However, there is no indication in the literature that small variations in the crystallographic structure of aragonite could exhibit an environmental signal. This study suggests that an association exists between the crystallographic structure of the corals and parameters associated with the El Niño Southern Oscillation. The association is suggested to be between the Southern Oscillation Index and the corals of the outer-shelf, and between Mean Sea Level Pressure and the corals of the inner-shelf. The cause of the anomalous behaviour of the crystallographic variations in the coral is presently not known, but it is unlikely the association is due to analytical error in two such comprehensive data sets. It is also unlikely to be as simple as variations in temperature or salinity, because the corals would be expected to respond in a similar manner to such stimuli. The fact that the behaviour is contrasting for the two environments suggests a more complex interaction. It was suggested in Chapter 7 that the relationship could be caused by the migration of different water masses (and associated temperature, salinity, nutrient and chemical variations) during the active phase of the ENSO cycle. This suggestion is based on the research of Druffel & Griffin (1993). While variations in the isotopic record do not necessarily imply similar changes in the chemical or morphological record, the results suggest the implications are worthy of further study. The lack of conformity in the coral-inferred temperature estimates from the outer- and inner-shelf samples could be due to the same events.

ENSO activity is associated with a breakdown of the southeasterly trades, a weakening of the equatorial easterly winds and the strengthening of the westerlies above Queensland (e.g. Quinn *et al.* 1978; Rasmusson & Carpenter, 1982; Rasmusson & Wallace 1983). This interrupts the predominantly northwards movement of the East Australian Current. For a short period current flow along the inner-shelf of the northern Great Barrier Reef changes to the south, moving off the shelf through the Trinity Passage (south of Green Island). Under such conditions, a different water mass with a different chemical composition could be transported from the equatorial area to the north and northwest of Australia into the inner-shelf waters of the Great Barrier Reef. This change in water may be reflected in the chemical composition and morphological structure of the Green Island sample. The incursion of two different water masses into the study area, both of which are driven by ENSO activity, could explain the correlation irregularities between the Green Island and No Name Reef data sets and parameters associated with the Southern Oscillation. Extension of the study to different locations could prove useful in understanding large-scale oceanic circulation patterns associated with the Southern Oscillation. X-ray Diffractometry (XRD) is an inexpensive, relatively quick method of analysis, and comparison of the results with the more precise, but more expensive, isotopic records from the same samples would be interesting.

8.3 CONCLUSIONS FROM THE RESEARCH

It is concluded that massive long-lived corals provide a suitable avenue for the reconstruction of paleoenvironmental and paleoclimatic signals. The information to be gained from these corals is restricted only by present physiological understanding of coral growth and trace element variations.

It is further concluded that significant quantities of phosphate are delivered into the marine environment through the Barron and Mossman River catchments. This has the potential to influence corals in the path of the flood plume. It is considered that the coral inferred environmental record from the Green Island sample provides evidence of anthropogenic change associated with the use of agricultural fertiliser on the nearby mainland post-1950.

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