Progressive Vadose Diagenesis in Quaternary Reef Tracts, Barbados, West Indies.

Thesis submitted for the degree of Doctor of Philosophy at the University of Leicester

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Abstract

The role of time on the diagenetic alteration of reef facies, within the vadose zone on Barbados, has been investigated in this thesis. Models purporting progressive vadose diagenesis have been forwarded by workers including Gavish & Friedman (1969) and Reeckmann & Gill (1981), who all suggest that the degree of diagenetic alteration follows similar sequential steps, but establishing the ages when the various changes occur have been hampered by a lack of absolute dates. To overcome these problems, this study was carried out in Barbados, where coral reef deposits have been extensively dated radiometrically and eight discrete sea level stands ranging in age from 80ka to 640 ka have been identified (Bender et al., 1979).

Within this study the following reef zones were identified: the fore reef, the coral head zone, the reef crest, the rubble zone and back reef sands. Sediments were grouped together according to their position within the reef tract to give a greater understanding of the variability which exists within and between deposits.

Petrological analyses of 750 samples in thin section, supplemented by SEM and cathodoluminescence studies have identified a number of diagenetic alteration products. These include the dissolution and replacement of original grains, changes in porosity and cement formation. ICP, XRD, XRF and microprobe studies have also been employed to determine any chemical differences within selected coral samples over time. This research indicates that the simplistic models, which are restricted to aeolianites and calcarenites, proposed by Gavish & Friedman (1969) and Reeckmann & Gill (1981) cannot be directly applied to Barbados.

Reef deposits displayed diagenetic variability at differing scales between coral species and reef sediments within single reef tracts (as well as between different reef tracts). Therefore the role of rock fabric between the coral zones is an important consideration in the identification of sequential changes, and it complicates the application of simple time control models, developed for carbonate sands, that have been developed by others.
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Chapter 1 - Introduction

1.1 Introduction

This thesis is an investigation into early vadose, subaerial (freshwater) carbonate diagenesis, within sediments of Quaternary age, formed in the shallow water reef environment of Barbados. Alteration in the vadose zone can be isolated and studied here, as the reef tracts were formed during high sea stands, with subsequent falls in sea level superimposed on a tectonically rising coastline, resulting in well preserved reef terraces that have had very limited exposure to marine and phreatic environments, (Mesolella, 1967). The nature of coral diagenesis can be studied over time as corals have a fairly uniform initial geochemical signature, (Milliman, 1974) therefore the nature of alteration in the vadose environment can be studied. This investigation was restricted to carbonate reef facies of different ages that have undergone similar environmental conditions, in order that temporal trends could be researched.

The nature and rate of diagenetic changes were studied, firstly by field observation, then followed by laboratory analysis of 750 samples that were collected from Barbados, during March-April 1996 and March-April 1997.

Diagenesis involves the dissolution and replacement of unstable mineralogies as well as lithification and was a collective term that can be broadly defined as “...all physiochemical, biochemical and physical processes modifying sediments between deposition and lithification at low temperatures and pressures, characteristic of surface and near surface environments.” Chilinger et al. (1967) as cited in Gavish & Friedman (p. 980, 1969). However, as diagenetic pathways are controlled by: 1) the composition of the original sediments, 2) fluid composition and flow, 3) the physical and chemical processes involved, and 4) time (Scoffin, 1987), diagenetic products can vary widely.

Aragonite (scleractinian corals and gastropods) and high-Mg calcite (calcifying algae, foraminifera, bryozoa and echinoderm plates) precipitated in the marine environment, are relatively unstable in the subaerial environment and over time alter to the more
stable calcite polymorph low Mg-calcite. It was the aim of this research to focus on the
time taken for the carbonate sediments to reach a more stable end product.

In order to study the effects of time in early vadose diagenesis other factors that
influence the system need to be identified and quantified. Gardner & McLaren (1993)
recognised that there were a number of important ‘controls’ on diagenesis, which result
in both spatial and temporal heterogeneity, see Figure 1.1.

*Figure 1.1: Interactions between macro, meso and micro scale variables controlling
early carbonate diagenesis. (from Gardner & McLaren, 1994)*

The idea of progressive diagenesis in the vadose environment was first formulated by
Friedman (1964) working in Israel. The model was subsequently developed by Land et
al. (1967) working in Bermuda, Gavish & Friedman (1969) working in Israel, and
Reeckmann & Gill (1981) working in Australia and remain generally accepted today
(See Chapter 2). However, these models were formulated in predominantly calcareous
sandstones, which have a different fabric than the reef-associated sediments present on
Barbados.
The findings of Gardner & McLaren (1993) have questioned the application of progressive vadose diagenetic models outside the areas in which they were developed. This study has attempted to address the problem that early vadose diagenesis still lacks both a unifying spatial and temporal framework for study, with the creation of a regionally-based model of diagenetic change, within which a more rigorous and reliable dating of deposits exists.

A better understanding of environmental and diagenetic contexts and diagenetic processes may allow greater scope for a refined regional model based on the reef facies on Barbados to be developed. The uplifted reef terraces of Barbados were an ideal location for such a study, as they have all been sequentially uplifted from the sea. Previous work on the island identified a staircase of eight discrete coral reef tracts, which have been extensively dated radiometrically, (see Chapter 2) and range in age from 80ka to 640 ka. The large-scale effects of climate on diagenesis (Reeckmann & Gill, 1981) were also simplified with a study conducted on an island which was 32km long and 23km across at its widest dimension.

1.2 Organisation of the thesis

After a general introduction to the topic, Chapter two comprises the literature review. This begins with an introduction to the main processes of cementation in the vadose environment; and is followed by an overview of the nature of modern and diagenetically altered corals. This leads on to an investigation of the current models of progressive diagenesis, which suggest a set sequence of morphological development of cement types develop over time in the vadose zone. Chapter two will also examine previous studies of diagenesis on Barbados and the dating methods that have been employed on the island. The literature review clearly illustrates the need for a systematic study of the nature and extent of early vadose diagenesis in reef sediments.

The fieldwork carried out in this project is discussed in Chapter three. Firstly there is a consideration of the Quaternary history of Barbados, including tectonic, sea level and
climatic changes. The chapter then continues with an evaluation of why the specific study locations have been selected and the field sampling rationale followed.

Chapter four describes the wide range of laboratory methods that were employed. Analyses of the deposits falls into two main categories: (1) Mineralogical analyses - these include the use of stains, peels, point counting, cathodoluminescence and SEM techniques; and (2) Chemical analyses - these include ICP, microprobe, X-ray diffraction and X-ray fluorescence.

Chapters five and six contain the results of the petrologic and geochemical analyses. The nature of geochemical alteration and cementation is described and the rates of vadose diagenesis in the deposits studied for this research are assessed. This is brought together in Chapter seven, which gives an evaluation of the sequential development found in cement types and diagenetic alteration of the corals and reef sediments. Finally Chapter eight concludes the thesis with a summary of the main findings.

1.3 Research Aims

There are several aims to this research that will be explored in this thesis:

1. To observe the nature and extent of early vadose diagenesis in reef and reef-associated sediments;

2. To try to quantify the role and importance of time on early carbonate diagenesis in the uplifted coral reef tracts on Barbados;

3. To develop a model of early vadose diagenetic change that is applicable to Barbados.
Chapter 2 – Literature Review

2.1 Introduction

“It is a truism of carbonate petrology that ancient carbonate rocks are composed of the stable minerals calcite and dolomite, whereas their Recent sediment analogs are predominantly composed of the unstable minerals aragonite and high-Mg calcite” Matthews (1968, p1010). However, Matthews (1968) has also stated that Pleistocene carbonate sediments exposed to the subaerial environment can be of stable mineralogy and within the relatively short timeframe represented by the Quaternary (p1010). Stabilisation has been recorded as occurring within 125ka in Israel, (Gavish & Friedman, 1969) but within 700 ka in Australia (Reeckmann & Gill, 1981). Therefore, an investigative study of the timeframe over which diagenetic alteration can be achieved within carbonates in the vadose zone is possible, by means of a comparison of modern carbonate sediments with sediments that are at various stages of alteration.

The study of vadose carbonate diagenesis mainly concerns sediments that originated in shallow, tropical, marine environments, such as the carbonate reefs forming around and uplifted onto the island of Barbados. The transformation of a freshly deposited carbonate facies in the shallow marine environment into a fully stabilised rock, once uplifted into the subaerial zone, is a complex process (Schroeder, 1988; Scoffin 1987) with many diagenetic routes, depending upon the initial sediment composition, environmental conditions and time.

The bio-clasts that make up the carbonate rocks on Barbados have differing mineralogies at time of precipitation. (See Table 2.1). However, Jamieson (1953), Harker & Tuttle (1955) and Graf & Goldsmith (1955) have shown that only low-Mg calcite (<4% MgCO₃) in solid solution is relatively stable under subaerial conditions. A general stability sequence for the CaCO₃ minerals composing carbonate sediments under natural conditions appears to be as follows; low-Mg calcite > aragonite > high-Mg calcite (Chave, 1954). Therefore the exposure of reef sediments composed of
aragonite and high-Mg calcite to the subaerial environment, results in a number of processes, especially dissolution, recrystallisation and subsequent cementation.

Table 2.1: The mineralogy of major groups of carbonate secreting organisms on Barbados.

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<td>Scleractinian corals</td>
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<td>Bryozoans</td>
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<td>Brachiopods</td>
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<td>Molluscs</td>
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<td>Echinoderms</td>
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2.2 Coral Growth

The reef biotic environment is complex containing corals, algae, sea-grasses, sponges, alcyonarians, bryozoans, echinoderms, tunicates, foraminiferids, diatoms, molluscs, burrowing decapods and fish, (Bathurst, 1975). These organisms all influence the formation and distribution of sediments that make up the reefs. The major reef builders are scleractinian hermatypic corals with skeletons entirely composed of calcium carbonate. The most extensive distribution of hermatypic corals are found in the intertropical Indo-Pacific with over 30 genera. Coral growth is not so prolific in the Caribbean, but it is still important with more than 20 hermatypic genera. (Guilcher, 1988). Of the areas covered by coral reefs and associated communities living at depths of less than 30 m, Smith (1978) calculated that 14% are located in the Caribbean Sea and North Atlantic.

Schroeder & Zankl (1974) found that reef rocks are formed by the interaction of construction and destruction by organisms, sedimentation, cementation, and mechanical
breakdown. Reef formation is dynamic with every available internal and external surface of the reef continuously subject to modification by reef-forming processes. These continue to operate and interact as long as the reef remains in its original environment. In areas of active uplift, such as Barbados, reefs flourish at times of high sea stands, when the eustatic rise of sea level slightly exceeds the tectonic rise of the substrate (Gascoyne & Harmon, 1992).

Goreau (1959) found that modern West Indian reefs in general are, on the whole, very much smaller than their Indo-Pacific counterparts, though the density of coral growth within the reefs are comparable. The Caribbean is remarkably homogeneous with regard to the shallow water scleractinia, with no important regional differences in the reef coral populations and no corals have yet been found that are peculiar to any one locality. The corals reefs off the coast of Jamaica are representative of the Caribbean, with a deep coral head zone dominated by Montastrea annularis, a fore reef composed almost exclusively of Acropora cervicornis, a buttress zone composed of some Acropora palmata and flattened Montastrea annularis heads, a reef crest composed of A. palmata, a breaker zone of dead A. palmata and a shallow reef flat. On Barbados fringe reefs flourish on the leeward side of the island.

Coral growth is dependent on many parameters such as water temperature, salinity and purity. Optimal conditions for reef building occurs between about 30°N and 30°S and in water depths down to 50m, although some other species are able to live in more northerly latitudes and at greater depths. In the Barbados near shore environment, reefs grow on the insular shelf, and most of the accumulating sediments are carbonates (Acker & Stearn, 1990). The coral zonation present on a reef is produced as each coral species has its own optimal conditions. The Caribbean reef-crest coral, A. palmata, is generally restricted to the upper 5m of the water and dominates the reef crest community in many locations. Woodhead (1971) reported that A. palmata has optimum conditions for growth in the shallow water environment and does not grow at depths exceeding 18m at Heron Island, Australia. Because of reduced illumination, hermatypic corals are thought to grow more slowly in deeper water than near the surface. However, Barnes (1973) found that the optimum depth for calcification in M. annularis was between 20 and 25m.
The coral colony shape is commonly related to environmental and other factors such as degree of illumination, water turbulence and interspecific competition (Martindale, 1992). In addition to corals, coralline red algae, bryozoa and foraminifera are also important contributors to the reef framework. Red algae are found to form thick crusts which fuse individual corals, and is therefore instrumental in forming continuous pillar structures, which reinforce the structure (Zankl & Schroeder, 1972; Martindale, 1992). Coralline algae are found at all depths in the reef and unlike corals, are composed of high-Mg calcite precipitated within and between cell walls. (Milliman, 1974). Most bryozoa occur at depths of 10-30m, (Martindale, 1992) whilst encrusting foraminifera (consisting of 8-16% MgCO₃ high-Mg calcite, Milliman, 1974) are found at all depths, away from exposed brightly lit environments.

The dominance of each coral species within the reef environment varies spatially, Weber & White (1977) found that within the Caribbean region, M. annularis was the major contributor to framework construction in both modern and fossil coral reefs. In Florida A. palmata was recognised as most important reef builder by Ginsburg (1956) and Shinn (1963). In Jamaican reefs, Goreau (1959) identified M. annularis as the dominant contributor to the framework of the reefs, with A. palmata of secondary importance. In the uplifted Pleistocene tracts on Barbados, while M. annularis and A. palmata were major contributors, A. cervicornis was equally important as a framework builder (Mesolella, 1967).

A. palmata is one of the fastest growing corals in a reef environment and is often found in an interlocking reef framework on the windward side of Caribbean islands. It is well preserved in the fossil record as its massive size minimises post depositional transport and compaction. (Bard et al., 1990a). However, Woodley (1992) believes that the extensive proliferation of A. palmata characteristic of the upper zones of West Indian reefs indicates a reef community in the later stages of development, as a climax stand, with the luxuriant Acropora stands of classical description atypical. This conclusion was based on the A. palmata thickets in Jamaica described by Goreau (1959) that were demolished by hurricanes in 1980 and 1988 and as yet have not had time to recover. A. palmata cover has now fallen to zero on the reef crest and A. cervicornis stands have fallen to only 3.6% of total coral on the fore-reef (previously 45%). However, the failure
of the reef to recover successfully has been attributed to a decline in herbivores, in part due to overfishing (Perry, 1996); a modern problem that is not reflected in fossil reefs.

The uplifted Pleistocene reef terraces on Barbados are seen by Mesolella (1967) to record the zonation of corals, in sections cut perpendicular to the reef tract trends. The zonation is composed of the following four major elements shown in Figure 2.1:

(i) The coral-head zone – deep fore reef,
(ii) The A. cervicornis zone – fore reef slope,
(iii) The A. palmata zone – reef crest,
(iv) The back reef.

*Figure 2.1: Schematic coral reef zonation of the uplifted Pleistocene reefs on Barbados.*

Exposures at the base of the terraces are composed largely of coral species, which tend to form massive coral heads. At several localities, *M. annularis* makes up as much as 50% of the total exposure. However, at other localities, *M. annularis* composes only 10 – 15 % of the total exposure and *Siderastrea siderea*, *Siderastrea radians*, *Diploria strigosa*, and *Diploria labyrinthiformis* are equally important. The individual species
occur in clumps with first one species being important and then another. Coralline algae are not abundant in this zone but at times form thick crusts on the upper surfaces of the coral heads.

Moving upward and back into the reef terrace, the zone of coral heads gives way gradually to a zone composed almost exclusively of *A. cervicornis*. At times *A. cervicornis* makes up as much as 75-80% of the total exposure. Coralline algae often form thin coatings on the branches. Near the upper portions of the *A. cervicornis* zone *M. annularis*, *Siderastrea sp.* and *Diploria sp.* are frequently scattered in among the *A. cervicornis*. The *M. annularis* here has the growth form of heads and tall thin 'pipes' and appear to be analogous to the 'buttress zone' reported for recent West Indian reefs along the north coast of Jamaica. (Goreau, 1959).

Near the crest the *A. cervicornis* zone grades into a zone almost exclusively composed of *A. palmata*, however this zone was not recorded in all sequences. The *A. palmata* increases in size and overall abundance towards the central portions of the zone often making up to 70% of the exposure. Coralline algae are most abundant in this zone with crusts reaching 5-8cm thick on some of the *A. palmata* branches. Moving back from the crest *A. palmata* is gradually replaced by a wide variety of corals comparable to those found in the coral head zone and is analogous with the ‘rear zone’ as identified by Goreau (1959).

Mesolella *et al.* (1970) and James (1972) concluded that each uplifted terrace on Barbados represents an outer barrier reef, a protected lagoon, and an inner fringing reef. The barrier and fringing reefs are dominated by *A. palmata* and the lagoon by *M. annularis*. Present day reefs off the west coast of Barbados do not exhibit this zonation and analogues from other islands, e.g. Jamaica, (Goreau, 1959) have been used to interpret the Pleistocene reef palaeocology. By analogy with recent West Indian reefs, it was assumed that the crest of any reef terrace with a well developed *A. palmata* zone can be taken to represent mean low tide level as related to that particular reef. The average depth ranges of the Barbados Pleistocene reefs agree particularly well with depth ranges and coral zonation reported for the various coral zones of recent West Indian reefs of Jamaica, (Goreau, 1959). This coral zonation has occurred numerous
times during the Pleistocene in the uplifted Barbados reefs. Thus, similar zonations in Recent West Indian reefs are not solely a Recent phenomena.

2.3 Diagenetic Environments

Four main diagenetic realms may be distinguished based upon the nature of the pore-filling aqueous phase, the subaerial vadose zone (above the height of the water table), the subaerial phreatic zone (below the height of the water table), the marine zone and the burial zone (Folk, 1973). Land (1970) recognised the need to subdivide the subaerial environment into two component parts based on large variations in the rate of alteration and nature of the alteration products found between the vadose and phreatic zones. Prior to this, studies of diagenetic alteration (Friedman, 1964; Land, et al., 1967) treated the subaerial environment as a single diagenetic environment.

The depth of the vadose zone depends upon climate, vegetation, thickness of soil and height above sea level. Though the identification of the boundary between the vadose zone and the phreatic zone is complicated, as the water table boundary is gradational and fluctuates over time, the “simple transition from marine environment to vadose environment attendant to eustatic regression or tectonic uplift offers in one geologically simple event ample opportunity for numerous “stages” of diagenetic modification to the sediment.” (Matthews, 1971). The subsurface (burial) realm is the deepest and most extensive diagenetic environment, but will not be considered in this study as the carbonate sediments on Barbados have only been exposed to near surface conditions.

The interaction of gradual tectonic uplift and glacio-eustatic sea level fluctuations on Barbados allows us to make realistic approximations of the diagenetic history to which the limestone sediments have been subjected, and the total time the sediment has been exposed to each environment (Steinen & Matthews, 1973).

Matthews (1974) and Pingitore (1976) were able to distinguish between locations on Barbados that are dominated by phreatic histories and others by vadose histories, determined by cement morphologies and rates of geochemical alteration. The diagenetic
rate was reported to be higher in localities dominated by a phreatic history than at sites
where vadose conditions prevailed. The following map of Barbados (Figure 2.2)
produced by Matthews (1968) shows the topography and mineralogical stability of the
Barbados coral cap determined by XRD determinations. However, the 'considerable'
climatic variability proposed by Matthews (on an island with maximum dimensions of
32km and 23km), resulting in vadose histories on the South Coast and phreatic
conditions in the west coast is questionable. Increased rainfall in the topographically
higher central region and flowing to the west coast (as outlined in chapter 3), should
have little effect on surface exposures, as rainfall would permeate through the porous
coral cap at high elevations down to the groundwater table. Therefore water availability
to the upper vadose zone should be comparable between the west coast and Christ
Church. Possible factors to explain any apparent differences in rates of alteration
between regions will be investigated in Chapters 5 and 6.
In Figure 2.1 the open circles represent localities where aragonite has been sampled. Closed circles represent localities where only low-Mg calcite or dolomite have been collected. The shaded area represents that portion of the island where significant quantities of unstable mineralogy still persists. Whereas much of the coral cap is composed of stable mineralogy, unstable mineralogy exists in young terraces throughout the range of climatic variability exhibited on the island. The low rainfall-high evaporation in the Christ Church region retains unstable mineralogies to greater elevations than that found in the west coast.
2.4 Alteration in the marine environment

Before sediments are exposed to subaerial conditions, diagenetic alteration may occur in the marine environment. Tucker (1991) noted that diagenetic processes may be going on concurrently with reef growth. Marine diagenetic processes include dissolution, cementation and micritisation. (Bathurst, 1975). Marine cements may be composed of aragonite and high Mg-calcite, which reduce the porosity within chambers of corals. The porosity may also be reduced by the infilling of voids by sand and clay-sized carbonate detritus (micrite).

The term micrite (Folk, 1959) refers to ‘microcrystalline calcite ooze’ (p.8) deposited in low energy environments and are composed of crystals ‘1-4 microns in diameter, generally subtranslucent with a faint brownish cast in thin section’. Friedman & Sanders (1978) believe that micrite should refer strictly to ‘lithified mechanically deposited lime mud’ (p.565) as distinct from a precipitated cement. However the term ‘micritic cement’ has been used (Hook et al. 1984) and Milliman et al. (1985) believe that micrite (in addition to an oozelike matrix), may include cement and/or diagenetic envelopes (formed through the processes of micritisation). As micrite formation is polygenetic, the exact origin is difficult to ascertain after diagenesis (Tucker & Wright, 1990) and therefore ‘the term micrite should be used as a generic term for microcrystalline calcite and should not be restricted to refer to micrite-grade matrix’. (Tucker & Wright, 1990, p. 17).

Marine cements are predominantly of acicular aragonite or cryptocrystalline high-Mg calcite, as high Mg$^{2+}$ content of sea water seems to inhibit low-Mg calcite precipitation in favour of aragonite (Folk & Land, 1975). Longman (1980) identified that cementation in the marine environment may be divided into two end members. One end member has little water circulation, which would result in micritisation and minor intragranular cementation, and the second has good circulation resulting in extensive intragranular and cavity-filling cementation with fibrous aragonite and micritic Mg-calcite as the dominant cements.
Lighty (1985) working in Florida noted a high degree of variability in Holocene submarine cementation resulting in different diagenetic products inside adjacent cavities. The distribution of high-Mg calcite submarine cements within the Florida barrier reef was facies related, the most significant amount of cementation generally occurred in those reef environments that had higher rates of agitation and/or lower sedimentation rates or framework accumulation rates (every facies except the back-reef coral head facies). However, on Jamaica (Land & Goreau, 1970) laminated pelmicritic crusts of high-Mg calcite were found to depths of 70m and internal sediments in reef cavities were cemented. In both Bermudan (Ginsburg et al. 1968) and Jamaican (Land & Goreau, 1970) reef borings of burrowing bivalves and sponges were filled with cemented geopetal sediment overlain by cement. The presence of high-Mg calcite as a reef cement within modern reefs has been reported on Barbados by Macintyre et al. (1968).

In the modern reef environment off Barbados, Stentoft (1994) found that the beach rock that is widespread along the present west coast of Barbados, lacked planktonic foraminifera and was rich in rounded skeletal grains from shallow water scleractinians and molluscs, unlike sediments collected at depth. Therefore the allochems present in the uplifted sediments on Barbados can be used to indicate where in the reef they were deposited. Cementation in the modern, shallow water reef environment was found to be only a minor process with the degree of cementation found to increase with decreasing amounts of mud, resulting in submarine hardgrounds within sediments at depths of over 165m.

Pingitore (1970) noted acicular crystals composed of aragonite in corallite chambers within the subaerially exposed reef sediments on Barbados. Aragonitic needles were found to comprise 0-5% of the unaltered corals examined and were of marine origin, precipitated prior to sedimentary detritus infilling primary voids. The presence of sedimentary detritus was found to significantly reduce the porosity and permeability of the rocks. Pingitore (1976) found the mechanical filling with bio-micrite (lime mud) was an important process, particularly in the central zones of the reef (A. cervicornis and M. annularis). In contrast precipitation of aragonite needles was generally a minor process best developed in the reef-crest zone (A. palmata zone) indicating that the
physiochemical or biochemical conditions of shallow, agitated water were best suited for aragonite precipitation. Pingitore (1976) also found the aragonite needles were almost never preserved once uplifted into the vadose zone, with aragonite needles only recorded in altered corals in exceptional cases.

James (1971) noted that within corals examined on the North Coast of Barbados, encrusting biota formed a permeability barrier and *A. palmata* corals occur in a high agitation zone with an open framework that allows the development of uniform thin cement crusts in the marine environment. Crusts may act locally as dense protective seals, preserving primary porosity during later stages of subsurface diagenesis. These rims and crusts have been observed to still retain their dense peloidal texture after alteration to low Mg-calcite.

Steinen (1974) found very thin micritic crusts associated with a marine origin at the base of a core collected from the south coast of Barbados. As cements formed in the marine environment are composed of the unstable mineralogies aragonite and high-Mg calcite, the preservation of marine cements in sediments once exposed to the vadose environment requires further study.

Further evidence of marine cementation prior to uplift was found in the study by Allan & Matthews (1982). They suggested that cements with a positive covariance between $\delta^{13}$C and $\delta^{18}$O within a single carbonate generation indicates that the cements were precipitated in a marine/meteoric water mixing zone and that this could be used to identify the diagenetic origin of cements.

Dolomites have been found in the southeast of Barbados in what is known as the Golden Grove Terrace. Humphrey (1988) and Humphrey & Kimbell (1990) concluded that the dolomites were precipitated in a marine mixing zone with both algae and some corals replaced with dolomite. However, Machel & Burton (1994) believe that dolomitisation did in fact occur after a brief period of subaerial exposure and/or after a marine hiatus but prior to deposition of the overlying reef facies. Considering that other outcrops and quarries nearby do not contain dolomite, it is highly unlikely that dolomitisation extends.
much beyond Golden Grove. Dolomite has not been reported on the rest of the island and so has not been studied within the confines of this project.

2.5 Processes of carbonate cementation in the meteoric environment

Cementation is the major diagenetic process producing a hard-rock limestone from loose sediment and taking place principally where there is a significant throughput of low-Mg calcite supersaturated pore fluid. (Tucker, 1991). For this study the term 'cement' includes all passively precipitated, space-filling crystals which grow attached to a grain surface surrounding a pore space, the most common cementing agent is calcium carbonate. However, in all diagenetic zones it is widely recognised that the main sources of cement for many limestones is unknown, (Bathurst, 1975).

Arthur et al. (1982) stated that the cement fabric is a major method of recognising the original cement mineralogy, its rate of precipitation and whether it originated in the marine, vadose or phreatic environment. Coral reef rocks are composed of the following calcium carbonate polymorphs: aragonite, high-Mg calcite and low-Mg calcite. As aragonite is more soluble it will be more prone to dissolution than low-Mg calcite in the meteoric environment. When the pore waters are supersaturated with respect to CaCO$_3$ the less soluble polymorph (low-Mg calcite) will tend to precipitate out. This is a process of autolithification whereby aragonite is dissolved out of the rock and subsequently low-Mg calcite cement is precipitated into the pores, (Bathurst, 1975).

Traditional ideas on the typical cements thought to precipitate in the vadose zone have recently been questioned by McLaren (1993). These cements include pendant/gravity cements, drapestone cements, meniscus cements, rim cements and needle-fibre cements with pore-filling cements generally absent. The findings of McLaren (1993) are summarised below in Table 2.2, and they demonstrate that the type of cement formed in the vadose environment are more complex than earlier reviews suggest.
Table 2.2: Typical cement types found in a range of environments by previous researchers. (from McLaren, 1991)

<table>
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<th>Author</th>
<th>Site</th>
<th>Environment</th>
<th>Age</th>
<th>Formation</th>
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<th>Cement Type</th>
<th>Gravity</th>
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<th>Port-filling</th>
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Pendant gravity cements result from the precipitation from saturated waters held on the underside of grains and have been described as typical the vadose environment by many reviews of vadose diagenesis including Longman, 1980; Moore, 1989; Tucker & Wright, 1990; Morse & MacKenzie, 1990. However, this table shows that few researchers have found gravity cements in the vadose zone and where noted are restricted to arid and semi-arid regions, with no workers on Barbados noting their presence.
Drapestone cements are thought to occur on the upper surfaces of grains due to the dripping of water from overlying grains. Badiozamani et al. (1977), in an experimental study to simulate cementation from evaporation, found drapestone cements were precipitated out. However, drapestone cements have only been noted in a single study of vadose diagenesis by Buchbinder & Friedman, (1980).

Meniscus cements are concentrated where capillary water is present at grain contacts. Badiozamani et al. (1977) produced meniscus cements in the laboratory and concluded that meniscus cements are a valid criterion for distinguishing between vadose and phreatic cementation, substantiating the conclusions of Dunham (1969) and Budd & Land (1990). However, they are not noted in any studies of vadose diagenesis on Barbados.

Rim cements are commonly bladed, equant or syntaxial in shape. Dunham (1971) noted that rim cements may favour development on one side of a grain as a result of the formation of pendant or drapestone cements. Rim cements have been noted on Barbados but they are not limited to the vadose environment: Steinen & Matthews (1973), Steinen (1974) and Pingitore (1976) have all found rim cements precipitated in the phreatic environment and therefore rim cementation is not diagnostic as a vadose precipitate.

Needle-fibre cements have elongate crystal habits (length-to-width ratio exceeds 6:1) and are not commonly included in reviews of vadose diagenesis. However, needle-fibre cements ('Whisker' cements) are commonly recorded in studies of vadose diagenesis including acicular needles within calcareous crusts on Barbados (James 1972; Harrison 1977), typically in subspherical secondary cavities as randomly distributed straight fibres 1–4 μm wide and hundreds of microns long and as tangentially orientated lathe-shaped crystals coating pore-walls on the south coast. (Steinen, 1974). Badiozamani et al. (1977) produced somewhat different fibrous aragonite crystals that were completely inorganic in origin, precipitated in lab-simulated vadose conditions.

Pore-filling and replacement cements are not commonly cited as vadose precipitates in reviews of vadose diagenesis, as the upper vadose zone is seen as a zone of dissolution rather than of cementation. (Longman, 1980). This view persists despite pore-filling
cements being widely noted by individual studies, including on Barbados (Matthews, 1968, 1971; Pingitore, 1976). An evaluation of the cementation processes in the vadose zone on Barbados therefore needs to consider the rock fabric as well as local environmental conditions.

2.6 Cementation and replacement on Barbados

Cementation in the vadose zone on Barbados is dependent on the pore fluid flow with alteration related to the rate and path of water movement determined by the porosity and permeability of the sediment, and the availability of calcite nuclei for the cement to precipitated out on. The movement of pore water occurs in response to fluid-potential gradients, and a cycle is set up involving rainfall, seepage, subsurface flow within reservoirs, outflow at the surface, and evaporation (Matthews, 1968). Evaporation in the vadose zone near ancient and present subaerial exposure surfaces on Barbados has resulted in the enrichment in the δ¹⁸O of diagenetic calcites (Videtch & Matthews, 1880; Allen & Matthews, 1982).

In the absence of water the aragonite to calcite transformation essentially does not occur at near surface temperatures and pressures. When the pore waters are greatly undersaturated with respect to calcite, total dissolution of aragonite will generally occur. Steinen (1982) noted that bio-clasts originally composed of aragonite have been replaced with drusy sparite through the dissolution of aragonite and the later precipitation of calcite into the void. However, Harris & Matthews (1968) found that when the pore waters are only slightly undersaturated an efficient solution-reprecipitation process occurs across a thin reaction film within a single crystal without an intermediate cavity phase, a process known as 'calcitisation' with relics of the internal structure of the shell remaining. Steinen (1982) found that the neomorphic cement is composed of an irregular mosaic of small and large calcite crystals, with wavy, curved or straight intercrystalline boundaries and a brownish colouration.

Cementation within corals differs to that within the reef-associated sediments with Pingitore (1971) finding very little spar cement (averaging less than 1% of total rock
volume by point counting and only present in a third of the samples) within unrecrystallised *A. palmata* pores. However, in altered *A. palmata* corals, spar cement was present in every sample averaging 10% of total rock volume. Pingitore (1971) concluded that the majority of spar cement precipitated during the inversion of the coral skeleton with even the most recently recrystallised samples containing the same quantities of spar as the oldest samples. Pingitore also proposed that since calcite is less dense than aragonite (2.93g/cc vs. 2.71g/cc) material will be left over after the volume-for-volume inversion. This 8% excess by volume would then be available to be precipitated as a spar pore-filling cement, therefore one third of the macroporosity could be plugged with calcite spar without invoking an external source of precipitate.

Pingitore (1976) noted two types of coral replacement: (1) fabric selective mosaics concluded to be of vadose origin, and (2) cross-cutting mosaics believed to be of phreatic origin. The phreatic mosaics are composed of large, generally equant calcite crystals, often reaching several millimetres in maximum apparent dimension whereas crystal size in the vadose mosaics rarely exceed 100μm. However, James (1974) observed these two cementation types and assigned them both to the vadose zone. Fabric selective mosaics are formed by the solution-reprecipitation process occurring within a single crystal; whereas James (1974) found that cross-cutting mosaics are formed when alteration proceeds though an intermediate chalk stage, which preserves the basic arrangement of pores and the skeleton. The contact between blocky rhombic calcite and needle aragonite in these corals was transitional across a zone of chalky aragonite, varying in depth from a few microns to several centimetres. The calcite replacement crystals were found to be up to 5mm in size, with the original texture commonly preserved in ghost form.

Matthews (1968) found that cementation and replacement occurred more rapidly within reef-associated sediments rather than in large corals, as calcite nuclei (on which cements are precipitated) were present in the reef sediments whereas they were absent in corals, as they were entirely composed of aragonite. Therefore recrystallisation and cementation would occur in the matrix, whereas the corals remain aragonite and tend only to dissolve. Matthews also suggested that calcium carbonate is only locally mobilised during the development of secondary porosity, with aragonite which had undergone
dissolution, likely to be reprecipitated nearby, as calcite void filling. This conclusion was based on the lack of a systematic relationship between total porosity and secondary porosity within biosparites. Matthews also noted that the reef-associated sediments tend to stabilise more rapidly than large corals. James (1974) also found that calcretes examined from the west coast were altered by 125ka old with the textures of the more reactive finer reef-associated material completely changing, whereas textures were often partially or wholly retained in coral skeletons.

James (1971) noted that cements in reef sediments collected from calcretes on the north of Barbados were composed of high-Mg calcite. These samples were cemented in the vadose zone but had been subjected to sea spray. However, a subsequent study by Pittman (1974) did not find any high-Mg calcite cements in any of the samples collected from Barbados.

Diagenesis in the phreatic zone is considered to be relatively more rapid when compared to vadose diagenesis because of constant water movement in very large quantities (Land, 1970). The west coast of Barbados today supports an extensive fresh water lens at depth (Mesolella, 1968; Harris, 1971) that is believed to have been in existence for at least 300ka (Mesolella, 1968). The efficiency of this phreatic lens in altering unstable carbonate minerals in the near past was proposed by Pingitore (1976) who noted a general absence of high-Mg calcite and aragonite in even the youngest uplifted terraces in that region. However, a more rapid rate of alteration in near surface sediments would not be expected due to the presence of a phreatic lens at depth, therefore different explanations for the apparent regional differences will be examined in Chapters 5 and 6.

2.7 Porosity change

Porosity can be divided into two main types: primary (depositional) and secondary (diagenetic). Three common types of primary porosity are listed below.

a) Framework porosity, formed by rigid carbonate skeletons such as corals, stromatoporids and algae, especially in reef environments.
b) Interparticle porosity in carbonate sands, which is dependent on grain size distribution and shape.

c) Porosity in carbonate muds provided by fenestrae (birdseyes) and stromatactis.

Secondary porosity includes the following.

a) Molds, vugs and caverns formed by dissolution of grains and rock, commonly through leaching by meteoric ground waters.

b) Intercrystalline porosity produced through dolomitisation.

c) Fracture porosity, formed through tectonic movements and pressures, and by collapse and brecciation of limestone as a result of dissolution.

Porosity is commonly facies controlled. Pittman (1974) noted that porosity and permeability changes in Pleistocene corals are controlled either directly or indirectly by marine and fresh-water diagenetic processes. All coral have primary voids that originally were occupied by living coral tissue; also other irregularly shaped, but rounded macropores and micropores among the aragonite crystals. Two types of secondary pores were identified, borings by organisms of microscopic and macroscopic size and dissolution voids. The latter range from microscopic features such as dissolution of aragonite crystals in the skeleton to large features that affect entire coral colonies. The transition of aragonite to calcite was found to increase permeability but reduce the porosity of corals. Martin et al. (1986) found that the skeletal porosity and permeability play important roles in controlling rates of neomorphism. Greater porosity apparently allows for more uniform replacement of the coral structure, while greater density gives rise to selective alteration and migration of the neomorphic front across the coral.

Pittman (1974) found that the replacement of aragonitic coral skeletons with low-Mg calcite was also associated with a corresponding increase in permeability, which ranged from 443% for *A. palmata* to 1,374% for *M. annularis*. However, replacement results in a decrease in porosity ranging from 9% for *M. annularis* to 28% for *A. palmata* (for
specimens orientated parallel to structural grain). Permeability increases even though porosity decreases as recrystallisation of aragonite to calcite results in fewer, but more open, grain contacts. Marine cement and infill of sand and clay sized carbonate detritus reduces porosity within the chambers of a coral. In the freshwater environment porosity is affected by recrystallisation, the growth of sparry calcite and dissolution.

The distribution of both primary and secondary porosities within different parts of the reef tract requires investigation as the treatment of the reef as a homogeneous body is too simplistic. Differences in porosity have been noted between coral species as well as the reef-associated sediments.

### 2.8 Absolute dating in Barbados

#### 2.81 U-series dating

The most commonly used method of absolute dating of carbonates employs the U-series decay sequence. U-series methods are based on the measurement of the radioactive decay of $^{238}\text{U}$ and $^{235}\text{U}$, and their daughter products. Corals have proved to be suitable for absolute dating techniques as they incorporate oceanic uranium in the same isotopic composition as seawater (Thurber, 1963), and uranium concentrations in fossil corals do not differ significantly from that in recent corals (Veeh, 1966). The seawater $^{234}\text{U}/^{238}\text{U}$ activity ratio in the world ocean has a uniform value of $1.14 \pm 0.03(2\sigma)$ (Ku, et al., 1977). A modern *A. palmata* sample collected from the west coast of Barbados has activity ratios $^{234}\text{U}/^{238}\text{U}$ of $1.14 \pm 0.01$ and $^{230}\text{Th}/^{234}\text{U}$ of $<0.002$ (Ku, 1968) supporting this value. *A. palmata* is particularly useful in dating studies as its massive size minimises post depositional transport and compaction, and its abundance and generally pristine aragonite skeleton make sampling for $^{230}\text{Th}/^{234}\text{U}$ age dating relatively easy. (Bard et al., 1990a).

Since uranium has a long residence time in the sea, in the order of 400ka, the activity ratios of $^{234}\text{U}/^{238}\text{U}$ can be seen as constant over the U-series dating timeframe and can be used as a control to determine if the coral is suitable for dating. Higher ratios would indicate that the sample has undergone diagenetic alteration and therefore any dates
would be incorrect. Because no aragonitic coral sample from Barbados has ever been documented with an initial $\delta^{234}$U value less than the modern value, it can be assumed that the samples with the lowest values experienced the least alteration and provide the most accurate records of past marine $\delta^{234}$U values (Gallup et al., 1994).

Burnett & Veeh (1992) have found that in order to gain a reliable age from absolute dating techniques there should be as follows.

1. No evidence of recrystallisation and/or deposition of void filling cement. This is because recrystallisation increases the chances for uranium remobilisation and cementation would introduce secondary uranium and thorium unrelated to the true age of the original carbonate material.

2. The uranium content in the sample should not differ significantly from that in the contemporary equivalent. This is based on the rationale that the uranium concentration in sea water has remained constant, and that the processes governing the incorporation of uranium into the carbonate skeletons at the time of their formation are well defined and have not changed for the respective species. However, though this is true over short periods, Broecker (1974) has proposed that the significantly lower uranium concentration in apparently unaltered corals of Miocene age reflects a lower uranium concentration in sea water at that time. The mechanism by which uranium is incorporated into coral is still not well understood. There is, therefore, some uncertainty in assuming consistency of these processes over the long term.

3. The sample should be free of $^{232}$Th, since $^{232}$Th would indicate the addition of $^{230}$Th that has entered the system along with material of detrital origin which may also contain $^{230}$Th and/or U.

4. $^{234}$U/$^{238}$U, $^{231}$Pa/$^{235}$U and $^{239}$Th/$^{234}$U activity ratios in a given sample should be internally consistent.

5. The uranium-series ages should be consistent with the stratigraphic position of the samples, as well as internally consistent within well defined stratigraphic units.
U-series dating can theoretically be applied to date materials up to 350ka after which time the $^{230}\text{Th}/^{234}\text{U}$ ratio becomes indistinguishable from its equilibrium value of unity. However, a study of over 100 corals have indicated that “reliable” ages can only be obtained for carefully selected coral samples up to 150ka old and that corals older than 150ka do not act as closed systems, (Burnett & Veeh, 1992). Henderson et al. (1993) have also demonstrated that in two corals on Barbados, (one 129ka and the second 260ka years old), diagenetic addition of $^{234}\text{U}$ may give a calculated age 3.1ka younger for the first coral and 48.3ka less than the real age for the second coral. Therefore 150ka should be seen as an upper limit for U-series methods.

### 2.82 $^{230}\text{Th}/^{234}\text{U}$ ages

The first published absolute dates on Barbados were carried out by Broecker et al. (1968), using the $^{230}\text{Th}$ growth (alpha spectrometry) method on corals. The three youngest terraces on the island gave documented ages of 82ka ± 2,000, 103ka ± 3,000 and 122ka ± 4,000 year high stands of the sea. From an assumed sea level of +6m for the First High Cliff, Broecker et al. (1968) calculated palaeo-sea levels of -13 to -16m, 82ka years ago and -10 to -13m, 103ka years ago.

Mesolella et al. (1969) noted that corals suitable for radiometric dating could be collected from Barbados (samples >5% calcite were rejected for dating) to a height of 500 feet (Second High Cliff), with corals situated above this height affected by diagenetic processes. However, dates were only obtained for the five youngest terraces (see Table 2.3 for terrace chronology) giving ages of about 82ka, 105ka, 125ka, 170ka and 230ka, due to difficulties in establishing reliable dates >200ka using the $^{230}\text{Th}/^{234}\text{U}$ method. Dating terraces inland from the First High Cliff (125Ka) was hampered as radiometric dating did not allow a precise discrimination of individual reef tracts of slightly differing age. Hence a knowledge of uplift rates and Milankovitch’s astronomical theory was used to estimate an age of 5-600ka for the second high cliff and approximately 700ka for the oldest terraces on the island. Only samples from reef tracts that were distinct morphostratigraphic units, with defined facies relationships, so that the relation of the sample to paleo-sea level was clear, were dated by Mesolella (1967).
The dates obtained by Mesolella et al. (1969) correlated to high eustatic sea stands (Shackleton & Opdyke, 1973), which suggested that the Barbados reef terraces were not just a tectonic phenomena, but the product of world-wide eustatic changes in sea level. Age estimates from a database of over 300 corals from around the globe (Smart & Richards, 1992) give ages of 81.5 ka, 102.5 ka and a double peak of 123.5 and 129.0 ka for the last interglacial maxima. These confirm that the lower terraces in Barbados correlate to eustatic high stands of sea level rather than local tectonic events. A prolonged period of relatively low sea level between 82ka and the Holocene transgression was postulated by Mesolella et al. (1969) to account for the absence of a terrace younger than 82ka.

Table 2.3: Tentative correlation of Barbados reef ages with O18 record of core V28-238

<table>
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<th>Skinner (1988) ESR ages (ka)</th>
<th>Isotope Stage (Shackleton &amp; Opdyke, 1973)</th>
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<td>Kent</td>
<td>Bourne</td>
<td>280</td>
<td>270</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td>St. David</td>
<td>Walker</td>
<td>Undated</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cottage Vale</td>
<td>490</td>
<td>13</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Second High Cliff</td>
<td>460</td>
<td>13</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hill View</td>
<td>520</td>
<td>305</td>
<td>13</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Drax Hall</td>
<td>590</td>
<td>460</td>
<td>17 or 19</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Guinea</td>
<td>640</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

2.83 Mass Spectrometry

A major advance in uranium-series dating of marine carbonates has been the application of isotope dilution mass spectrometry, resulting in a significant reduction of the analytical errors in the measurement of $^{238}$U, $^{234}$U and $^{230}$Th and hence an improvement in the precision of uranium-series age analysis. In addition, this method permits the
analysis of much smaller uranium concentrations (30x smaller) and their decay products in comparison with alpha spectrometry, with a ~ 10x shorter data acquisition time and a 4 to 10 times higher precision, (Chen et al., 1986). The reduction in the analytical error should extend the upper dating limit of the $^{230}$Th growth method significantly beyond the present practical age limit, perhaps as far as 500 ka (Edwards et al., 1987). However, much will depend on the success of dealing effectively with problems caused by diagenesis, especially in older corals.

$\alpha$-counting and mass spectrometric methods are compared in Table 2.4. In general there is good correlation between the two methods, except the results obtained by Edwards (1987) which varies significantly for the Second Terrace with a date of 112ka ±1ka putting this sea level high stand at the time of the solar minimum. It is believed that the sample dated by Edwards may have undergone some alteration as the ratio of $^{234}$U/$^{238}$U of 1.17-1.18 is anomalously high and so this date is possibly unreliable.

Table 2.4: A comparison of $\alpha$-counting and mass spectrometric methods of dating the three youngest terraces on Barbados.

<table>
<thead>
<tr>
<th>U-Series method</th>
<th>$\alpha$-counting</th>
<th>mass spectrometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Author</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Broecker et al. (1968)</td>
<td>82</td>
<td>87.7</td>
</tr>
<tr>
<td>Mesolella et al. (1969)</td>
<td>82</td>
<td>81</td>
</tr>
<tr>
<td>Bender et al. (1979)</td>
<td>82</td>
<td>88.2</td>
</tr>
<tr>
<td>Edwards et al. (1987)</td>
<td>112</td>
<td>100.5</td>
</tr>
<tr>
<td>Ku et al. (1990)</td>
<td>104.6</td>
<td>104.3</td>
</tr>
<tr>
<td>Bard et al. (1990b)</td>
<td>125.1</td>
<td>127.9</td>
</tr>
<tr>
<td>Gallup et al. (1994)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Despite the good correlation presented here, Bard et al. (1990b) found that all corals older that 70ka have initial ratios greater than that of present seawater, a pattern also recorded by Edwards (1987) and Ku et al. (1990). One possible explanation is that all corals have been contaminated by exogenous uranium early in their evolution and that all $^{230}$Th ages are essentially correct. An alternative explanation is that the $^{234}$U/$^{238}$U ratio of the seawater changed by ~1.5% since 100ka BP. However, when comparing results interlaboratory comparisons should also be considered (Harmon et al. 1979) as a
lack of standardisation between laboratories with regard to spikes, spectral resolutions, half-lives, and even the age equation can result in large error bands. Ku et al. (1990) has therefore suggested that a more realistic estimate for the overall precision ($\pm 1\sigma$) of U-series dates in the literature would be $\pm 10-15$ka years at 120ka rather than the commonly assigned values of $\pm 5-10$ka for the individual dates, which were based on counting statistical uncertainties only.

### 2.84 $^{231}$Pa ages

Ku (1968) used the dates obtained by Broecker et al. (1968) to investigate the feasibility of the $^{231}$Pa growth method by correlating the $^{231}$Pa ages with $^{230}$Th/$^{234}$U ages (see Table 2.5). However, problems arose as the half-life of $^{231}$Pa could be taken as 34.3ka (Van Winkle et al. 1949) or 32.48ka (Kirby, 1961). The former was used as the dates are in better agreement with $^{230}$Th ages than if a half-life of 32,480 years was used; but more research is needed before these dates can be reliably accepted.

### Table 2.5: Analytical results of $^{230}$Th and $^{231}$Pa ages from Barbados (Ku, 1968)

<table>
<thead>
<tr>
<th>Terrace</th>
<th>$^{230}$Th age ($\times 10^3$ yr)</th>
<th>$^{231}$Pa half life</th>
<th>$^{231}$Pa age ($\times 10^3$ yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(living)</td>
<td>$&lt; 0.2$</td>
<td>(1) 34,300 years</td>
<td>(1) 215 + $\infty$ / - 42</td>
</tr>
<tr>
<td>Worthing</td>
<td>79 ± 2</td>
<td>(2) 32,480 years</td>
<td>(2) 204 + $\infty$ / - 39</td>
</tr>
<tr>
<td>Ventnor</td>
<td>105 ± 3</td>
<td>(1)</td>
<td>104 ± 8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(2)</td>
<td>98 ± 7</td>
</tr>
<tr>
<td>First High Cliff</td>
<td>125 ± 5</td>
<td>(1)</td>
<td>120 ± 10</td>
</tr>
<tr>
<td>Kendal Hill</td>
<td>200 ± 12</td>
<td>(2)</td>
<td>113 ± 10</td>
</tr>
</tbody>
</table>

A discontinuous reef terrace at a height of 0-4.5m above sea level, on the northwest coast, was found by James et al. (1971) in addition to the established chronology. This terrace was dated at approximately 60,000 ± 2,000 years B.P. by $^{230}$Th/$^{231}$Pa methods.
As this young terrace was absent from the west coast of the island, James et al. (1971) proposed that the northern part of the island had been uplifted more than the west coast, as the Ventnor terrace (105,000 years B.P.) was found to occur at approximately 18m above sea level in the west coast but at a height of 33m along the northwest coast. This tilting has possibly resulted in the 60ka terrace being at or just below sea level along the western coast and is as yet undetected and not exposed to subaerial conditions.

James et al. (1971) proposed that the 60ka terrace represented the sea level high stand between 60,000 and 65,000 years ago. The younger high stands may be represented as part of the shallow-water erosional terrace that extends as much as a mile offshore from the west coast (Macintyre, 1970). However, evidence for a high sea level stand prior to the 82ka was not found in this location by Radtke et al. (1988) whose subsequent ESR and U-series dates in this region indicates an Isotope Stage 5 age (either substage 5a or 5c). They concluded that the north coast of Barbados had not undergone a tectonic history different from that of the rest of the island and the $^{230}$Th/$^{231}$Pa determination was incorrect.

More recently, Edwards et al. (1997) have applied the $^{231}$Pa dating technique by thermal ionisation mass spectroscopy (TIMS) to the terraces on Barbados. The TIMS technique had yielded $^{231}$Pa ages that are believed to be 10 times more precise than those determined by decay counting. Prior to the TIMS technique, the main impediment for $^{231}$Pa dating was the inability to measure $^{231}$Pa with sufficient precision by radioactive decay counting techniques. $^{231}$Pa measurements were applied to 13 samples on Barbados to test $^{230}$Th ages. Five of these samples were found to have concordant ages and those with discordant ages all plot above concordia indicating diagenetic processes had occurred. Edwards et al. (1997) stated that a net U loss or Pa and Th gain and addition of a high $^{234}$U would result in both $^{231}$Pa and $^{230}$Th ages giving older values. If the same diagenetic processes affected the other Barbados samples with discordant ages, then $^{231}$Pa and $^{230}$-Th ages of all Barbados samples with discordant ages are upper bounds on their true age.
2.85 He/U dating

Bender et al. (1973, 1979) used the He/U dating method to determine the ages of reef tracts older than Isotope Stage 5e (First High Cliff) on Barbados. Helium analyses were carried out using the acid dissolution, isotope dilution method of Bender (1970), where the age of the sample is deduced from direct measurement of the helium formed from alpha particles given off in the decay process. The potential for He/U to date corals over a longer time period than U-series was found in a study of corals from the Caloosahatchee, Pincrest, Chipola and Gosport formations, ranging in age from early Pliocene to Eocene, whose He/U ages were in accord with those independently estimated from stratigraphic relationships (Bender, 1970, 1973).

Bender et al. (1973) analysed six samples collected at the next major reef tract at a higher location than the 200ka complex (fourth stand) which gave dates ranging from 333ka to 348ka, with one sample dated at 375ka (± 6% analytical uncertainty). However, two samples collected further inland (fifth stand) gave anomalously low ages of 315ka and 357ka, which were not consistent with the stratigraphy and it is implausible to conclude that these samples are in reality younger than the last. Problems with this dating method are also apparent in older samples with corals from the sixth high sea stand, giving ages of 490ka and 520ka, which also did not fit in with the other dates obtained. In an attempt to address problematic ages Bender et al. (1973) presented three possibilities for these inconsistent dates:

(1) the reef was formed during a low sea level stand;
(2) the corals (*M. annularis* and *Diploria sp.*) formed in deep water during a high sea stand and cannot be dated to any sea level datum; or
(3) the corals are contaminated by helium from the much older Tertiary basement immediately underlying the coral cap.

However, which of these theories, if any, was correct is still unclear. Skinner (1988) has stated that due to the potential for escape of gaseous helium from the coral matrix, He/U ages should be treated as minimum ages. Bender et al. (1973) also found large internal inconsistencies in samples from the Second High Cliff with ages ranging from 484ka to
662ka. It was therefore concluded that the usefulness and accuracy of the He/U method was limited as:

1. the stratigraphy on Barbados was not completely resolved;
2. $^{230}$Th/U dates over 200ka (for comparative purposes) have high uncertainty; or
3. He/U dates were only based on a few samples.

A subsequent study of the reef tracts on Barbados by Bender et al. (1979) revealed nine reef tracts in the Christ Church region, seven in the Clermont Nose area and ten in Saint George's Valley (See Table 2.5). The ages of these terraces were determined either using the $^{230}$Th/U method or the $^4$He/U method, but inconsistencies remain apparent as the younger age obtained for the St. David's terrace in comparison to the Kent Terrace could not be correct. However, marine transgressions were supported by He/U dating methods as within the Kingsland-Aberdare terraces (Christ Church) it was shown that the topographically higher Kingsland terrace is younger than the Aberdare terrace and they were separated by a period of subaerial exposure. Also in Saint George's Valley, Dayrells terrace has been inundated and is overlapped by the younger Rowans terrace. It was suggested by Bender et al. (1979) that even aragonitic corals older than 150ka have taken up excess $^{230}$Th, while corals older than 250ka contain excess $^{234}$U; therefore there were large degrees of uncertainty in age determinations for both U-series and He/U methods for samples over 150ka.

### 2.86 Electron Spin Resonance dating

More recently the relatively new microwave spectroscopy technique of Electron Spin Resonance (ESR) dating has been applied to the terraces on Barbados (Radtke et al., 1988; Radtke, 1989; Skinner, 1988). The ESR method is based on the measurement of the number of unpaired electrons trapped in the aragonite crystals created by the natural radiation resulting from radioactivity in the coral, with the intensity of the ESR signal increasing with age (Radtke et al., 1988). Ikeya & Ohmura (1983) working on the marine terraces in the Ryukyu Islands identified that ESR dating has a theoretical time range from a few hundred years to about a million years. Therefore, this method has the
potential to be accurately applied to non-recrystallised corals over a longer timeframe than previous methods.

Radtke et al. (1988) obtained the ESR dates for Barbados outlined in Table 2.6. These dates were found to be in agreement with $^{230}\text{Th}/^{234}\text{U}$ methods (Bender et al., 1979), but for samples over 300ka there is a strong tendency for the ESR ages to be greater than the He/U ages, suggesting a loss of helium from the corals (See Table 2.7). However, as samples over 300ka were dated using only a very small sample set, (only one or two analyses for both ESR and He/U) the stratigraphic assignment of these units should be considered tentative. The precision was found to be about ±10 to 15% for samples from isotope stages 5-9. The laboratory uncertainty of an ESR result on corals is mainly due to the uncertainty in the accumulated dose determination, which is in the range of 10-20%. However, this is only an estimate as there is currently no mathematical treatment available to calculate the confidence interval of a single AD determination (Radtke & Grün, 1988).

Table 2.6: ESR ages of the coral terraces on Barbados (Radtke et al. 1988)

<table>
<thead>
<tr>
<th>West Coast (Thorpe)</th>
<th>ESR ages</th>
<th>West Coast (Clermont nose)</th>
<th>ESR ages</th>
<th>Christ Church</th>
<th>ESR ages</th>
<th>Saint George’s Valley</th>
<th>ESR ages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Worthing</td>
<td>92.7</td>
<td>Worthing</td>
<td>96.6</td>
<td>Worthing</td>
<td>91.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ventnor</td>
<td>117.6</td>
<td>Ventnor</td>
<td>242</td>
<td>Kendal Hill</td>
<td>227.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>First High Cliff</td>
<td>134</td>
<td>First High Cliff</td>
<td>135.2</td>
<td>First High Cliff</td>
<td>133.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Durants</td>
<td>213.5</td>
<td>Durants</td>
<td>242</td>
<td>Kendal Hill</td>
<td>227.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cave Hill</td>
<td>Cave Hill</td>
<td>227</td>
<td>Kingsland</td>
<td>208.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thorpe</td>
<td>350</td>
<td>Thorpe</td>
<td>307</td>
<td>Aberdare</td>
<td>261</td>
<td>Windsor</td>
<td>310</td>
</tr>
<tr>
<td>Husbands</td>
<td>379.5</td>
<td>Husbands</td>
<td>Adams Castle</td>
<td>285.5</td>
<td>Dayrells</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kent</td>
<td>433</td>
<td>Bourne</td>
<td>St. David</td>
<td>625</td>
<td>Walker</td>
<td>642</td>
<td></td>
</tr>
<tr>
<td>St. David</td>
<td>625</td>
<td>Cottage Vale</td>
<td>585</td>
<td></td>
<td>Second High Cliff</td>
<td>425</td>
<td></td>
</tr>
<tr>
<td>Hill View</td>
<td>404</td>
<td>Drax Hall</td>
<td></td>
<td></td>
<td>Hill View</td>
<td>404</td>
<td></td>
</tr>
<tr>
<td>Guinea</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 2.7: Tentative correlation of Barbados reef tracts (with average ESR ages) with Oxygen-Isotope Stages (Imbrie et al. 1984) (from Radtke et al. 1988)

<table>
<thead>
<tr>
<th>Boundaries [1000 yr.]</th>
<th>Stage 5 71-128</th>
<th>Stage 7 186-245</th>
<th>Stage 9 303-339</th>
<th>Stage 11 362-423</th>
<th>Stage 13 478-524</th>
<th>Stage 15 565-620</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bender et al. (1979)</td>
<td>Worthing</td>
<td>Kendal Hill</td>
<td>Adams Castle</td>
<td>St. David</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rendezvous Hill</td>
<td>Ventnor</td>
<td>Kingsland</td>
<td>Kent</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Aberdare</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Durants</td>
<td>Husbands</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cave Hill</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Thorpe</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Radtke et al. (1988)</td>
<td>Worthing</td>
<td>Kendal Hill</td>
<td>Adams Castle</td>
<td>Kent</td>
<td>St. David</td>
<td></td>
</tr>
<tr>
<td>Rendezvous Hill</td>
<td>Ventnor</td>
<td>Kingsland/</td>
<td></td>
<td>Kent</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Aberdare I</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Kingsland/</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Aberdare II</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Durants</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cave Hill</td>
<td>Thorpe</td>
<td>Husbands</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The oldest ages calculated on Barbados were in the order of 800 to 900 ka in Cluff's Bay on the northwest coast of the island, and are believed to support reef initiation on the island. Radtke et al. (1988) found that recrystallisation seems to have only a limited effect on the ESR as samples with aragonite concentrations down to 60% did not show a trend towards younger ages compared to samples with concentrations of 95-100%. However, as recrystallisation is accompanied by U-migration so samples with aragonite concentrations lower than 95% must be avoided. Inconsistencies have arisen between the results of Bender et al. (1979) and Radtke et al. (1988) and are evidenced in Thorpe, Kent, Husbands and St. David terraces. Also, ESR methods of dating corals from the Saint George's Valley gave erroneous ages and a correlation between these two chronologies was not possible.

Skinner (1988) also applied the ESR dating method to corals on Barbados. The results of this study are given in Table 2.3 and are concluded to be accurate to at least 300ka. The results of the two oldest samples were found to be problematic as both appear
significantly younger than the dates obtained by the He/U method (Bender et al. 1979), which was opposite to that found by Radtke et al. (1988). It was proposed that the low ages were due to a fading of the ESR signal. However, a fading of the signal was not found in the study by Radtke et al. (1988) who obtained ESR ages as old as 908ka on Barbados.

2.87 Comparison of methods

Since the late 1960's the coral reef tracts on Barbados have come under extensive study resulting in a well established timeframe provided by uranium methods and ESR determinations, with the terraces becoming successively older with height and distance inland.

The correlation between U-series, He/U and ESR ages and the stratigraphy on Barbados is dependent on the determination of accurate uplift rates. Both the U-series and the ESR dates have proposed slightly different tectonic regimes, with the proposed increase in the rate of uplift prior to 125ka (Bender et al. 1979) not required with the ESR age determinations which give an older age for the same terraces. However, as both ESR studies and He/U determinations have given some results that are clearly inconsistent with the stratigraphy it is difficult to accept or reject ages from one method over the other.

The difficulty in establishing an unambiguous timeframe for the coral on Barbados is related to the quality and errors associated with absolute dating techniques. New techniques that are applied to the terrace sequence on Barbados are judged on their ability to support the older established dates despite the possibility that the new methods may be correct and the errors associated with the older methods are not fully scrutinised. Also the unquestioned value of coral as a suitable material for dating needs to be treated with caution. The variation in $^{234}$U activity ratios argues that the assumption that coral acts as a closed system over time is not necessarily true. As the ages obtained on Barbados do generally agree with the stratigraphy, the precise resolution may require
further study with the development of new techniques, but the dates we have at present provide one of the best chrono-sequences anywhere in the world.

### 2.9 Models of progressive diagenesis

It is generally accepted that much of the cementation in carbonate rocks occurs very early in their diagenetic history and is due primarily to fresh water exposure (Milliman, 1974; Bathurst, 1975; Longman, 1980). Friedman (1964) working in Australia, first proposed the idea of progressive diagenesis occurring within sediments exposed to vadose conditions, with stabilisation occurring in 5 stages. Stage 1 involves the precipitation of rim and meniscus cements composed of low-Mg calcite. The cement source was identified as coming from the early dissolution of aragonitic shells. Stage 2 involves the conversion of high-Mg calcite allochems to low-Mg calcite without any noticeable fabric change. Stage 3 involves the continued leaching of aragonite forming moldic porosity. Stage 4 involves the infilling of the molds by drusy low-Mg calcite. The fifth and final stage involves the precipitation of low-Mg calcite as pore-filling cement. This model was developed and expanded into different environments through the work of Land et al. (1967) in Bermuda, Gavish & Friedman (1969) in Israel, and Reeckmann & Gill (1981) in Australia. However, all these models are all formulated within carbonate sands, and as yet no models produced for the progressive alteration of the reef-associated sediments typical of those found on Barbados.

Only a single model, proposed by Gvirtzman & Friedman (1977) in the southern Sinai Peninsula, considered alteration within emerged coral heads dated to about 110 ka, 200-250 ka and older than 250 ka. Alteration is seen to occur along the four following stages. Stage 1 - Living scleractinian coral. Organic tissue is essentially preserved, most of the pores were interskeletal and calcite is absent. By Stage 2 marine cements are introduced into the system and decomposition of organic material in submergent reefs begins. As organic material decomposes the nonconnected centrosclerodermite pores become progressively connected. micritic envelopes and aragonite or high-Mg calcite cements are precipitated and there is a decrease in the effective porosity as cement filled up to three quarters of the original interskeletal pores. Subaerial conditions are
experienced by Stage 3, where leaching of sclerodermites occurs, with the connected voids leached and enlarged with a corresponding increase in permeability. Void filling and cement that may have formed at stage 2 are removed leaving only negligible traces (leaching progresses until all the skeletal elements are entirely dissolved). Micritic envelopes and high-Mg calcite cements alter to low-Mg calcite. In Stage 4 precipitation of low-Mg calcite occurs through meteoric fresh waters. All the corals are replaced with a low-Mg calcite drusy cement, precipitated on both sides of micritic envelopes. The total volume of calcite is considerably less than the original volume of aragonite with the porosity created in stage 3 retained. (See Table 2.8).

Table 2.8: Diagenetic alteration of corals. (from Gvirtzman & Friedman, 1977)

<table>
<thead>
<tr>
<th>Fabrics</th>
<th>Stage I</th>
<th>Stage II</th>
<th>Stage III</th>
<th>Stage IV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Interskeletal void filling</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>aragonite cement</td>
<td>Negligible</td>
<td>Well developed</td>
<td>Relics only</td>
<td>Absent</td>
</tr>
<tr>
<td>magnesian-calcite cement</td>
<td>Negligible</td>
<td>Moderate to well developed</td>
<td>Relics only</td>
<td>Absent</td>
</tr>
<tr>
<td>micritic envelope</td>
<td>Negligible</td>
<td>Moderate</td>
<td>Well preserved</td>
<td>Well preserved</td>
</tr>
<tr>
<td>Organic tissue</td>
<td>Present</td>
<td>Decomposing</td>
<td>Absent</td>
<td>Absent</td>
</tr>
<tr>
<td>Centers of sclerodermites</td>
<td>Original pores preserved</td>
<td>Original pores preserved</td>
<td>Pores modified by leaching to hollow skeletal elements</td>
<td>Sclerodermites nonexistent</td>
</tr>
<tr>
<td>Void filling of low-magnesium calcite</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>interskeletal voids</td>
<td>Absent</td>
<td>Negligible</td>
<td>Negligible</td>
<td>Negligible to moderate</td>
</tr>
<tr>
<td>intraskeletal voids</td>
<td>Absent</td>
<td>Negligible</td>
<td>Moderate to well developed</td>
<td></td>
</tr>
</tbody>
</table>

1 Based on poritoids
2 Based on faviids

Models of progressive vadose diagenesis within calcareous sands all suggest that a set sequence of morphological development of cements and geochemical alteration of the carbonate rock occurs with progressive vadose diagenesis, as outlined in Table 2.9. The models have three components: the diagenetic product; the diagenetic processes proposed to account for the product; and, the rates of diagenesis.
Table 2.9: Models of progressive vadose diagenesis. (from Gardner & McLaren, 1993).

<table>
<thead>
<tr>
<th>Author Location</th>
<th>Diagenesis</th>
<th>Stage 1</th>
<th>Stage 2</th>
<th>Stage 3</th>
<th>Stage 4</th>
<th>Stage 5</th>
<th>Stage 6</th>
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</thead>
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<tr>
<td>Friedman (1964)</td>
<td>Israel</td>
<td>a. product</td>
<td>meniscus and rim cement early aragonite dissolution</td>
<td>low-Mg calcite allochems loss of Mg$^{2+}$</td>
<td>secondary porosity moulds infilled</td>
<td>pore-filling cement low-Mg calcite precipitation</td>
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</tr>
<tr>
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<td></td>
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<td>Land et al. (1967)</td>
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<td>unconsolidated sediments</td>
<td>meniscus cement (external source)</td>
<td>low-Mg calcite allochems loss of Mg$^{2+}$</td>
<td>pore-filling cement dissolution of aragonite</td>
<td>total loss of aragonite reprecipitation</td>
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<td>Israel</td>
<td></td>
<td>d. time</td>
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</tr>
<tr>
<td>Reeckmann &amp; Gill (1981)</td>
<td>Australia</td>
<td>a. product</td>
<td>unconsolidated sediments</td>
<td>meniscus cement (external)</td>
<td>pore-filling cement dissolution of aragonite</td>
<td>total occlusion of pores by low-Mg calcite</td>
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</tbody>
</table>

All the models developed in calcareous sands commence from an original unconsolidated sandy sediment comprising aragonite (molluscs, corals, Halimeda) and high-Mg calcite (foraminifera, coralline algae, echinoderms) bio-clasts. Stage 2 (Land et al., 1967) involves the formation of a partially lithified limestone with meniscus and rim cements and, more rarely, a pendant-type cement on the bases of larger grains. Dunham (1971) suggests that this implies low-Mg calcite precipitation in the vadose zone from water localised around points of grain contact. Gavish & Friedman (1969) quote a reduction in porosity from 35% to 20% at this stage and the loss of Mg$^{2+}$ from high-Mg calcite, which Friedman (1964) & Land et al. (1967) recorded as a separate stage. The next stage involves local aragonite dissolution and loss of Sr and reprecipitation as low-Mg calcite cement as pore-filling cement. This proceeds until all the pores are occluded. However, the model proposed by Land et al. (1967) culminates in the production of a well lithified rock with c.20% porosity. A further phase of cementation is thus required to reduce the porosity to less than 5%, the typical value of ancient limestones. The sequential stages in the progressive diagenesis of a marine carbonate sand consisting of
aragonite and high-Mg calcite as proposed by Gavish & Friedman (1969) as shown in Figure 2.3.

Figure 2.3: Progressive vadose diagenetic as proposed by Gavish & Friedman (1969), amended to include cement types. (from Gardner & McLaren, 1993)

One of the main differences noted between the models is the proposed timeframe for alteration, with stabilisation given as occurring in 130ka in the Gavish & Friedman (1969) model and in 700ka in the Reeckmann & Gill (1981) model. The time taken to reach stabilisation in Australia (Reeckmann & Gill, 1981) takes seven times longer despite containing 90-95% carbonates and being located in a wetter environment (700-750 mm a⁻¹). However, none of the deposits of pre-Holocene age have been
radiometrically dated in the Gavish & Friedman (1969) model and there were no dates beyond the last interglacial for the rocks used to develop the Reeckmann & Gill (1981) model. Therefore the timeframe may be open to conjecture in both studies, necessitating the need for a study where the timeframe is well established.

Other apparent differences in the rate of alteration can be seen in the literature. as though Gavish & Friedman (1969) proposed that by 7 to 10ka all high Mg-calcite has been lost from the system, Evans & Ginsburg (1987) have found that in the 130ka Miami Limestone, the skeletal components had retained much of their original mineralogy. Mitchell (1986), Richter (1976) and Ward (1975) all found evidence of high-Mg calcite allochens in deposits of 125ka age even though these should be totally stabilised (Stage 3 age) according to the Gavish & Friedman (1969) model. Evidence from Barbados suggests that sediments situated in a vadose diagenetic environment for the past +100 ka will have experienced only relatively slight diagenetic modification including the removal of magnesium from high-Mg calcite, the precipitation of low Mg-calcite and some minor dissolution, (Steinen & Matthews 1973). However, wide variations were noted between the west coast and the Christ Church region on the south coast. Therefore, as deposits of similar age were not found to be at similar stages of alteration, the models are not applicable outside of the areas for which they were developed and new regionally based models are required in order to understand the differences that occur in different natural environments.

These models also propose that a set sequence of alteration events exist with little overlap between the stages. For example, Gavish & Friedman (1969) implied that high Mg-calcite was lost before aragonite. However a comparison of these models with the reported findings on Barbados suggests that the sequences comprising early progressive diagenesis is far more complex. As Matthews (1968) noted, well cemented deposits that contain little evidence of aragonite dissolution or even the conversion of high-Mg calcite to low-Mg calcite. Budd (1984) also found evidence of aragonite dissolution in Holocene rock samples from Schooner Cays, where high-Mg calcite was still present. Van Kauwenbergh & Bain (1983) found that, ultimately, the persistence of aragonite may be more dependent on the porosity and density of aragonite constituents rather than its relative stability with respect to high-Mg calcite. Where the sediments contain
significant proportions of high-Mg calcite red algae, the cements would reflect this influence. Therefore progressive diagenesis cannot simply be categorised as a series of discrete steps and carbonate diagenesis could be more correctly assessed as a dynamic system. Furthermore Buddemeir & Oberndorfer (1986) challenged the idea of a set sequence of diagenetic alteration products and concluded that several diagenetic processes occur parallel to each other because they found well flushed pores of various dimensions existing next to stagnant ones.

Walter (1985) examined the relative reactivities of aragonite, high-Mg calcite, and low-Mg calcite in dissolution experiments using crushed samples of skeletal grains. He concluded that microstructure complexity controls the relative reactivities of carbonate grains and may override differences in mineralogic stability. Aragonite grains having more complex microstructures can dissolve more rapidly than the reportedly less stable magnesium calcites inferring that the difference of their reactive surface areas apparently is greater than that of their thermodynamic stabilities. Therefore models indicating that Mg is lost from the system prior to aragonite dissolution need re-evaluation.

Gavish & Friedman also proposed that rim and meniscus cements develop before pore-filling cements, with the latter not forming until Stage 3 (80 to 125ka). However, a large number of workers including Budd (1984), Halley & Harris (1979), Gardner (1986) and Ward (1973, 1975) have all found evidence of pore-filling cements in Holocene sediments. Therefore, it would seem that the sequence of morphological development of cement types and mineral inversion devised in Israel by Gavish & Friedman (1969) and reinforced by Gvirtzman & Friedman (1977) also working in Israel is not supported by research carried out in similar sediments elsewhere in the world. Land (1970) questioned his own temporal sequence when he noted that the zone of cementation (phreatic or vadose) is important in determining the type of fabric produced. He concluded that even though the Belmont rocks have been exposed to vadose diagenesis for nearly half the Pleistocene Epoch, most of the diagenesis and cementation was contemporaneous with deposition. The later vadose overprint, in spite of the long time involved, has been relatively ineffective in altering and cementing the rocks.
The variations in the nature of alteration and the temporal scales suggested, may well be because of the large number of different environments from which the deposits have come. A knowledge of spatial variations is important in any study of the timeframe over which diagenetic alteration of the rock takes place but “...however, readily apparent as they may be, spatial variations have been largely ignored in studies concerned with diagenesis, or the porosity development in carbonate rocks.” (Schroeder, 1988 p.184).

Despite the problems outlined in temporal models of vadose diagenesis, they still receive support, such as by Tucker & Wright (1990, p.342). If time is the main influence on late Quaternary vadose diagenesis then it would be expected that first, sediments of similar character and age would be cemented to roughly the same degree, and, secondly that deposits of similar character but of varying ages would have varying amounts of cement, with older deposits consistently showing more diagenetic alteration. The role of time on progressive vadose diagenesis therefore requires evaluation of internal variations in an area exposed to vadose conditions for most of its history, where the time sequence is well established and variations in lithology and climate are minimised. (Gardner & McLaren, 1993)

2.10 Conclusion

A detailed review of the literature on carbonate diagenesis reveals that either a number of questions regarding progressive alteration in the vadose zone within reef sediments on Barbados, remain unanswered, or tentative conclusions based upon cement morphologies not indicative of reef carbonates remaining unquestioned. Therefore the aim of this thesis is to examine the internal variability of vadose diagenesis within a single lithology, in a single environment and to identify progressive alteration products within corals and reef-associated sediments.
Chapter 3 — Field Sites and Fieldwork

3.1 Introduction

This chapter will start with a brief account of the Quaternary geography and climate of Barbados and is followed by a description of the fieldwork/sampling rationale and procedure. Rock samples were collected during two field seasons with rock sections described in the field and the samples studied, both chemically and petrographically, once they were brought back to the laboratory (see Chapter 4).

3.2 Description of Barbados

Barbados is located at 13°10 North, 59°35 West, approximately 145km east of the Windward Islands of the Lesser Antilles island chain in the southern Caribbean sea, and about 400km NNE from the coast of South America (Figure 3.1).

Barbados is part of the Barbados ridge complex, formed by the east-west convergence between the North American and Caribbean plates over the past 40-50ma. It is the only non-volcanic island in the Lesser Antilles Island chain and represents the emergent portion of the Barbados submarine ridge, exposing the crestal zone of a broad accretionary prism of the Lesser Antilles forearc, resulting in the active uplifting of the coastline (Speed & Larue, 1982).

Barbados is presently about 32km long and 23km across at its widest dimension and during the past 1ma (Taylor & Mann, 1991), a series of coral terraces were tectonically uplifted to form much of the island as it is seen today. This has resulted in between 80 and 85% of the 430km² surface area, consisting of Pleistocene coralline limestone (Stentoft, 1994). The remainder of the island known as the ‘Scotland District’ is composed of Tertiary strata and forms a topographic high in the east of the island. The Tertiary Scotland Sandstone hosts oil and gas that are produced from several small reservoirs at depths of 1000-2000 m (Barker et al., 1988, Payne et al., 1988). The fossil reefs capping the rest of the island, attain a maximum thickness of
more than 130m in the Southeast, thinning to less than 30m on the Clermont – Mount Hillaby anticline and the geometries of individual reef-tracts record interaction of rates of (1) reef growth, (2) glacio-eustatic sea level fluctuations, and (3) tectonism (Mesolella et al., 1970).

**Figure 3.1: Map of the Lesser Antillean showing older (eastern) and younger (western) volcanic arcs.** Subaerially exposed geology of each island is given (after Martin-Kaye, 1969). Also indicated is 100 fm contour – the approximate extent of carbonate shelf on older islands. (After Adey & Burke, 1977).
Prior to the study by Mesolella et al. (1969) the formation of the terraces on Barbados had been the subject of conjecture. "Erosionalists" (e.g. Trechmann, 1933, 1937; Senn, 1944, 1946, 1948; Weyl, 1965) believed that the coral cap was formed in its entirety prior to uplift, then during upward doming of the great coral sheet, terraces were developed by wave abrasion and faulting. "Depositionalists" (e.g. Schomburgk, 1848; Jukes-Brown & Harrison, 1891; Russell & McIntyre, 1965. Russell, 1966) believed that the terraces represented individual reef tracts which formed periodically around the emerging island and that the terraces become progressively older with increased elevation. They were also of the opinion that the terraces resulted from short periods of uplift between longer periods of rest. Mesolella et al. (1969) demonstrated that the uplifted reef tracts on Barbados, are an accumulation of fringing reefs, with a distinctive fore-reef, reef-crest and back-reef facies, formed during eustatic sea level highs, superimposed along a tectonically rising coast. Reef facies contain characteristic coral species as shown in Plates 3.1 – 3.4.

The current coastal outline of Barbados was not evident at the onset of coral reef formation (Figure 3.2), but as the reef tract trends conform to the outlines of high areas of the Tertiary foundation, the 'Scotland District' was present throughout the development history of the coral cap (Mesolella, 1968).
Plate 3.1: Massive *M. annularis* coral head characteristic of the coral head zone in the deep fore reef.

Plate 3.2: *A. cervicornis* coral characteristic of the fore reef slope.
Plate 3.3: A. palmata coral characteristic of the reef crest.

Plate 3.4: Small M. annularis coral heads characteristic of the back reef facies.
Figure 3.2: Paleogeographical history of Barbados

- --- Reef tracts
- ---- Erosional escarpment
- ...... Submerged bank
- --- Cliff

--- 5 miles
The youngest deposits are found at the lowest elevations of the island, and are near the present coastline, with older terraces found at successively higher elevations (Figure 3.3). Many of the individual terrace units form distinct topographic features that can be traced across the landscape whilst others are discontinuous and have little topographic expression. Two in particular stand out, one known as the First High Cliff (Isotope Stage 5e) (Plate 3.5) is found in the range of +35m above sea level. The second major terrace, known as the Second High Cliff (Oxygen Isotope Stage 13) (Plate 3.6) is found at an approximate height of +150m above sea level, however, the morphology has partially been modified by marine erosion.

The present height of each terrace is a result of uplift plus sea level change, with variations along the trend of an individual terrace caused by deformation that has occurred since the reef tract emerged from the sea. For example the First High Cliff is found at altitudes ranging from +15m above sea level, in the Northwest extreme of the terrace to +61m above sea level in the Clermont-Mount Hillaby anticline. Uplift rates based on these heights range from 0.07 to 0.44 mm/year, with the assumption of a palaeo-sea level 125ka BP six metres higher than today. (Taylor & Mann, 1991)
Figure 3.3: Geomorphological cross section of Barbados: figures in parenthesis indicate approximate dates of emergence from the sea. (from Bird et al., 1979)

Figure 3.4: Altitude (in metres) of sea ward edges of Quaternary reef terraces. (from Taylor & Mann, 1991)
Plate 3.5: First High Cliff rising steeply behind a house on the West Coast.

Plate 3.6: Second High Cliff viewed from Saint George’s Valley
3.3 Sea level and Climate change during the Quaternary

In order to be certain that the reef tracts on Barbados have always been in the vadose zone it is necessary to have a knowledge of the sea level and climatic history.

The Pleistocene is characterised by a number of alternations between colder glacial and warmer interglacials. These climatic variations resulted in eustatic changes in sea level, as a response to the removal of large quantities of water from the ocean basins to form glaciers (lowering of sea level), and the subsequent melting of these glaciers, during warmer periods (raising of sea level). These oscillations are recorded in the marine oxygen isotope record, which represents a history of the changing temperature and oxygen isotopic composition of the seawater (See Figure 3.5).

*Figure 3.5: Palaeodepths of Barbados corals plotted against $^{230}$Th ages (dots) measured by mass spectrometry (modified from Bard et al., 1990b). The palaeosea-level curve, which was constructed by applying linear corrections for uplift by normalising the last interglacial high sea stand to 7 m above present sea level, is shown with respect to normalised $\delta^{18}O$ curves for deep-sea sediments (dashed lines) and the 65°N summer insolation curve (solid line). (After Gascoyne & Harmon, 1992)*
The sequence of Pleistocene sea levels in the Caribbean was first proposed by Emiliani (1966) who reconstructed a continuous, generalised palaeotemperature curve for the past 425,000 years in the Caribbean, revealing eight complete glacial and interglacial temperature cycles. This palaeotemperature curve was subsequently expanded by 25% by Broecker et al. (1968) so that Isotope Substage 5e corresponds to an age of 125,000 yr. BP. This expansion was supported by the dating projects carried out on Barbados, as reviewed in Chapter 2.

Emiliani (1966) estimated that the $\delta^{18}O$ variation in amplitude corresponded to a 5-6°C change in temperature between glacials (21-22°C) and interglacials (26-27°C). However, Shackleton (1967), found that isotopic changes in foraminiferal tests were not due entirely to temperature changes, but were indicative of changing terrestrial ice volumes. Schroeder et al. (1970) in a study of corals on Barbados, reported that uranium was not uniformly distributed in a given coral, but concentrated in bands, with a correlation found between annual cycles in U/Ca and temperature. The U/Ca data suggested that Barbados temperatures during the last three interglacial periods were similar to today, with temperatures during glacial periods (Isotope Stages 2 and 4) 4-6°C below modern values. They also concluded that temperatures rose from glacial to interglacial values early in the last deglaciation. In addition to palaeotemperature variations Bonatti & Gartner (1973), in a study of a deep sea sediment core, used isotopic variations to conclude that during Pleistocene glacials conditions of relatively high aridity prevailed during temperature minima in the Caribbean basin, while more humid conditions prevailed during the interglacials.

Fairbanks & Matthews (1978) found terrestrial evidence of a minimum temperature change of 2°C on Barbados between Isotope Stage 6 (glacial) and Isotope Stage 5e (interglacial), through the record of oxygen isotopes in A. palmata corals. They also indicated that the temperature decline in surface waters around Barbados lagged behind major global ice-volume buildup during the regressive phase of Oxygen Isotope Stage 6 and 55m of sea level lowering could have occurred before local temperature began to decrease. More recent studies by Guilderson et al. (1994) noted larger palaeotemperature variations in the tropical sea surface temperature, thermodynamically recorded in Barbados corals collected off the south coast.
Temperatures were calculated to be 5°C colder than present values, 19,000 years ago during the glacial minima. Results from Barbados also indicate that the western tropical Atlantic is sensitive to climate change on glacial-interglacial time scales and is capable of changing quite rapidly, as evidenced by a 4°C shift between 13,7000 and 12,000 years ago. These studies indicate that glacials and interglacials have followed similar cycles and climatic conditions that may influence diagenesis have not changed over the timeframe represented on Barbados.

3.4 Present Climate

Barbados presently experiences a subhumid to humid tropical climate, with small seasonal variations in the mean average temperatures, ranging from 24-28°C and a dry season that lasts from approximately December to May. Mean annual precipitation ranges from about 1000-1230mm on the north and south coasts to 1750-2120mm in the Scotland District (Rouse & Watts, 1966).

Kimbell & Humphrey (1994) have found that orographic effects concentrate rainfall on the topographically higher, central part of the island and it is in this region that the maximum rainfall is generated. The clouds generated by the high elevations of the ‘Scotland District’ are then carried towards the west of the island by prevailing winds. This results in the Central West Coast being a relatively wet area. Consequently in comparison, relatively dry conditions occur in the vadose zone along the north and south coasts. Matthews (1968) suggested that present rainfall and surface evaporation data indicates that there may be gross differences in the availability of water to the vadose zone, which has resulted in carbonate rocks exposed to vadose conditions in the West Coast reaching stabilisation earlier than comparable deposits in Christ Church.

Runoff from the coral cap on Barbados is low with rainfall percolating downward though the porous limestones. The dominant control over the distribution of groundwater is the contrast between the highly permeable Pleistocene coral cap and the underlying low permeability of the Tertiary Oceanic Formation (Humphrey, 1988). Rainfall passes through a deep vadose zone in the older rocks at higher
elevations with the depth of the vadose zone shallowing towards the coast. Percolating rainfall then proceeds to move coastward along the contact between the limestone and the underlying impermeable Tertiary sedimentary rocks.

3.5 Sampling procedure

The staircase chronology of the fossil reef tracts on Barbados allows for the direct study of time dependent problems (within rocks of similar lithologies that have been exposed to similar environmental conditions but for increasing lengths of time). However, one of the main problems with this type of research the large number of variables affecting early diagenetic change.

A random sampling procedure of the terraces was inappropriate for this project as time constraints limited the amount of samples and outcrops that could be examined. Therefore this project builds upon prior knowledge, notably on the work carried out by Matthews and other members of Brown University under his direction, as outlined in Chapter 2. As a consequence, purposive sampling was carried out in order to examine the effect of time and fabric, whilst at the same time choosing sites that minimised the effect of other variables. Though this approach may not be an ideal form of sampling, for subsequent statistical analysis, such an approach was felt to be necessary given the extensive field research.

Even though the reef tracts originated in the marine environment tectonic uplift has enabled this research to adopt a systematic study of diagenesis in the vadose zone. The coral tracts studied have been exposed to vadose conditions for most of their existence with any exposures that have been in the phreatic zone (today or at any time in the Holocene) being avoided. Vadose histories can be accurately determined on Barbados, as O-isotope studies on sea level change have shown that sea level is believed to have been rarely higher than present, excepting the high at 125ka where sea level was between 4 and 6 metres higher, and possibly 200ka where Harman et al. (1983), working in Bermuda, determined a high of 20-50 cm above present. Therefore, reefs formed during high sea level stands would be left stranded in the vadose zone when sea levels fell during glacials. Tectonic uplift in the order of 0.07 to
0.44 mm/year, Taylor and Mann (1991) with 30 mm/ka an average estimate (Mesolella, 1970; Bender et al., 1979) would result in the terraces remaining above sea level when sea levels rose again. Where dating projects (e.g. Bender et al., 1979) indicate a sea level transgression resulting in the resubmergence of a terrace (Kingsland-Aberdare complex; Dayrells and Rowans terraces), the reef tract exposure was not sampled to avoid complexities. This is because the diagenetic history is not comparable with other vadose sequences on the island.

As there are a large number of variables affecting early diagenetic change it was necessary to minimise the number of potential controls, in order that meaningful results could be obtained. Therefore, sampling was restricted to exposures that met certain criteria. These are outlined below:

Sites studied were located exclusively in the vadose zone, within well dated sequences, with different parts of the reef tracts represented for each age group. Favourable exposures exhibited little or no surficial weathering as, although weathering is a part of vadose diagenesis, it has occurred post-initial diagenesis. Also any cements observed in weathered sediments may not reflect typical early vadose diagenesis. It was necessary to sample weathered exposures in a number of locations due to the lack of available freshly exposed samples in key outcrops and to allow comparisons with the literature. Weathered samples were, where possible, also examined in conjunction with samples that had been freshly exposed so that the differences in the degree of alteration products could be noted and reviewed. Sites with no overlying soil and vegetation layer were preferred with all sampling avoiding the soil zone and the area immediately below it. Exposures under the direct influence of sea spray were also avoided in this sampling strategy. The number of samples collected from a site was dependent on the extent and variability of the exposure so that the samples collected were representative of the whole face.

Intensive sampling was carried out mainly within the West Coast, Christ Church and Saint George's Valley regions, as shown in Figure 3.6. Over the two sampling seasons 53 exposures were examined with 750 samples collected in total (see Table 3.1). It was found to be preferable to concentrate on these sites in detail, with previous studies on the island outlining patterns of alteration within very small, limited data
sets, which may not necessarily be representative of the whole facies. Exposures were sampled at regular intervals in either the vertical or the horizontal plane, in order to examine the nature of alteration down through the rock and also to cover different fabrics within different parts of the reef tract.

**Table 3.1: Samples collected in the field**

<table>
<thead>
<tr>
<th>Age (Isotope Stage)</th>
<th>Back reef zone (rubble)</th>
<th>Coral head zone (M. annularis and Diploria sp.)</th>
<th>Fore-reef zone (A. cervicornis)</th>
<th>Reef crest zone (A. palmata)</th>
<th>Back reef</th>
<th>Total</th>
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<td>21</td>
<td>26</td>
<td>125</td>
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</table>

At each location a field sketch was drawn and the following points noted:

- Section name,
- Grid reference,
- Type of exposure,
- Direction of face,
- Age of the face,
- Age of tract,
- Height and length of tract,
- Number of samples collected and the location within the exposure,
- Major morphological forms evident.
- Location description.
- Nature of bedrock including bed thickness.
- Position in reef.
- Coral species present and their abundance.

Texture including size, shape and sorting of sediments,
Matrix/clast supported,
Degree of cementation,
Unconformities,
Colour,
Sedimentary structures present,
Karstic features including pipes and wash,
Presence of palaeosols/calcretes,
Variability within the section,
Presence of sea spray,
Nearness to ground water table,
Sample proximity to surface/roots/rhizoliths.

A field description of all the exposures sampled is given in Appendix 1.
Figure 3.6: Exposures sampled (reef trends after Pittman, 1974)

Reef trends
First High Cliff reef - Isotope Stage 5e
Second High Cliff reef - Isotope Stage 13
Pre-Pleistocene sedimentary rocks
Sample site
3.51 Reconnaissance field visit, Spring 1996

A four-week preliminary study was undertaken in March – April 1996. On this visit the terrace stratigraphy was mapped and suitable locations for the collection of samples were identified. This visit incorporated a study of all of the key sites identified by Mesolella (1968); Bender et al. (1979) and Radtke et al. (1988) so that well dated sequences with an established stratigraphy could be investigated (see Plate 3.7). A number of site types were found to be accessible, notably road cuts (Plate 3.8), quarries (Plate 3.9) and building sites (Plate 3.10) as well as natural exposures. In total 309 samples were collected from 25 outcrops.

3.52 Second field visit, Spring 1997

A second four-week study was carried out March – April 1997. This visit involved the identification of a number of new sites in addition to those visited on the preliminary study. Continuing the rationale of the preliminary visit, 441 samples were collected from 34 sites. As a result of the two visits 750 samples have been collected in total.
Plate 3.7: Sample of A. palmata from Guinea Plantation (Isotope Stage 15 (+)) where cores have been taken from at least two previous studies.
Plate 3.8: An example of a road cutting. (DS)

Plate 3.9: A quarry exposure. (CAR)

Plate 3.10: A building site exposure. (GAS)
Chapter 4 – Laboratory Methods

4.1 Introduction

The coral reef exposures on Barbados were initially described in the field before samples were collected for more detailed analysis in the laboratory. This chapter outlines the following analytical methods employed in this project:

1) Microscope techniques;
   ♦ Thin sectioning
   ♦ Point counting
   ♦ Stains
   ♦ Peels
2) Scanning electron microscope;
3) Microprobe;
4) X-ray powder diffraction;
5) X-ray fluorescence;
6) Inductively coupled plasma spectrometry; and
7) Cathodoluminescence.

Table 4.1 shows which laboratory techniques were applied to each section that was sampled.
Table 4.1: Laboratory techniques applied to each section

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<th>Microprobe</th>
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4.2 Microscope Techniques

All of the samples collected in the field were examined in thin section, with petrographic studies forming the core of this research. Both descriptive and quantitative studies were employed.

4.21 Thin sectioning

All the samples collected from Barbados were prepared and thin sections made, as follows:

1. Dry samples were cut into slices, with dimensions 20 x 50 x 10 mm and labelled.
2. Slices were impregnated under vacuum with araldite.
3. Cured slices were ground and polished.
4. Polished slices were glued onto polished glass slides as follows:
   (25 x 76 mm) – petrographic work, and
   (25 x 48 mm) – electron microprobe and cathodoluminescence work.
5. Slices are then cut and ground down to 30µm, in preparation for petrologic studies

The thin sections were not given cover slips as the analyses carried out on the electron microprobe, the cathodoluminescence work and staining needed to be applied directly to the rock surface. Different analytical techniques were therefore carried out on the same section so that the results could be compared.

4.22 Point counting

The samples were studied in thin section, under a microscope at X10 and X25 magnifications. A system of 500 point counts, identifying grains, pores and cements, evenly distributed over each slide was employed. Point counting involves the identification of the feature found directly under the cross hair, after which the slide moves on a set distance along predetermined lines until the target number is reached. This was used to determine the percentage of the various constituents and pore spaces
present and was calculated as a percentage of the total bulk rock volume. The following features were identified and their proportional presence within the slide noted (see Table 4.2).

**Table 4.2: Point counting categories**

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**Clasts**

Coral, bryozoa, foraminifera, coralline algae and skeletal fragments represent fresh unaltered allochems in the rock. Micritic clasts are generally unidentifiable fragments, this may be due to diagenetic alteration and the micritisation of grains or the deposition of pelletal grains. Quartz fragments were noted in a few of the sections and represent material transported from the Tertiary bedrock in the East of the island.

Corals secrete a skeleton of aragonite and mollusc fragments are also initially composed of aragonite, whereas red algae, encrusting algae, brachiopods, bryozoa and forams tending to be composed of high-Mg calcite. However, once uplifted into the vadose environment, the metastable minerals aragonite and high-Mg calcite, preferentially alter to low-Mg calcite. The identification of each of these minerals is therefore crucial to the determination of the degree of alteration that the rock has undergone.

**Pores**

Primary porosity includes primary pores within coral heads and other bio-clasts (intraskeletal pores), as well as primary pores in between allochems (inter-skeletal pores).
Secondary pores are the result of diagenetic alteration and the dissolution of unstable mineralogies. Dissolution in many instances is fabric selective and moldic pores develop preserving the original clast shape.

Cement

Bio-micrite is also a primary marine product deposited in high energy environments such as in the reef-crest and fore-reef, both within and between allochems. In the vadose zone primary pore-filling cements are precipitated within original unaltered pores and for this study have been sub-divided into rim cements and pore-filling cements. Secondary pore-filling cements are replacement cements formed subsequent to aragonite dissolution and have been subdivided into replacement drusy calcite cement, and neomorphic spar where the original fabric of the allochem has been retained. Micrite is a cement where the crystal size is less than 4µm and can be of biological or inorganic origin. It can be in the form of micritic envelopes, a pelletal fabric, or as a result of the micritisation of primary fabrics.

Studying cement formation in thin section can be problematic as the orientation of the sample is crucial in the identification of a) infilling of the pores with bio-micrite in the marine environment prior to uplift, and b) certain cement types, notably gravity or drapestone cements. In the field and again on the slide, the way up was marked on the sample and the sectioned samples were cut along the vertical axis (from top to bottom). Corals were also sectioned horizontal to the growth form to compare cement types and distributions as it was hoped that dual sectioning should reduce misidentifications due to the samples being 3D in reality but only studied in 2D.

The classification of cement types was determined by the size and location of the cement crystals. Rim cements were defined by this project as a zone of crystals developed as a clear rim around a clast and included syntaxial cement, with primary pore-filling cements extending into and often obscuring pores both within and between clasts. Secondary cements were found to be either precipitated in secondary pores or neomorphically replacing a clast or previous cement generation without an interim pore
space developing. Micritic cements were also observed but could not be accurately
defined as either a primary or a secondary precipitate and were grouped into an
individual category.

In addition to point counting, visual descriptions were also made of the slides to identify
clast orientation, sample homogeneity and whether the deposits were clast or matrix
supported. However, a textural analysis was not possible in the timeframe allowed as
only unaltered bio-clasts from Isotope Stage 5 were identifiable, with increasing
alteration obscuring original grain boundaries and the aim was to measure what was
present prior to alteration rather than what is present now.

4.23 Staining

The distinction between the optical properties of low-Mg calcite, high-Mg calcite and
aragonite is very difficult to determine in thin section. It was resolved by using staining
techniques, where a chemical reaction results in the production of a coloured precipitate
on a specific mineral surface. For this project the presence of different forms of calcium
carbonate was used to indicate the degree of diagenetic alteration that the rock has
undergone.

**Fiegl’s solution**

Aragonite can be identified from calcite with the use of a stain developed by Fiegl
(1937), though sensitive, this stain is not always reliable (Miller, 1988a). The recipe for
Fiegl’s solution is given in Appendix 2. The thin section was immersed in Fiegl’s
solution for 10 minutes at 20°C after which time the aragonite is stained black while
calcite remains unstained.

**Titan Yellow**

Calcites containing more than 3% MgCO₃ can be identified using a permanent Titan
yellow stain developed by Choquette and Trusell (1978) (see Appendix 2). Choquette
and Trusell (1978) identified that stain intensity was proportional (determined
qualitatively) to the Mg content of the calcite. Calcite with 5-8% MgCO\textsubscript{3} is stained a pink to pale red colour, which intensifies to a deep red colour for high Mg-calcite.

*Alizarin red S*

Calcite was identified with the use of a stain developed by Dickson (1965, 1966) (see Appendix 2). The stain dyes calcite pale pink to red, whereas dolomite does not stain at all. Dickson (1966) also noted that this stain could be used to differentiate between slightly different types of calcite, as different bioclasts stain with differing intensities. The optic orientation of sparry cement crystals can also be determined as crystals normal to the c-axis are stained pale pink, with those parallel to the axis stained a deep pink.

Although staining gives a visual clue as to carbonate mineralogy, it is only qualitative and not always successful. Geochemical techniques including ICP, XRD, XRF and microprobe analyses were also used to give precise element chemistry.

**4.24 Peels**

In addition to staining thin sections, rock samples themselves were stained, and peels taken. This enabled the production of different stain peels for the same specimen, with the previous stain removed, by re-polishing the sample (see Appendix 2).

Peels were used as an initial method to identify crystal shell mineralogy on impregnated samples, without permanently damaging the thin section, through etching. Several peels could also be applied to each individual sample with only minimal grinding required between each stain. However, the solvent used to make the peel can cause a diffusion of the stain, and because the stain is a surface precipitate, some detail of the underlying etched fabric was lost when taking a peel.
4.3 Scanning electron microscope

The SEM enabled the study of 3-D grain relationships, as unlike petrologic studies a block of fresh, uncut sample were coated in gold or carbon and then examined at a significantly higher magnification range (x20-100,000). It is possible to look down pores, identify the smallest minerals, and examine the distribution of these minerals within the pores. A review of the SEM technique is given in Trewin (1988). For this study a Hitachi S-520 scanning electron microscope was employed (see Appendix 2).

SEM analysis was used to complement the thin section analysis as features, especially the cement morphology, that could not be seen in the two dimensional slice could be observed. However, features could only be noted and photographed in a qualitative manner. As only very small samples could be studied it was difficult to know how representative such samples were, therefore several sub-samples from each whole rock sample were studied to examine small scale variations. The carbonate rocks tended to be only poorly coated with either gold or carbon and the samples were sometimes too charged to produce an image.

4.4 Microprobe

The microprobe allowed the determination of the chemical composition within a small beam (15μm in diameter), allowing the geochemical analysis of mineral grains or parts of grains. Polished thin sections of coral and red algae were carbon coated and placed under an electron beam. An average of 30 points were identified and analysed on each slide. A review of the use of microprobes is given in Reed (1975). The microprobe specifications for analysing carbonate samples in this study are outlined in Appendix 2. The microscope image on the microprobe only displayed the sample mineralogy with all carbonate minerals viewed as white, with pores black, preventing the identification of cements and bio-clasts for analysis. Microprobe work was therefore limited to fresh and altered corals and samples composed exclusively of cemented red algae. Red algae grains were analysed to examine mineralogical variations from the centre to the edge of the grains, as unlike the ICP, the microprobe allowed cements and clasts to be evaluated.
separately. It was not possible with this machine to determine the variations in the fabric between the corals.

4.5 X-ray diffraction (XRD)

X-ray diffraction was used to distinguish between the three CaCO$_3$ minerals: aragonite, high Mg-calcite and low Mg-calcite in selected coral samples. The determination of the chemical composition of carbonate minerals is an important tool supporting petrological techniques and XRD analyses can also determine the suitability of corals for dating techniques (see review in Chapter two). Details of XRD theory is outlined in Hardy & Tucker (1988).

A Phillips PW1729 X-ray generator was used with a PW1716 diffractometer and a PW1050/25 detector. The XRD uses a copper element to detect K$_\alpha$ radiation with 40KkV 30mA operating conditions. The peak heights were measured between a scan range of 10°2\(\theta\) and 55°2\(\theta\).

The X-ray peak heights were measured and from this it was possible to determine the various percentages of aragonite and calcite using the reference intensity ratio method, (a computer programme based on the work of Chung, 1974). The programme was unable to differentiate between high-Mg calcite and low-Mg calcite as the two peaks overlapped so microprobe and staining techniques were used to differentiate between the two calcite polymorphs. Errors in the XRD peak intensity may also result from grinding as the crystallite may be damaged by strain caused by overgrinding and powder fractions that are too coarse (Gavish & Friedman, 1973).

4.6 X-ray fluorescence (XRF)

X-ray fluorescence was used to examine the proportion of Sr, U, and Th within selected coral samples using an ARL8420+. The same samples were used for the XRD and ICP
analyses to allow direct comparisons of the methods and sample results. Details of the XRF technique are outlined in Tertian & Claisse (1982).

The X-ray emissions from international reference materials were measured to produce a calibration curve, against which the coral samples in this study were compared. The concentration of U and Th is of most interest in this study but Sr concentrations were measured by both the XRF and the ICP to compare the two methods of analysis.

4.7 Inductively Coupled Plasma Spectrometry (ICP)

The coral samples were analysed using a simultaneous Philips PV 8060 ICP-OES. Inductively coupled plasma optical emission spectrometry was used to examine the proportion of Ca, Fe, Mg, Mn, Na, and Sr from selected coral samples in solution. A review of ICP techniques is given in Thompson & Walsh (1983).

In an aid to improve representativeness, large samples were crushed and a small subsample was selected from within them. These same crushed samples were used in the XRD and XRF analyses.

4.8 Cathodoluminescence (CL)

Cathodoluminescence is the emission of light from the sample as a result of the excitation of the minerals by electrons (Miller, 1988). The conditions for luminescence often occur in impure crystalline substances where the impurities act as the luminescent centres. The intensity of light emitting from any particular point will be proportional primarily to the surface density of luminescent centres. Cathodoluminescence was used to determine whether diagenetic alteration had proceeded under vadose conditions, as Niemann & Read (1988) found that the oxidised states of Fe$^{2+}$ and Mn$^{2+}$ can not be incorporated in to the calcite lattice of vadose cements. As manganese is a common activator and iron is a common quencher, the presence and luminescence of these
elements can therefore be used to identify alteration that has proceeded outside of the vadose zone.

For this project the Cold Cathode Luminescence Model 8200 Mk II was used. The CL stage uses an electron beam to produce cathodoluminescence in susceptible materials. The view area of the polished thin sections is 50x70mm and as luminescence in certain samples is extremely dim, the samples were viewed in a darkened room. The vacuum pump was set on the floor so that vibrations transmitted to the microscope were minimised. When the vacuum in the chamber was sufficiently low for the electron beam to strike and hold, a current was transmitted through the sample. Once the target voltage was reached, sufficient luminescence could be generated to observe the target through the microscope.

Selected samples were examined using the CL, where the amount, location and intensity of the luminescence was noted and photographed.
Chapter 5 – Geochemical variations within coral sediments on Barbados

5.1 Introduction

This section of the thesis is concerned with an examination of the geochemical alteration of coral and reef associated sediments and offers possible explanations for the variations found in progressively older exposures. Consideration of within-site variability, as well as regional differences, have been undertaken.

The geochemistry of 68 coral samples was determined for Mg, Ca, Fe, Mn, Na, and Sr using the ICP. CaO, MgO, FeO, MnO, and SrO were analysed in 22 samples using the microprobe. Sr, U, and Th concentrations were analysed for 18 samples with the XRF. In the same 18 coral samples as those analysed with the microprobe, the proportion of aragonite, high-Mg calcite and low-Mg calcite was determined using the XRD. The presence of aragonite, high-Mg calcite and low-Mg calcite in both coral samples and reef associated sediments were also determined using staining techniques. Finally, cathodoluminescence studies were also carried out within selected samples to confirm a vadose origin of the pore-filling and replacement cements.

The corals were examined using the microprobe to test the following hypotheses:
(1) Does dissolution and alteration begin in the primary pores and extend inwards into the coral?
(2) Does alteration begin where pores are empty rather than in pores that have been previously infilled with bio-micrite during formation?
(3) Do different coral species alter at different rates?

5.2 Preservation of high-Mg calcite

This section will examine the length of time that high-Mg calcite is preserved in the vadose zone on Barbados. The marine organisms that secrete a skeleton initially composed of high-Mg calcite examined in this study, include red algae, encrusting
algae, echinoderms, foraminifers, bryozoa and brachiopod shells, as well as the biomicrite precipitated in primary pores in the marine environment. The preservation of high-Mg calcite was determined by staining techniques (Plates 5.1 and 5.2) and is outlined in Table 5.1.

Table 5.1: Preservation of high-Mg calcite in samples collected on Barbados as determined by staining techniques.

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<th>Region</th>
<th>Exposure (see Figure A6)</th>
<th>Red algae</th>
<th>Encrusting algae</th>
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<th>Echinoderms</th>
<th>Foraminifers</th>
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Plate 5.1: Red algae composed of high-Mg calcite (stained with Titan Yellow).

Plate 5.2: Micritic envelopes (SP3) composed of high-Mg calcite (stained with Titan Yellow).
**Isotope Stage 5a**

High-Mg calcite in bio-micrite and bio-clasts is abundant in Isotope Stage 5a, except within echinoderms, which have all altered to low-Mg calcite indicating that this process must occur prior to Isotope Stage 5a (80ka). Some exposures have had some minor loss of high-Mg calcite where porosity values are very high, including GAS1.4 from Christ Church. GAS1.4 is a sample of *Diploria sp.* coral surrounded by altered encrusting algae. The porosity values are very high in this sample with 40.6% of the total bulk rock volume by point count comprising primary pores and 4.4% secondary pores. In contrast a sample of *A. palmata* collected from the same exposure (GAS 1.2) contains 4.4% primary pores and 0.6% secondary pores, and is surrounded by unaltered encrusting algae. As the porosity values are much higher in the sample of *Diploria sp.*, fabric rather than time may be the most important variable in this case as an increased flow of water through a sample will accelerate alteration processes (Matthews, 1968).

Samples from exposure SP2 (Christ Church) were devoid of high-Mg calcite and it is possible that alteration may have occurred in the phreatic zone, as samples were collected below the present ground surface in an exposure less than 10m above the present sea level. This site was sampled as there are few unweathered exposures of Isotope Stage 5a age on the island and, as it was not near to the present water table, past phreatic conditions were not identifiable in the field.

No differences between Christ Church and the west coast were noted, contrary to the results of Matthews, (1968) who proposed that stabilisation of high-Mg calcite had occurred by Isotope Stage 5a on the west coast. A re-evaluation of outcrops visited by Matthews was hampered as all of these exposures were heavily weathered (as were most of the exposures on the west coast). The single fresh (recently cut) exposure on the west coast (CH) was found to contain unaltered bio-micrite and bio-clasts and was comparable to exposures visited at Christ Church. A review of weathered exposures has been evaluated separately at the end of this section.
Isotope Stage 5c

The Ventnor terrace (5c) was not well exposed in the west coast and so all samples of this age were collected from Christ Church. However, all of the exposures in Christ Church had undergone some surficial weathering. They will be discussed at the end of this section.

Isotope Stage 5e

Exposures of Isotope Stage 5e age were well represented but again there were no very fresh exposures in the west coast, but as exposures HEY and BRF had only undergone minor weathering, the bio-micrite and bio-clasts present were not unaltered. Unaltered bio-clasts and bio-micrite are abundant in Christ Church with exposure CMO showing exceptional preservation with samples containing unaltered echinoderm fragments, in addition to the other unaltered bio-clasts present. In the vicinity of the unaltered echinoderm all pores were filled with bio-micrite and all bio-clasts were composed of high-Mg calcite. Therefore, low porosities may have limited the flow of meteoric waters through the deposit thereby retarding the rate of alteration. The exposure OI showed partial stabilisation with the foraminifera present altered to low-Mg calcite. However these were not of sufficient abundance in the reef sediments to examine in detail.

Isotope Stage 7

Exposures from this age group demonstrate differential stabilisation, but unaltered red algae and bio-micrite are all found in exposures from Christ Church, the west coast, and Saint George's Valley. In addition, unaltered brachiopod shell fragments were noted in CAR (Saint George's Valley). However, in OQ1 (Christ Church) the bio-micrite was altered to low-Mg calcite, but in two adjacent transects from the same exposure (OQ2 and OQ3) high-Mg was present. Similarly WR1.2 (Saint George's Valley) contains unaltered red algae where the bio-micrite (composed of high-Mg calcite) surrounds the red algae, but elsewhere on the slide it has stabilised to low-Mg calcite.
**Isotope Stage 9**

At Christ Church, WIL contains bio-micrite and encrusting algae composed of high-Mg calcite with the bryozoa present stabilised to low-Mg calcite. In Saint George's Valley there is variable preservation of high-Mg calcite, with the majority of the red algae unaltered in EDG but the other bio-clasts and the bio-micrite were all altered. In the road cut DS, high-Mg calcite was found in the bio-micrite and red algae in DS1.1 and DS1.7, but the micritic envelopes in DS1.5 were composed of low-Mg calcite. The quarry HQ contained foraminifera that were dyed a deep pink around their edges but not in the centre of the grain, with the encrusting algae in sample 1.3 composed of high-Mg calcite. No high-Mg calcite was found in the exposures LEQ, CNQ and EBZ, nor EN on the west coast.

**Isotope Stage 11-15**

All the samples collected from these age groups have undergone alteration and there is no high-Mg calcite present.

**Weathering**

Two samples analysed for high-Mg calcite from the weathered exposure EG, (Isotope Stage 5a) do not contain any high-Mg calcite. However, the red algae surrounding a sample of *A. cervicornis* coral was altered at the surface, but is still composed of high-Mg calcite along one side, deeper into the exposure (away from the weathering front). When these results are compared with the freshly exposed outcrop CH also from the west coast, where no alteration has taken place, it corroborates the fact that if studying vadose diagenesis *sensu stricto* then sampling must occur away from weathered exposure surfaces.

The Ventnor terrace (Isotope Stage 5c) was not well exposed on the west coast and so all samples of this age were collected from Christ Church. However, although the exposures had undergone some surficial weathering some high-Mg calcite fabrics remain. In SP3 stabilisation was limited to a single brachiopod shell fragment, in the
vicinity of a second unaltered fragment. The exposure INCH, in addition to stabilised brachiopod fragments also contained bryozoa that had stabilised to low-Mg calcite.

The preservation of high-Mg calcite was more complex in SP1 (Isotope Stage 5c), with alteration more pronounced with depth in the section. Sample SP1.1 (base of exposure) had no high-Mg calcite present, SP 1.4 (1m above base) contained unaltered red algae composed of high-Mg calcite, whereas in SP 1.6 (1.5m above base) abundant high-Mg calcite bio-clasts were found. These results show that the presence of high-Mg calcite at this site decreases with depth in the exposure. This trend was also found in EH (Isotope Stage 5e) located on the west coast. High-Mg calcite present at the top of an exposure but not at the base would indicate that any rainfall running down an exposed surface attains a maximum efficiency (for alteration) not directly below the surface but at a depth within the exposure. Increased alteration with depth was limited to exposures that had undergone surficial weathering, indicating that evapotranspiration was not the dominant process. This finding disagrees with the ideas of McLaren (1993) and Longman (1980) who suggested that the top of the vadose zone is a zone of solution with alteration most pronounced at the top of the section and may explain why pedogenic calcretes are not abundant on Barbados.

Perhaps the weathering effect can be seen most clearly at Rendezvous Hill (1st High Cliff). The exposures RVH and RH were from the same part of a single reef tract and the only difference between them was the degree of surficial weathering. RH was sampled in 1996 when it was the only exposure available and was situated in an old road cut. By 1997 a large fresh exposure was being cut though the RVH terrace and was sampled during the second field visit. The samples from RVH contain bio-micrite, red algae, encrusting algae and bryozoa composed of high-Mg calcite, but as a result of surficial weathering, there is no high-Mg calcite on the samples from RH.

Samples of Isotope Stage 7 age from DEP on the Southeast Coast of the island and EJ on the west coast contain red algae composed of high-Mg calcite, with samples from RAG (on the southeast coast) containing unaltered bio-micrite. The moderately weathered exposure RR1 (Christ Church) had no high-Mg calcite present at the base of the exposure, but sample RR1.5 near the top of the exposure contained unaltered red algae. In RR2, a less weathered part of the cutting, patches of the bio-micrite present
were composed of high-Mg calcite. In Saint George's Valley, there is no high-Mg calcite at all in the heavily weathered LEH. These results indicate that red algae and biomicrite have the greatest preservation potential, especially when they are in close juxtaposition to each other, but the proportion of unaltered bio-clasts decreases as weathering increases.

An analysis of a range of different locations on Barbados has highlighted the importance of only analysing completely unweathered sites as the dissolitional effects of weathering can easily be mistaken for dissolution and alteration that has proceeded in the vadose zone.

**Summary**

- The rate of alteration varies among different biogenic fragments. Encrusting algae and red algae appear to be preserved the longest (Isotope Stage 9) followed by biomicrite (Isotope Stage 9). High-Mg calcite brachiopod shell fragments were found in samples up to Isotope Stage 7. However as bryozoa and foraminifera are not very common it is difficult to ascertain whether they alter at the same rate or are preserved for longer or shorter lengths of time than brachiopods. Echinoderm fragments alter very rapidly with stabilisation generally occurring prior to Isotope Stage 5a.

- There is only one sample with an unaltered echinoderm fragment present (CMO – 5e). The single crystal structure of the echinoderm fragments results in rapid alteration. However, this contrasts with the findings of Purdy (1968) who noted that coralline algae have an isotropic crystal fabric and are the first to undergo mineralogic change when compared to echinoderm fragments which have an anisotropic crystal face.

- Bio-micrite does not show a simple pattern of stabilisation with time.

- Alteration proceeds at a faster rate where isolated high-Mg calcite biogenic fragments are located in a porous rock.
• Many of the mineralogically stabilised coralline algae and echinoderm fragments appear unaltered under the microscope. The change from high-Mg calcite to low-Mg calcite without a textural change was first identified by Friedman (1964) in Bermuda and Israel and was termed paramorphic replacement.

• Weathered exposures reach stabilisation at a faster rate than unweathered exposures.

• Stabilisation of high-Mg calcite has occurred in all samples by Isotope stage 9.

5.3 Preservation of aragonite

This section will examine the time scale over which aragonite is preserved once uplifted into the vadose zone on Barbados. The marine organisms that secrete a skeleton initially composed of aragonite, include corals such as *A. palmata*, *A. cervicornis*, *M. annularis*, *Siderastrea sp.*, *P. porites* and *Diploria sp.*, mollusc shell fragments and cements precipitated in the marine environment. The preservation of aragonite as determined by XRD techniques is outlined in Table 5.2, and by staining techniques in Table 5.3.

Table 5.2: XRD results of aragonite preservation within selected coral samples

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Table 5.3: Preservation of Aragonite, as determined by staining techniques

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- **>75% unaltered aragonite present**
- **0% aragonite present**
- **Variable preservation of aragonite**
**Isotope Stage 5a**

All the corals and identifiable shell fragments from Christ Church and the west coast were composed of aragonite. There were no cements composed of aragonite in any of the exposures examined which indicates that if any were precipitated in the marine environment they have altered prior to Isotope stage 5a (80 ka).

**Isotope Stage 5c**

Aragonite coral and shell fragments were present in samples from SP1 and INCH. However, SP3 did not contain any corals or shell fragments composed of aragonite.

**Isotope Stage 5e**

Exposures from Christ Church and west coast all contained unaltered coral and shell fragments composed of aragonite with little evidence of any solution.

**Isotope Stage 7**

The only evidence for coral alteration in Christ Church was along the edge of a single sample of *A. palmata* (OQ2.2), but there is no alteration in the centre of the coral according to XRD studies. In Saint George’s Valley unstable mineralogies persist in CAR and WR but in exposure WAR both the coral and the bio-clasts are stabilised to low-Mg calcite.

**Isotope Stage 9**

The *A. palmata* coral in the freshly exposed section WIL (Christ Church) has not undergone any alteration, in addition there are few unaltered shell fragments present. In contrast, the *M. annularis* coral analysed by XRD studies from EN (west coast) and the mollusc shell fragments have totally stabilised to low-Mg calcite. However a sample of
Diploria sp. coral from this same exposure was found to be only partially altered. In Saint George’s Valley no unstable mineralogies remain.

**Isotope Stage 11**

Mollusc shell fragments from the fresh exposure STD (Christ Church) have undergone alteration, but a sample of *M. annularis* coral has not totally stabilised as it still contains 10% aragonite. In CQ (Saint George's Valley) there were small amounts of aragonite still present (<1%) but the majority of the bio-clasts had been replaced with low-Mg calcite.

**Isotope Stage 13**

In CV (Saint George's Valley) a sample of *A. palmata* was chalky in appearance and XRD analysis found this sample was stabilised to low-Mg calcite. However, Fiegl’s solution dyed large patches of it black (indicating that aragonite is present). This is the only sample in this age group to possibly contain aragonite. There are no unstable mineralogies evident in older exposures on the island.

**Weathering**

Aragonite in samples as young as Isotope Stage 5a (EG) have undergone alteration in weathered exposures. In samples of Isotope Stage 5c only aragonite bio-clasts had undergone dissolution but not replacement, with unstable mineralogies remaining in corals. RVH (fresh) and RH (weathered) were from the same part of a single reef tract from Christ Church, and were of Isotope Stage 5e age. RVH has undergone some partial alteration as XRD results show that 13% of the coral sample is composed of low-Mg calcite but the corals were totally replaced in RH (or dissolved out by weathering and no longer present in the rock outcrop leaving vuggy porosity). In the west coast, HEY had undergone some minor weathering, but XRD studies indicate that the *M. annularis* coral has not altered at all. However, in the heavily weathered exposure EH, both the coral and the bio-clasts had altered. This degree of alteration is not replicated in other
exposures on the west coast and so weathering rather than alteration in the phreatic zone, as suggested by Matthews (1968), has accelerated the rate of stabilisation. No weathered exposures of Isotope Stage 7 in age contained aragonite.

Summary

• There are no aragonitic cements in any of the samples analysed.

• In the samples studied the rate of alteration varies among different coral species. *A. palmata* is preserved the longest (Isotope Stage 13 - CV) followed by *Diploria sp.* (Isotope Stage 9 - EN) followed by *M. annularis* (Isotope Stage 7 - OQ).

• Weathered exposures alter at a faster rate than unweathered exposures.

• This study noted that unaltered reef associated sediments were found in samples of Isotope Stage 9 in a fresh quarry in the west coast despite Matthews indicating that in this region total stabilisation was reached by Isotope Stage 5e and in the west coast aragonite stabilised at a much faster rate than in Christ Church.

• Generally corals do remain unaltered for longer periods of time than reef associated sediments as the number of aragonite bio-clasts older than Isotope Stage 5e are very small, supporting one finding of Matthews (1968).

5.4 Mg concentrations in coral samples

The results of ICP and microprobe analyses on the concentration and distribution of Mg within corals do not show a decrease in corals over time, despite this element being used by previous models of vadose diagenesis (Gavish & Friedman, 1969 and Reeckmann & Gill, 1981) to indicate the first stage of alteration. The Mg content of corals analysed using the ICP in this study is shown in Figure 5.1 and Figure 5.2 displays the average values obtained for the Christ Church, west coast and Saint George’s Valley areas for each age group. The ICP gives bulk rock values of Mg content in the coral, with the microprobe (Figure 5.3) able to differentiate between Mg in coral, bio-micrite, spar cement and red algae.
Figure 5.1: Mg concentrations within selected coral samples as determined by ICP-OES analysis

![Magnesium content of selected coral samples](image)

Figure 5.2: Regional variations in Mg concentrations within selected coral samples as determined by ICP-OES analysis

![Regional variations in Mg concentrations](image)

Figure 5.3: Mg concentrations within selected coral samples as determined by microprobe analysis

![Distribution of Mg in selected coral samples](image)
**Isotope Stage 5a**

In unaltered samples of Isotope Stage 5a the Mg concentration varied from 700 ppm to 3525 ppm in the Christ Church region, and 1678 ppm to 2394 ppm in the west coast samples. These values vary markedly from an average of 900 ppm in unaltered corals (Pingitore, 1976) and living corals. Cross & Cross (1983) also working in Barbados found a systematic difference in the Mg content between living *A. palmata* (1022 ppm) and *M. annularis* (1456 ppm). Microprobe analysis indicates that 90% of the Mg is located in the micritic matrix component of the sample. The average Mg concentrations in the six samples without bio-micrite present is 777 ppm (standard deviation 76 ppm) whereas the average for the nine samples containing bio-micrite is 1954 ppm (standard deviation 733 ppm). The high standard deviation between the samples containing bio-micrite reflects the varying quantities of marine mud present. Variation was noted in the distribution of Mg between weathered and freshly exposed corals, with weathered corals containing on average 0.81% MgO against 0.26% in samples from fresh exposures. No variation in MgO distribution was noted within a coral head except for a single *A. palmata* (MCR2.13), where the MgO proportion was greater near to the pores (0.38%) than away from them (0.29%).

**Isotope Stage 5e**

In samples from Christ Church some variation was noted between samples with OI1.4 containing 982 ppm and OI1.5 containing 2307 ppm. Neither sample showed any signs of alteration with the variation related to the presence of bio-micrite in the pore spaces with 7% and 37% of the total bulk rock volume by point count, respectively. Therefore in bulk rock analyses the relationship between bio-micrite and Mg should not be underestimated.

**Isotope Stage 7**

All the corals collected from this age group were from Christ Church due to the lack of freshly exposed outcrops in the west coast. The average Mg content was low at 979
ppm despite all these samples containing bio-micrite in the coral pore spaces. This indicates that diagenetic processes have preferentially removed Mg from the bio-micrite. However, a sample of cemented red algae (El 1.1) collected from the west coast still contains very high Mg concentrations, indicating that alteration does not proceed faster on the west coast when compared to Christ Church. This conclusion is only based on the ICP evidence of a single sample and therefore requires substantiation from more freshly cut exposures in the west coast.

Isotope Stage 9

The lowest concentration of Mg was found in an unaltered sample of *A. palmata* collected from WIL in the Christ Church region at 644 ppm. The highest was from an altered sample of *M. annularis* collected from CNQ in the west coast at 3263 ppm. Therefore diagenesis not only results in the removal of Mg from high-Mg calcite but microprobe results indicate that Mg is incorporated into the recrystallised coral cements on Barbados, a trend also found on Barbados by Pingitore (1976), with bio-clasts composed of high-Mg calcite seen as the source of the Mg. The proportion of Mg within the altered corals is fairly constant at 0.6% of the total bulk rock volume in this age group and in the subsequent older samples. However, experimental studies by Schroeder (1969) indicate that Mg is lost from the aragonite structure during diagenesis and Cross & Cross (1983), also working in Barbados, found a strong tendency for corals to progressively lose Mg throughout diagenesis.

Regional differences, or differences relating to coral species, cannot be used to explain the difference between the high value for the *M. annularis* sample analysed from CNQ at 3263 ppm and the Mg concentration for a *M. annularis* sample from EN (also from the west coast) at 894 ppm. Both values are outside the range of vadose and phreatic alteration values proposed by Pingitore (1976). Pingitore (1976) found corals altered under phreatic conditions contained on average 2600 ppm Mg (standard deviation 170 ppm), whereas corals that had been subjected to solely vadose conditions contained on average 1850 ppm (standard deviation 190 ppm). This present study has found that large variations in Mg concentration are evident and the determination of vadose histories is more complex than Pingitore (1976) has suggested.
Mg changes with relation to diagenetic alteration found in this study differ significantly from the findings of both Pingitore (1976) who noted an increase in Mg from unaltered and altered corals, and Cross & Cross (1983) who noted a decrease. These two views contradict each other despite both studies being carried out on Barbadian corals. Both studies suffer due to the small data sets involved, with only single samples collected from each outcrop examined. This research has tried to address the problem of small data sets by examining several corals from each outcrop where possible, which has highlighted a large degree of internal variation not previously noted. Pingitore’s (1976) presumption that all corals in the west coast were altered in the phreatic zone and all corals in Christ Church were altered in the vadose zone was not upheld in this study. Pingitore (1976) based his results on the selective sampling of corals with either fabric selective (vadose), or non-fabric selective (phreatic) cement morphologies, whereas this study is based on random analysis of corals, regardless of location.

**Isotope Stage 11**

Only a single freshly exposed coral sample (Mg content of 1260 ppm) was examined for the Isotope Stage 11 terrace and is comparable to results from Isotope Stage 9.

**Isotope Stage 13**

There is little variation in the Mg content between Saint George's Valley and the west coast. In the west coast Mg concentrations varying from 1066 ppm to 1781 ppm (both extremes were found in a single outcrop - ER) with a mean of 1414 ppm and a standard deviation 272 ppm. Only a single sample was analysed from Saint George's Valley CV6, which had a value very close to the mean of the west coast at 1440 ppm.

**Isotope Stage 15**

Mg concentrations in the oldest corals are similar to each other with a mean of 1770 ppm (standard deviation 177 ppm) for the west coast and 1661 ppm (standard deviation 167 ppm) for samples from Saint George’s Valley. The lack of variation between the
coral samples indicates that the samples have reached values in equilibrium with their present environment.

Weathering

Samples collected from Isotope Stage 5c had all undergone surficial weathering and Mg concentrations varied widely. The Mg was found to be lowest in a sample of *A. cervicornis* at 739 ppm and highest in a sample of *P. porites* at 2459 ppm even though both were collected from the same site in Christ Church (SP1). The sample of *A. cervicornis* with low Mg content does not contain any bio-micrite in the pores, and this rather than the degree of weathering seems to control Mg concentrations within this exposure.

The difference between the weathered road cut RH and the freshly cut exposure RVH is again apparent with average Mg concentrations of 2674 ppm and 1332 ppm respectively, despite both being from the same outcrop. Only weathered samples were analysed from the west coast but high values were again noted with a mean of 3044 ppm (standard deviation 1216 ppm).

Only two coral samples were examined from the Isotope Stage 11 terrace. The Mg contents were very different with the *M. annularis* sample from the fresh exposure STD in Christ Church having a value of 1260 ppm and the *A. palmata* sample collected from the weathered exposure BE in the St. George’s Valley having a value of 3542 ppm.

Summary

- Mg concentrations in unweathered samples are very variable and does not follow a distinctive pattern of change over time. (see Figure 5.1 and Table 5.4).

- The degree of scatter decreases with age and all diagenetically altered values lie between 1100 and 2000 ppm (Isotope Stages 11 and greater).

- Higher Mg concentrations are related to the presence of bio-micrite in the coral pores and not to the coral species.
Table 5.4: Regional variation in Mg concentrations over time.

<table>
<thead>
<tr>
<th>Age (Isotope Stage)</th>
<th>Region</th>
<th>Samples</th>
<th>Mg (ppm)</th>
<th>Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>5a</td>
<td>Christ Church</td>
<td>11</td>
<td>1259</td>
<td>830</td>
</tr>
<tr>
<td>5a</td>
<td>West Coast</td>
<td>4</td>
<td>2099</td>
<td>340</td>
</tr>
<tr>
<td>5e</td>
<td>Christ Church</td>
<td>9</td>
<td>1248</td>
<td>558</td>
</tr>
<tr>
<td>5e</td>
<td>West Coast</td>
<td>3</td>
<td>3044</td>
<td>1216</td>
</tr>
<tr>
<td>7</td>
<td>Christ Church</td>
<td>7</td>
<td>938</td>
<td>60</td>
</tr>
<tr>
<td>9</td>
<td>Christ Church</td>
<td>1</td>
<td>644</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>West Coast</td>
<td>5</td>
<td>1436</td>
<td>174</td>
</tr>
<tr>
<td>9</td>
<td>Saint George's Valley</td>
<td>5</td>
<td>2193</td>
<td>726</td>
</tr>
<tr>
<td>11</td>
<td>Christ Church</td>
<td>1</td>
<td>1260</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>West Coast</td>
<td>7</td>
<td>1407</td>
<td>250</td>
</tr>
<tr>
<td>13</td>
<td>Saint George's Valley</td>
<td>1</td>
<td>1440</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>West Coast</td>
<td>4</td>
<td>1770</td>
<td>177</td>
</tr>
<tr>
<td>15</td>
<td>Saint George's Valley</td>
<td>4</td>
<td>1661</td>
<td>167</td>
</tr>
</tbody>
</table>

- In general the west coast only has higher Mg values than samples in Christ Church when the outcrops have been exposed to weathering processes.

- Bio-micrite containing high levels of Mg are found in samples upto Isotope Stage 9 (DS)

- Mg is lost from the bio-micrite over time but is incorporated into the coral lattice during diagenesis, which is why there is no noticeable change in the average concentration over time (Table 5.5).

Table 5.5: Proportion of MgO present in the micrite and coral components as determined by microprobe analysis.

<table>
<thead>
<tr>
<th>Age (Isotope Stage)</th>
<th>Sample</th>
<th>Diagenesis</th>
<th>Micrite (% Mg)</th>
<th>Coral (% Mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5a</td>
<td>CH 2.9</td>
<td>unaltered</td>
<td>1.25</td>
<td>0.18</td>
</tr>
<tr>
<td>5a</td>
<td>MCR 2.13</td>
<td>unaltered</td>
<td>1.37</td>
<td>0.33</td>
</tr>
<tr>
<td>5a</td>
<td>MCR 2.10</td>
<td>unaltered</td>
<td>1.74</td>
<td>0.28</td>
</tr>
<tr>
<td>5e</td>
<td>RVH 1.15</td>
<td>unaltered</td>
<td>0.33</td>
<td>0.19</td>
</tr>
<tr>
<td>7</td>
<td>OQ 1.8</td>
<td>unaltered</td>
<td>1.68</td>
<td>0.26</td>
</tr>
<tr>
<td>7</td>
<td>OQ 2.5</td>
<td>unaltered</td>
<td>1.30</td>
<td>0.16</td>
</tr>
<tr>
<td>9</td>
<td>WIL 1.1</td>
<td>unaltered</td>
<td>0.47</td>
<td>0.18</td>
</tr>
<tr>
<td>9</td>
<td>DS 1.4</td>
<td>altered</td>
<td>2.50</td>
<td>0.64</td>
</tr>
<tr>
<td>11</td>
<td>STD 1.5</td>
<td>altered</td>
<td>1.06</td>
<td>0.62</td>
</tr>
<tr>
<td>13</td>
<td>BESS 1.11</td>
<td>altered</td>
<td>1.10</td>
<td>0.59</td>
</tr>
<tr>
<td>15</td>
<td>APES 1.11</td>
<td>altered</td>
<td>1.70</td>
<td>0.52</td>
</tr>
<tr>
<td>15</td>
<td>GQ-V</td>
<td>altered</td>
<td>0.67</td>
<td>0.63</td>
</tr>
</tbody>
</table>
5.5 Strontium concentration

Aragonite precipitated into warm shallow waters is likely to contain about 2500-9500 ppm Sr (molluscs ~2500, corals ~8000, bio-micrite and cements ~8000-9500 ppm Sr\(^{2+}\), Scoffin, 1987). When marine sediments and corals composed of aragonite are transformed to calcite, Sr is depleted from the calcite structure and enters the meteoric waters. Figures 5.4 and 5.5 show the Sr concentration of selected corals, looking at the change in samples of various ages as well as differences related to the coral species, as determined by ICP studies. Sr concentrations were also determined using the XRF and Figure 5.6 shows a comparison of these two methods in determining the actual Sr concentration.

Within this study it was found that the ICP results were consistently lower than both the results obtained using the XRF and the results quoted in the literature. The peak intensity curves of Ca and Sr are very similar and some of the Sr may have been incorrectly identified as part of the Ca peak. A correction procedure was applied to the results however, it seems that this was not sufficient. It was not possible in this study to recalibrate the machine and run the samples through again. The results are still significant as though the numbers are lower than expected the trend is still valid and corresponds well to the XRF results.
Figure 5.4: Sr concentrations within selected coral samples as determined by ICP-OES analysis

![Graph showing Sr concentrations within selected coral samples](image)

Figure 5.5: A comparison of Sr concentrations in different coral species as analysed using the ICP-OES.

![Average strontium content of different coral species](image)

Figure 5.6: A comparison of Sr concentrations within selected coral samples analysed using the ICP-OES and the XRF

![Comparison of XRF and ICP values for strontium concentration within selected coral samples](image)
**Isotope Stage 5a**

In unaltered samples of Isotope Stage 5a age, ICP results indicate that the Sr concentration is fairly constant with little internal or regional variation with the mean Sr content in Christ Church is 4780 ppm (standard deviation 186 ppm) and in the west coast it is 4670 ppm (standard deviation 168 ppm). Samples analysed with the XRF have given very different results with an average of 7944 ppm (standard deviation 536 ppm) in Christ Church and 6830 ppm in a single sample analysed from the west coast. Values obtained on the XRF were found to be almost double those achieved on the ICP (Figure 5.6). As the trends between the two methods are comparable despite the different actual values, differences in the analytical procedure must be responsible for the varying results. Microprobe analysis indicates that the Sr is concentrated in the coral and in the pore-filling cement, with these values three times greater than that found within the micrite.

**Isotope Stage 5e**

The ICP Sr concentrations in this age group do to vary from those found in younger terraces in all unaltered samples. XRF results show the same trends within the samples but XRF concentrations are still nearly twice as high as the ICP results.

**Isotope Stage 7**

All the corals collected from this age group were from Christ Church. There was no evidence of loss of Sr in fresh exposures.

**Isotope Stage 9**

The Sr concentration in samples from this age group shows a large drop from those of Isotope Stage 7 age and younger in all but one sample (W1L from Christ Church with 4687 ppm - ICP and 8356 ppm -XRF). Samples on the west coast exhibit a large variability with EN having ICP values ranging from 1029 - 3078 ppm and CNQ1.5
having a value of 541 ppm. In the Saint George’s Valley values range from 794 ppm (LEQ) to 1882 ppm (DS). XRF values support the trends found for unaltered coral analysed from WIL although the actual values are twice as high as those obtained by ICP analysis. However in EN2.8 (a diagenetically altered sample) the Mg content is similar using both techniques.

**Isotope Stage 11**

Only a single fresh coral sample was examined from this age group, a sample of *M. annularis* from STD in Christ Church. It had a value of 1149 ppm.

**Isotope Stage 13**

Sr concentrations by Isotope Stage 13 are generally low with CV6 in Christ Church containing 185 ppm. This suggests that Sr has been lost through the processes of diagenesis. In the west coast Sr concentrations are also low in comparison to unaltered rocks; values vary from 170 ppm to 1091 ppm.

**Isotope Stage 15**

Sr contents in the oldest corals sampled still exhibit variability with results varying markedly between the west coast and Saint George’s Valley. Samples from the west coast have an average of 414 ppm Sr whereas samples from Saint George’s Valley have a value of 1277 ppm.

**Weathering**

Despite the fact that samples from Isotope Stage 5c had all undergone surficial weathering, there was no change in the Sr concentrations from Isotope Stage 5a. However, this was not the case in samples from Isotope Stage 5e where RH2.1 (Christ Church) has much lower Sr concentrations with 1815 ppm than the average of 4373
ppm obtained for fresh samples from Christ Church. The exposure RH is weathered but a second sample analysed from this exposure has a value of 4366 ppm indicating that there are great internal variations related to differential weathering of the exposure. On the west coast (HEY) the Sr concentrations also vary in a single exposure from 2440 to 4268 ppm. The trends between the ICP and the XRF are the same in the weathered samples despite the differences in the actual values. Microprobe results indicate that the only loss of Sr within this age group (EH - west coast) and in Isotope Stage 7 (LEH - Saint George’s Valley), was in the weathered exposures. This occurred where both corals had been replaced with low-Mg calcite. Within Isotope Stage 11 there was also a difference between weathered and fresh exposures, with the *M. annularis* sample from STD in Christ Church having a value of 1149 ppm and the *A. palmata* sample collected from the weathered exposure BE in the St. George’s Valley having a value of 390 ppm.

**Summary**

- The youngest samples analysed are from Isotope Stage 5a, so the increase in Sr of 250 ppm between living to fossil (Isotope Stage 5e) *M. annularis* and *A. palmata* noted by Cross & Cross (1983) can only be investigated in samples of Isotope Stage 5a and over. Peak values were obtained from samples of Isotope Stages 5e, 7 and 9 (WIL) indicating that Sr has been taken in to the coral lattice, (but not in replaced corals) though this was variable. (See Table 5.6). Experimental studies by Schroeder (1969) also indicate that Sr increases slightly during diagenesis.

- Sr values decline sharply after Isotope Stage 7. Stable values are then reached in all corals by Isotope Stage 11 but in most samples by stage 9. The differences between the west coast and Christ Church noted by Pingitore (1976) and related to alteration in different diagenetic environments, were not supported by this study.

- Higher Sr values were found in *A. palmata* corals than *M. annularis* corals in unaltered samples (Table 5.7). This agrees with the findings of Cross & Cross (1983) who noted a difference in Sr content between living *A. palmata* (7094 ppm) and *M. annularis* (650 ppm).
Table 5.6: Sr concentrations in selected coral samples over time as determined by ICP-OES and XRF analysis.

<table>
<thead>
<tr>
<th>Age (Isotope Stage)</th>
<th>Region</th>
<th>ICP Samples</th>
<th>Mean Sr (ppm)</th>
<th>Standard Deviation</th>
<th>XRF Samples</th>
<th>Sr (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5a</td>
<td>Christ Church</td>
<td>11</td>
<td>47.80</td>
<td>186</td>
<td>2</td>
<td>78.51</td>
</tr>
<tr>
<td>5a</td>
<td>West Coast</td>
<td>4</td>
<td>46.70</td>
<td>168</td>
<td>1</td>
<td>68.30</td>
</tr>
<tr>
<td>5c</td>
<td>Christ Church</td>
<td>9</td>
<td>47.30</td>
<td>523</td>
<td>1</td>
<td>74.70</td>
</tr>
<tr>
<td>5c</td>
<td>Christ Church</td>
<td>-</td>
<td>48.05</td>
<td>632</td>
<td>1</td>
<td>82.30</td>
</tr>
<tr>
<td>9</td>
<td>Christ Church</td>
<td>1</td>
<td>46.87</td>
<td>1</td>
<td>1</td>
<td>26.12</td>
</tr>
<tr>
<td>9</td>
<td>West Coast</td>
<td>5</td>
<td>53.98</td>
<td>959</td>
<td>1</td>
<td>83.56</td>
</tr>
<tr>
<td>9</td>
<td>Saint George's Valley</td>
<td>5</td>
<td>108.9</td>
<td>475</td>
<td>1</td>
<td>293.1</td>
</tr>
<tr>
<td>11</td>
<td>Christ Church</td>
<td>1</td>
<td>11.49</td>
<td>1</td>
<td>1</td>
<td>120.5</td>
</tr>
<tr>
<td>13</td>
<td>West Coast</td>
<td>7</td>
<td>33.6</td>
<td>152</td>
<td>1</td>
<td>61.6</td>
</tr>
<tr>
<td>13</td>
<td>Saint George's Valley</td>
<td>1</td>
<td>185</td>
<td>1</td>
<td>1</td>
<td>129.5</td>
</tr>
<tr>
<td>15</td>
<td>West Coast</td>
<td>4</td>
<td>41.14</td>
<td>222</td>
<td>1</td>
<td>70.9</td>
</tr>
<tr>
<td>15</td>
<td>Saint George's Valley</td>
<td>4</td>
<td>12.77</td>
<td>81</td>
<td>1</td>
<td>192.7</td>
</tr>
</tbody>
</table>

Table 5.7: A comparison of Sr concentrations within different coral species over time.

<table>
<thead>
<tr>
<th>Age (Isotope Stage)</th>
<th>A. cervicornis standard deviation</th>
<th>A. palmata standard deviation</th>
<th>M. annularis standard deviation</th>
<th>Diploria sp. standard deviation</th>
<th>P. porites standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>5a</td>
<td>4890 114</td>
<td>4852 296</td>
<td>45.50 61</td>
<td>46.40 50</td>
<td>47.31 282</td>
</tr>
<tr>
<td>5c</td>
<td>5194 77</td>
<td>4585 340</td>
<td>48.50 53</td>
<td>57.92 433</td>
<td>43.61 137</td>
</tr>
<tr>
<td>5c</td>
<td>5194 77</td>
<td>5260 863</td>
<td>561 44.5</td>
<td>57.2 45.5</td>
<td>57.2 45.5</td>
</tr>
<tr>
<td>9</td>
<td>2651 2580*</td>
<td>1010 514</td>
<td>2108 879</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>1149 124</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>185 278</td>
<td>120 511</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>12 16</td>
<td>483 589</td>
<td>498 144</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* one sample was altered the other one was not

- Microprobe analysis indicates that there is twice as much Sr in the coral compared to the bio-micrite in corals from Isotope Stage 5a, but the proportion is the same in diagenetically altered samples indicating a loss from the coral lattice.
5.6 Calcium concentration

Calcium is the principle component of all carbonates. However, heterogeneities in the crystal lattice allow the incorporation of trace elements such as Sr and Mg into the aragonite crystal lattice as calcium carbonate is precipitated in the marine environment these elements are removed and other elements added during diagenesis. Figure 5.7 shows the Ca concentration in different coral species over time as determined by ICP analysis. Figure 5.8 shows the changing proportion in the concentration of Ca in the bulk rock samples as determined by microprobe studies.

Figure 5.7: Ca concentrations within selected coral samples as determined by ICP-OES analysis

![Calcium content of selected coral samples](image)

Figure 5.8: Calcium concentrations within selected coral samples as determined by microprobe analysis

![Proportion of Calcium in selected coral samples](image)
ICP results indicate that the distribution of Ca is fairly constant between the different coral species with no trends related to the location or the age of the corals. Microprobe results indicate that the proportion of calcium accounts for 98% of the total composition in samples of Oxygen Isotope Stage 5a and increases to 99% by Isotope Stage 13 as mineral stabilisation is reached and elements such as Sr and Mg are lost from the coral structure.

**Summary**

In aragonite, Sr and Mg substitute for Ca and, as these are removed by diagenetic processes, the proportion of Ca increases with time, though the actual content remains constant.

**5.7 Sodium concentration**

The role of Na as an indicator of diagenetic alteration will be examined in this section. Na is a principle element in the marine environment with a concentration of 10,500 mg l⁻¹ in sea water (Trudgill, 1985). Scoffin (1983) found that Na is present in modern carbonate sediments to levels of ~3000 ppm but drops to 200 ppm in ancient limestones following freshwater diagenesis. Figure 5.9 examines the concentration of Na in corals over time as determined by ICP analysis.

*Figure 5.9: Na concentrations within selected coral samples as determined by ICP-OES analysis*
Isotope Stage 5a

In unaltered samples of Isotope Stage 5a the Na concentration is high with no significant difference between Christ Church and the west coast. All the exposures from Isotope Stage 5a close to the present coastline. The average Na concentration is 4011 ppm in the Christ Church region, and 4086 ppm in the west coast. The Na content of the samples is more likely related to distance inland and exposure to the sea rather than due to diagenetic processes, with altered sediments (due to weathering) in close proximity to the current coastline, showing no significant change in the Na concentration.

Isotope Stage 5c

In samples collected from Isotope Stage 5c the Na content was equally high with a very high peak at 5917 ppm in a sample of *A. palmata*. The high Na concentration is believed to be related to the close proximity of the exposures to the sea.

Isotope Stage 5e

The Na content in fresh exposures from this age group have not changed from those of younger exposures, as though these samples are found further inland, the 1st High Cliff is a very prominent and exposed terrace.

Isotope Stage 9

All the corals collected from this age group were from the Christ Church region and Na concentrations in the fresh exposures are generally high.

Isotope Stage 9

Na concentrations are generally much lower in samples from this age group, except for a single sample of *A. palmata* from WIL in Christ Church, which has an anomalously high concentration with 3715 ppm. The high value is restricted to a single sample and
may indicate operator error. However, as the exposure WIL has only recently been exposed to the surface, the water flow dynamics in Christ Church may have restricted the loss of Na from the system. Na concentrations in samples from the west coast are low with a sample from CNQ containing no Na at all, with samples from EN containing on average 359 ppm. In Saint George’s Valley Na concentrations are low with this region well away from the present coast. The two samples analysed from LEQ do not contain any Na at all. Na concentrations from other exposures from Saint George’s Valley average out at 251 ppm.

**Isotope Stage 11**

There was very little Na (236 ppm) in the sample from the exposure STD. This exposure is located far inland away from any new Na source from the sea.

**Isotope Stage 13**

There is little Na in samples collected from this age group. Na concentrations vary from 0 ppm to 435 ppm in the west coast. The sample from CV in the Saint George’s Valley has a value of 84 ppm.

**Isotope Stage 15**

Na concentrations in these older corals, that are also the furthest inland, are the lowest out of all the age groups. There is no detectable Na in any of the samples from APES on the west coast and samples from Saint George’s Valley have an average of 105 ppm.

**Weathering**

In Isotope Stages 5a and 5c there is no change in the Na concentration between fresh and weathered exposures, with the position of the outcrop in relation to the sea rather than alteration being the dominant control. The Na content in Isotope Stage 5e did vary
between fresh and weathered exposures, with two samples showing a significant drop from the values obtained in younger outcrops. RH2.1 in Christ Church has much reduced Na levels at 771 ppm, however sample RH1.3 (part of the same exposure) has values of 5306 ppm. A similar pattern was found on the west coast where values range from 1105 – 5204 ppm, indicating that there are was still large internal variations within these sites. Samples analysed from the weathered exposures of Isotope Stage 7 age have lower concentrations with the average for WR at 3476 ppm, whereas the average for the fresh exposure OQ was 4723 ppm. By Isotope Stage 11 there was no detectable Na in BE from Saint George's Valley, but this value was comparable to the fresh exposure STD indicating that age and position rather than processes operating at different rates were important in samples from this age. There is no Na in samples of Isotope Stage 13 and older.

**Summary**

- Na concentrations in corals are high in samples up to Isotope Stage 7 and in one outcrop from Stage 9.

- In general, samples of Isotope Stage 9 and older do not contain any detectable Na as these are situated well away from any recent Na source in sea spray.

- Weathered coastal samples from Isotope Stage 5c contain high Na concentrations therefore exposure to the sea rather than diagenetic alteration controls the distribution of Na. This conclusion supports the work of McLaren (1995).

**5.8 Manganese and iron concentration**

Mn and Fe are not common in marine sediments but can enter the calcite lattice under reducing conditions. The Mn and Fe concentrations can therefore be used to determine if the sediments on Barbados were altered in the vadose zone or within the phreatic zone. Fe is also incorporated in the calcite lattice under burial conditions but this is outside of the scope of this current project. Figures 5.10 and 5.11 examine the variation over time in the Mn and Fe concentrations of selected corals as determined by ICP
analyses. Figures 5.12 and 5.13 show the results of microprobe analysis to determine where the Mn and Fe was located within the corals. Cathodoluminescence studies were also used to examine the proportion of Mn (an activator) and Fe (a quencher) within the reef samples.

**Figure 5.10: Mn concentrations within selected coral samples as determined by ICP-OES analysis**

![Manganese content of selected coral samples](image)

**Figure 5.11: Fe concentrations within selected coral samples as determined by ICP-OES analysis**

![Iron content of selected coral samples](image)
Figure 5.12: Mn concentrations within selected coral samples as determined by microprobe analysis

![Distribution of Manganese in selected samples](image)

Figure 5.13: Fe concentrations within selected coral samples as determined by microprobe analysis

![Distribution of Iron in selected coral samples](image)
**Isotope Stage 5a**

Coral samples from both Christ Church and the west coast were found to contain little Mn or Fe, confirming a vadose history for these sediments. Samples from this age group did not generally luminesce. However, in samples MCR 1.4 and 2.12 a single red algae and bryozoa were noted that did glow.

**Isotope Stage 5e**

In samples from Christ Church there is a small increase in the amount of Mn (with peaks in two samples from RVH), but Fe concentrations were generally low in freshly exposed faces. Internal variability is however apparent in OI, where concentrations varied from 81 to 162 ppm. Despite an increase in Mn there was no corresponding increase in luminescence.

**Isotope Stage 7**

ICP analyses were only available for the Christ Church region, where little Mn was present, but Fe values were more variable ranging from 10-152 ppm in OQ. However, luminescence was only significant in two samples composed of cemented red algae: OQ2.1 (Christ Church) and EI1.1 (west coast). A bright red glow was emitted from the red algae in both samples but in EI1.1 the bio-micrite also gave off a glow (see Plates 5.3 and 5.4). EI1.1 was found by microprobe results to contain quite considerable amounts of Mn and this is the only sample from Barbados that gave off a spectacular red glow over the whole of the area indicating that Mn was added to the sample during diagenesis. EJ1.4 (Plates 5.5 and 5.6) and CAR1.4 in the west coast gave off bright luminescent bands, as well as a dull glow associated with red algae, foraminifera, shell fragments and bryozoa.
Plate 5.3: Red algae (E11.1) under cathodoluminescence.

Plate 5.4: Red algae (E11.1) under plane polarised light.
Plate 5.5: Luminescent bands between cement generations (EJ1.4).

Plate 5.6: Sample EJ1.4 under plane polarised light.
Isotope Stage 9

Mn concentrations remain low in samples from this age group but the bio-micrite in WIL (Christ Church), EN (west coast), HQ, EDG and DS (Saint George's Valley) gave off a dull glow. In addition some of the bio-clasts also luminesced with no regional variations noted. There were, however, variations in the Fe concentration with Christ Church having an average of 31 ppm, the west coast with 94 ppm and Saint George’s Valley with 68 ppm. Within site variability is again a feature as the quarry exposure EN has values ranging from 22 – 133 ppm.

Isotope Stage 11

STD1.5 did not contain any significant amounts of Mn (4 ppm), and Fe contents were also low (75 ppm). Though the altered M. annularis itself does not glow, there is a lot of glow on this slide associated with the micrite component. Samples from CQ in Saint George’s Valley have apparently unaltered shell fragments that glow but luminescence was very limited within these samples.

Isotope Stage 13

ICP results do not indicate any increase in Mn or Fe content in this exposure from younger samples, nor any regional differences. However, there has been an increase in the proportion of the area giving off a luminescent glow. BESS 1.8 only contains on average 7 ppm Mn, but has a dull glow associated with red algae, bryozoa and a neomorphic shell fragment and bryozoa, there is also a bright band separating generations of cement. Samples from ER also on the west coast have larger Mn concentrations with an average 24 ppm Mn, but there is no increase in the intensity of the glow in these samples from BESS. In Saint George’s Valley CV only contains 4 ppm Mn, but there is a significant amount of luminescence related to relic features and where micrite is in contact with spar.
**Isotope Stage 15**

The oldest samples on the island have the greatest intensity and proportion of luminescence (Plate 5.7 – 5.9) but this is not supported by an increase in Mn concentrations or Fe concentrations and there is no evidence of alteration outside of the vadose zone.

**Weathering**

The weathered samples from the exposure SP2 (Isotope Stage 5c) from the Christ Church contained micrite and red algae that gave off a red luminescence. In the weathered exposure EG on the west coast some of the unaltered shell fragments gave off a bright luminescence as did some red algae. Alteration did not proceed in the phreatic zone as Mn concentrations were less than 5 ppm and Fe values were also low. In samples from Isotope Stage 5c, Fe concentrations were found to be more variable with Fe concentrations varying from 22 ppm to 114 ppm within SP1 in Christ Church (SP1).

There was no luminescence and Mn and Fe concentrations were low in samples from the exposure EH on the west coast. This is contrary to the findings of Matthews, (1968) who stated that all corals of Isotope Stage 5e age and older from the west coast had altered in a phreatic zone. In contrast, the weathered exposure RH (in Christ Church) did give off a dull glow within the bio-micrite and there were bright luminescent bands present. In addition Fe concentrations reached 365 ppm, which is much higher than the average of 161 ppm obtained for the west coast. These data further refute Matthew’s findings.

Weathered corals of Isotope Stage 7 age analysed using the ICP analysis were found to have large variations in the Fe concentrations, ranging from 11 to 392 ppm despite all the samples being located in Christ Church. There were also significant internal variations with WR1.5 containing 392 ppm whereas WR1.6 contains only 67 ppm. Microprobe results for the sample LEH 1.3 indicate that a peak concentration of Fe was found in the micrite component of the sample with no Fe in the weathered coral itself.
Plate 5.7: Luminescent intensity of micritised grains and micritic envelopes in APES 1.9.

Plate 5.8: APES 1.9 under plane polarised light.

Plate 5.9: Luminescent intensity of the micrite in APES1.2.
The weathered sample from exposure BE(1.4) does contain more Mn with 30 ppm, and there is a lot of luminescence on this slide (with sharp bright boundaries where micrite and spar meet) compared to the fresh exposure STD with 75 ppm. The Fe contents were also different with the *A. palmata* sample collected from the weathered exposure BE in the St. George’s Valley having a value of 210 ppm, whilst the *M. annularis* sample from STD in Christ Church had a value of 75 ppm.

**Summary**

- Luminescence was obtained despite the low Mn concentrations, therefore the Mn is not evenly distributed in the samples, but in concentrated bands corresponding to areas which luminesced.

- Mn is associated with Mg and is found in the red algae and within the bio-micrite and on the boundaries between bio-micrite and cement generations.

- Microprobe analyses had low Mn contents but most of the Mn present was located within the bio-micrite. EII.1 has a very bright luminescence within all of the red algae and bio-micrite but microprobe studies only indicate a high proportion of Mn within the bio-micrite.

- Mn concentrations are generally constant over time but the intensity and proportion of the sample that luminesces increases with age.

- There is no luminescent glow within any of the coral structures.

- Little Fe is found in corals from Isotope Stage 5a and 5c from either Christ Church or west coast.

- Fe content is variable with peaks found in weathered samples but these are not mirrored in other samples from the same outcrop.

- There is no significant variation between the west coast and Christ Church where only freshly exposed samples are analysed.
5.9 Uranium and Thorium concentrations

Uranium is taken into the aragonite lattice and a knowledge of the changes in the concentration of U is important for absolute dating purposes. Gvirtzman et al. (1973) stated that a constant U concentration of about 2 ppm was found in modern aragonitic scleractinian corals, regardless of occurrence, anatomy or taxonomy. However, the presence of up to 50% cement of aragonite or high-Mg calcite usually raised the U concentration of bulk samples of modern corals to about 3 ppm. Kaufman et al (1971) also suggested that there is little variation between modern and unaltered Pleistocene samples. Cross & Cross (1983) have also suggested that U concentrations in A. palmata outside of 3-4 ppm and M. annularis outside of 2-3 ppm have been subject to diagenetic effects at an unknown time after the death of the coral. Th is a daughter product of the decay of U and the values of U and Th can be used in conjunction to examine the timeframe over which the coral lattice is preserved. However, in this study Uranium concentrations in samples of Isotope Stage 5a age, were in the order of 6-8 ppm. The high values in apparently unaltered samples are outside the values obtained in U-series studies on Barbados (See Chapter 2) which indicates a calibration problem with the XRF used in this study.

Figure 5.14: U concentrations within selected coral samples as determined by XRF analysis
Samples from Isotope Stage 5a contain similar amounts of U in all the coral samples regardless of species. There is little variation in the U concentration within *A. palmata* corals despite alteration from aragonite to low-Mg calcite, except for the heavily weathered sample collected from Isotope Stage 11. However, in the *M. annularis* coral there is a decline associated with alteration from 7ppm to 2ppm.

**Figure 5.15: Th concentrations within selected coral samples as determined by XRF analysis**

There is no detectable Th present in samples of Isotope Stage 9 age and younger except a single sample of *M. annularis* with 1ppm (Isotope Stage 9). Th seems to be incorporated into the coral during or after alteration with samples of *A. palmata* containing increasing amount of Th from Isotope Stage 11 to 15 where a peak value of 2 ppm was noted. There is some Th in the altered *M. annularis* but values were less than 1 ppm.

**Summary**

- Despite the discrepancy between the values obtained in this study and reported U concentrations, *A. palmata* corals in this study did not show a change in U concentration following diagenetic alteration. This is dissimilar to *M. annularis*, which has implications for dating studies.
There is a variation in the U concentrations in the youngest samples analysed with dense corals such as *A. palmata* containing more U than more porous corals, such as *M. annularis*. Cross & Cross (1983) found that in live corals *A. palmata* corals contained on average 0.5 ppm more U than *M. annularis* corals. Also samples of fossil *M. annularis* corals contained U concentrations consistent with live samples, whereas fossil *A. palmata* corals contained systematically higher U concentrations than live *A. palmata*, a trend also paralleled (in samples of Isotope Stage 5a and over) within the limited data set in this study.

There is no detectable Th present in corals of Isotope Stage 7 and younger indicating that the corals had not undergone diagenetic alteration.

From Isotope Stage 9 the Th concentration increases steadily in the *A. palmata* coral with increasing alteration.

Th concentrations in *M. annularis* coral peaks in the altered coral Isotope Stage 9 but is not present in the fresh sample from STD (Christ Church) but again rises in Isotope Stage 13.

### 5.10 Conclusions

- The stabilisation of high-Mg calcite initially proceeds prior to the alteration of aragonite but is controlled by the physical structure of the biogenic fragments with the alteration of echinoderm fragments generally occurring first despite the perfect preservation of the structure at a petrological level.

- It is not possible to identify altered from unaltered high-Mg calcite bio-clasts petrologically.

- Altered coral can have good preservation of the original structure but are easily identifiable petrologically. aragonite bio-clasts are generally replaced with low-Mg calcite with no original structure remaining.

- Aragonite may remain unaltered for a longer period of time on Barbados than high-Mg calcite.
• The total stabilisation of high-Mg calcite (Isotope Stage 11) does not occur prior to the alteration of aragonite (Isotope Stage 9) refuting the models of progressive diagenesis outlined in Chapter 2).

• The rate of alteration also varies between different biogenic fragments initially composed of high-Mg calcite. Encrusting algae and red algae are preserved to Isotope Stage 9 whereas echinoderm fragments have generally stabilised prior to 80ka (the youngest exposures studied). Alteration proceeds at a faster rate where isolated high-Mg calcite biogenic fragments are located in a porous rock.

• Weathered exposures composed of both high-Mg calcite and aragonite reach stabilisation at a faster rate than unweathered exposures.

• There were no significant differences between the rate of alteration within fresh exposures on the west coast from Christ Church and Saint George’s Valley.

• Significant differences were noted in the rate of alteration between weathered and freshly exposed samples highlighting the need to only sample freshly exposed outcrops.

• Sr, Mg, Na and U to varying extents all show a strong temporal trend and can be used to distinguish between altered and unaltered carbonates.

• Fe and Mn concentrations do not indicate that alteration proceeded in the phreatic zone.

• There is a variation in the rate of alteration between different coral species with dense corals being preserved for a greater length of time than more porous corals.
Chapter 6 — Cementation and porosity change

6.1 Introduction

This chapter of the thesis examines the effect of diagenesis within the coral and reef associated sediments from Barbados. The degree of variability within single exposures and between different zones of the same reef, as well as temporal and spatial comparisons will be discussed. This will then allow an evaluation of previously developed models of vadose diagenesis in Chapter 7. If time is the main influence on late Quaternary vadose diagenesis then it is expected that first, sediments of similar character and age are cemented to similar degrees and, secondly, that deposits of similar character but of varying ages have varying amounts of cement, with older deposits consistently showing more diagenetic alteration.

The individual coral species and sediments have been grouped together according to their position in the reef tract for analysis. The following reef zones (as discussed in Chapter 2.3) are:

a) The coral head zone dominated by the massive corals *M. annularis* and *Diploria sp.*
b) The fore reef dominated by the coral *A. cervicornis.*
c) The reef crest dominated by the coral *A. palmata.*
d) The back reef dominated by carbonate sands and small isolated coral heads.
e) The rubble zone with broken coral fragments not preserved *in situ.*

6.2 Micrite

The rock matrix on Barbados is dominated by micrite. Bio-micrite is thought to be a primary sedimentary matrix (Steinen, 1974), precipitated in the marine environment initially with a high-Mg calcite structure. Bio-micrite is composed of a very fine (~4μm), dense, brown coloured mud and skeletal silt possibly formed by the breakdown of locally derived skeletal material (see Plates 6.1 and 6.2). In Isotope Stage 5a bio-micrite is very variable in its distribution and on average makes up 5.1% of the total
bulk rock volume by point count (standard deviation 3.1%) in the fore reef; 25.5% (standard deviation 11.3%) in the reef crest; and 3% (standard deviation 3.1%) in the back reef sands. Bio-micrite is predominantly found in the reef crest zone, partially filling the primary pores within and between corals and bio-clasts, and is found to coat clasts in samples of all ages (see Plate 6.3). However, with increasing age (generally by Isotope Stage 9 and older) the skeletal silt is replaced with microspar (4 – 10µm) and pseudospar (10 – 50µm), both partially and fully, as the micrite undergoes sparitisation (see Plate 6.4).

The term bio-micrite in this study represents the mechanically deposited ‘microcrystalline calcite ooze’ (Folk, 1959) containing silt-sized skeletal silt. Micrite has been categorised separately from bio-micrite, on the grounds that it does not contain any skeletal silt and shows evidence of being a biological precipitate (in the form of pellets and micritic envelopes, see Plate 5.8 in Chapter 5 and Plate 6.5). Micritic envelopes can be precipitated in both the marine (during the formation of the reef) and the vadose environments (Steinen, 1974); with pore-filling micrite precipitated in the marine environment usually having a pelletal texture and a dark brown colour.
Plate 6.1: Micrite obscuring the pores in CH2.7.

Plate 6.2: Bio-micrite containing skeletal silt in MCR2.15.

Plate 6.3: Micrite coating of a bryozoa fragment in SP 2.1
Plate 6.4: Sparitisation of the bio-micrite and micritisation of selected red algae in EDG1.6

Plate 6.5: Micritic envelopes preserving the original clast outlines in GQ3.4
Micritic envelopes have been defined as any cryptocrystalline opaque outline of a particle or skeleton, whether they originated as fillings of bored outer regions of skeletons or as coatings extending beyond the original outline of the bio-clast, whose outer parts may or may not have been bored (Friedman et al., 1971). Although micritic envelopes can be either aragonite or high-Mg calcite (Friedman et al., 1971), the envelopes on Barbados consist exclusively of high-Mg calcite and form an irregular, fuzzy boundary around a number of bio-clasts. Micritic envelopes composed exclusively of high-Mg calcite are also noted in the reef sediments of the Red Sea (Gvirtzman & Friedman, 1977) formed in the marine environment. However Steinen (1974), working on Barbados, has suggested that micritic envelopes are formed in both the marine and the vadose zone formed in the vadose environment, as the most extensive distribution was in the upper part of a single drilled core in Christ Church. If this is the case than they must have been precipitated early in the diagenetic history of the rock, as micritic envelopes are generally only identifiable in sediments where the pores are not infilled with bio-micrite. The presence of micrite has implications for primary cementation as pores infilled with micrite have a reduced area available for primary cement development. In the sediments studied in this project micritic envelopes are not a common feature but the distribution does decrease with age as they are lost due to replacement. In some instances micritic envelopes can be used to identify clasts that have been dissolved and replaced, as they preserve the shape of the original outline (see Plate 6.3). Micritic envelopes also seem to partially replace the very edge of bio-clasts rather than growing outwards into the pore space.

The micritisation of bio-clasts was found to occur with the proportion of micrite increasing with age as seen in Table 6.1. (internal variations and standard deviations are given in Appendix 2). Remains of partially micritised red algae and encrusting algae indicates that these are the most prone to micritisation of all the bio-clasts. Encrusting algae and red algae distributions range from isolated appearances within the sediment to being the only bio-clast making up the sample (e.g. OQ2.1 in the reef crest and El 1.2 in a sandy facies), but micritisation may occur in some grains but not in other adjacent algae (see Plate 6.4).
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<td>0.0</td>
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</tr>
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<td>0.0</td>
<td>0.0</td>
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</tr>
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<tr>
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The proportion of micrite increases substantially following alteration in the A. palmata, M. annularis and Diploria sp. corals, especially in those replaced with a drusy cement. This may indicate that either these corals originally contained greater quantities of bio-micrite than those currently of Isotope Stage 5a age, which has resulted in a different alteration pathway to those that did not contain bio-micrite, or that aragonite dissolution left organic material remaining, which subsequently underwent micritisation along the pores of the coral structure prior to replacement with drusy calcite. Micritisation of skeletal material has been identified as a fairly common diagenetic process in the marine environment (Bathurst 1966; Winland 1971) but the results of this study and that of James (1972) suggests that micritisation is a common process in the vadose environment as well.

6.3 Gravity (pendent) cement

No evidence of gravity cement has been found in any of the samples collected from Barbados. Samples collected in the field were marked with their exposure orientation, so any effects of gravity would be evident in the thin sections. Despite a wide range in both size and shape of the primary pore spaces found in the different corals and the reef associated sediments, there is no evidence of any cement draped on the underside of any grains.

Although gravity cement is often referred to in the literature as a “typical” vadose cement, it has not been commonly identified. In Pleistocene deposits gravity cements have only been identified in arid and semi-arid environments from Israel (Buchbinder & Friedman, 1980), Mexico (Ward, 1973; 1975) and Oman (Gardner, 1988). Schroeder (1973) revealed that gravity cements are “notably absent” in Pleistocene vadose cemented deposits from Bermuda, and suggested that this is a result of textural controls. McLaren (1993) analysed a wide variety of sediments with differing textures to see if texture acted as a control on the presence or absence of gravity cements. However, no gravity cements were found, as in this study, and the idea of gravity cement being described as a “typical” vadose cement type was questioned.
6.4 Meniscus Cement

Meniscus cements are also absent within the deposits studied. There are a number of possible reasons for the absence of meniscus cements, as many of the samples contain bio-micrite in the original pores. This is found at the grain to grain contacts where meniscus cements would be expected. The bio-clasts in the reef sediments are not generally spherical in shape. McLaren (1993) noted that meniscus cements are abundant particularly in oolitic sediments, and so variations in the sediment texture may hamper meniscus cement development. McLaren (1993) also noted that with increasing cementation, the abundance of meniscus cements decreased. This is due to a loss in the visual appearance as they became masked by pore-filling cements, rather than a real absence. Therefore so the samples on Barbados may have had any meniscus cement development masked prior to Isotope Stage 5a (80ka) the earliest sediments studied.

McLaren (1993) noted a relationship between texture and meniscus cement development, with poorly sorted sediments and very fine sands having significantly less meniscus cement than well sorted coarse sands. The rock fabric on Barbados is very variable with only a single exposure (CQ) composed of well sorted sands. Therefore this would be the only exposure out of all the outcrops examined where meniscus cements would be expected. The absence of meniscus cements within CQ may be due to later phases of cementation obscuring evidence for earlier cement generations as this outcrop is of Isotope Stage 11 age whereas the best development of meniscus cements is noted in samples of Holocene age by McLaren (1993).

James (1972) and Harrison (1974) did note the presence of meniscus cements on Barbados. However these were found within calcrites formed by processes that are not examined in this study of early vadose diagenesis. No other workers have recorded the presence of meniscus cements on Barbados. Therefore Steinen’s (1974) conclusion that samples collected from Christ Church had been subjected to solely phreatic conditions on the basis that no meniscus or gravitational cementation fabrics are found is now believed to be unsound.
6.5 Rim cement

Two types of rim cement are found on Barbados. The first type is a syntaxial rim cement that is precipitated in optical continuity with the crystals of the host grain (see Plate 6.6). The second type of rim cement surrounds bio-clasts and lines the pores of corals either in the form of rhombic blocks or scalenohedral spar (i.e. dog tooth crystals, see Plate 6.7).

Syntaxial overgrowths are not common within the samples collected from Barbados and are limited to echinoderm plates. Echinoderm fragments though scarce are noted within 27 exposures of which only 11 display syntaxial cements. Of the 27 exposures, the presence of syntaxial overgrowths has been recorded in Table 6.2.

Table 6.2: The occurrence of syntaxial cements around echinoderm plates

<table>
<thead>
<tr>
<th>Exposure</th>
<th>Age</th>
<th>Region</th>
<th>Reef tract position</th>
<th>Syntaxial overgrowths</th>
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<tr>
<td>MCR2</td>
<td>5a</td>
<td>Christ Church</td>
<td>Fore reef</td>
<td>Not present</td>
</tr>
<tr>
<td>CH</td>
<td>5a</td>
<td>West Coast</td>
<td>Reef crest</td>
<td>Not present</td>
</tr>
<tr>
<td>INCH</td>
<td>5c</td>
<td>Christ Church</td>
<td>Reef crest</td>
<td>Not present</td>
</tr>
<tr>
<td>SP1</td>
<td>5c</td>
<td>Christ Church</td>
<td>Reef / crest</td>
<td>Not present</td>
</tr>
<tr>
<td>CMO</td>
<td>5e</td>
<td>Christ Church</td>
<td>Reef crest</td>
<td>Not present</td>
</tr>
<tr>
<td>RVH</td>
<td>5e</td>
<td>Christ Church</td>
<td>Reef crest</td>
<td>Not present</td>
</tr>
<tr>
<td>E1</td>
<td>7</td>
<td>West Coast</td>
<td>Rubble</td>
<td>Not present</td>
</tr>
<tr>
<td>EJ</td>
<td>7</td>
<td>West Coast</td>
<td>Sands</td>
<td>Not present</td>
</tr>
<tr>
<td>CAR</td>
<td>7</td>
<td>Saint George’s Valley</td>
<td>Rubble</td>
<td>Present</td>
</tr>
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<td>LEH</td>
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<td>Saint George’s Valley</td>
<td>Coral head zone</td>
<td>Present</td>
</tr>
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<td>9</td>
<td>West Coast</td>
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<td>Rubble</td>
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<td>9</td>
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<td>Present</td>
</tr>
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<td>15</td>
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<td>Coral head zone</td>
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Plate 6.6: Syntaxial cement around an echinoderm plate (EDG1.2).

Plate 6.7: Rim cement development around encrusting algae (EDG1.7).
Of the exposures containing echinoderms, those of Isotope Stage 5e age and younger have no syntaxial overgrowths at all. Echinoderm plates with no syntaxial overgrowths are also found in all of the older age groups that were studied. Echinoderm plates from these exposures are all surrounded by bio-micrite, which appears to inhibit the growth of syntaxial cements.

Syntaxial cements are only found around echinoderm plates that are not surrounded by micrite. The cement crystal size is a function of the size of the surrounding pore space and so varies in size but reaches up to 600μm (EDG 1.2) (see Plate 6.6). Due to the very small number of echinoderm plates within the reef sediments syntaxial cements comprise a negligible amount of the bulk rock volume and for point counting purposes they have been grouped with other rim cements.

The study of any regional and temporal patterns of syntaxial cement precipitation is seriously limited by the infrequent distribution of the echinoderm plates. There does however, appear to be a direct relationship between the position in the reef tract of an exposure and the presence of syntaxial cements. Most of the exposures within the coral head zone contain syntaxial overgrowths, whereas echinoderm plates in the reef crest and fore reef have no overgrowths. The distribution of syntaxial cement appears to have a negative relationship to the distribution of bio-micrite, which is more prevalent in the reef crest and in the fore reef zone, and less prevalent in the coral head zone and in the sands.

McLaren (1991) found that syntaxial rim cements may be used as a characteristic feature of the vadose zone where suitable substrates are present. However, on Barbados syntaxial cement is not a common feature. The as samples contain bio-micrite in the pore spaces and this appears to act as an inhibitor to subsequent cement development and, within individual exposures, echinoderm fragments are found both with and without syntaxial overgrowths.

Rim cements that surround bio-clasts and line the pores of corals in the form of rhombic blocks or scalenohedral spar (dog tooth crystals) are more common, but still only make up 1% of the total bulk rock in reef associated sediments of Isotope Stage 5a age. No
notable regional variations are found and the distribution is reduced to 0.1 – 0.5% in older packstone, wackestone and grainstone samples.

The shape and distribution of the pores appear to be important to rim cement development, as can been demonstrated in the exposure MCR2 from Christ Church. The packstone reef associated sediments are composed of broken shell fragments and red algae (MCR2) and contain on average 0.8% rim cement, whereas the well sorted rounded back reef sands (MCR2) contain 4%. The coral samples from this location also contain varying amounts of rim cement with on average, the dense coral A. cervicornis containing 0.3%, A. palmata with 1.1% and the more porous M. annularis and Diploria sp. corals with 2.6%. A pattern of increased rim cement development in the corals M. annularis and Diploria sp. is reflected in other samples collected from Barbados as these corals have a large number of rounded pores. This appears to be the ideal shape for rim cement development. Rim cements are not mineralogically selective as they can be found surrounding both aragonite, calcite and quartz fragments and can also be precipitated on micritic envelopes and where bio-micrite does not entirely occlude the pore space.

In reef associated sediments from Isotope Stage 5c and older, rim cements comprise only 0.1 - 0.5% of the total bulk rock volume. However, in sandy units, the proportion of rim cement can be much higher, such as in SP3 (Isotope Stage 5c) and CQ (Isotope Stage 11) where the average proportion of rim cement reaches 3.1% and 6% of the total bulk rock volume respectively. Where rim cement development has preceded aragonite dissolution, rim cements remain, therefore low-Mg calcite rim cements do not appear to be prone to dissolution. Rim cements are not readily identifiable in older reef associated (non-sandy) sediments, due to subsequent sparitisation or pore-filling cements obscuring them, rather than a real decrease in abundance.

McLaren (1993) found that the number of generations of rim cement identified in aeolianites varied between one to three and the potential number of generations is limited by pore space. However, on Barbados, only a single, fine, rim cement layer in the order of 10-50\(\mu\)m is noted around clasts. In coral pores rim cements are mostly very fine and often cloudy in appearance, this is termed an incipient spar by Pittman (1974).
Rim cements are found mainly in primary pores but in samples from Isotope Stages 13 and 15, rim cement development has occurred in a limited number of secondary moldic pores following the dissolution or partial dissolution of a bio-clast (see Plate 6.8).

Rim cements have been frequently cited in the literature on vadose cemented deposits from a wide range of environments in addition to the subtropical climate found on Barbados. These include arid (Schlesinger, 1985); semi-arid (Yaalon, 1967); Mediterranean (Friedman, 1964; Georgiev, 1984) and temperate (Knox, 1977). The rim cements in this study are believed to be of vadose origin, as suturing of the void centres identified by Videtich & Matthews (1980) on Barbados, which would be indicative of precipitation in solution filled pores, are absent. As rim cement precipitation is not limited to the vadose zone, care needs to be taken in the use of rim cements in identifying the environment of precipitation. As rim cements are also precipitated in the marine environment and are composed of aragonite/high-Mg calcite with a needle-like habit, geochemical analyses and a knowledge of crystal morphology are needed to aid in the differentiation between the vadose and other rim cements.
Plate 6.8: Secondary rim cement development (BESS 1.9).
6.6 Primary Pore-filling Cement

Pore-filling cement has been shown to be a typical vadose cement (McLaren, 1993) and is common enough to be described as a characteristic feature of the vadose zone. However primary pore-filling cements are very variable in their distribution on Barbados. Temporal trends can be noted as well as variations related to the rock fabric. Primary pore-filling cement is not a major constituent in many of the exposures on Barbados due to the large volumes of bio-micrite having been precipitated and occluding most primary pores prior to subaerial exposure. However, the identification of primary pore-filling cement is limited to sediments that have not undergone dissolution of bio-clasts prior to cementation, unless micritic envelopes have preserved the original clast outlines. Therefore with increasing diagenetic alteration the correct identification of primary pore-filling cement becomes more difficult.

The fore reef and reef crest sediments of Isotope Stage 5a age (~80ka) are clast-supported (bio-clasts generally comprise in excess of 65% of the total bulk rock volume), with most of the primary pores being preserved and there is generally only minor, patchy pore-filling cement development. The amount of pore-filling cement in Christ Church is very limited, but varies with changes in the fabric. For example, the rounded back reef sands at MCR2 contain 3.5% (of the total bulk rock volume) pore-filling cement, whereas in the reef associated sediments only one (MCR 2.8) out of the five samples point counted contained any pore-filling cement at all. Primary pore-filling cement is also generally absent in the coral heads regardless of species, as the main phase of cementation occurs during/after recrystallisation. In the West Coast there is a small increase in the amount of pore-filling cement in CH, but it is still patchy in distribution and comprises less than 3% of the total bulk rock volume. There are no notable differences in the amount of pore-filling cement in either the corals or the reef associated sediments.

The main development of primary pore-filling cement can be seen in Isotope Stages 7 and 9. However, if these cements are precipitated in pores initially filled with micrite then they are the result of aggrading neomorphism or replacement cementation and are not a true primary pore-filling cements; even though they are located in pores that
appear to be primary in origin. The lack of primary pore-filling cements in reef associated sediments over Isotope Stage 9 (except the sands located in CQ of Isotope Stage 11 age) is due to the poor preservation of the original fabric. Secondary cementation becomes the dominant process. As most pore spaces are filled with bio-micrite, cementation may have been inhibited or masked.

The pore-filling cement crystals are generally equant in shape (see Plate 6.9). However, no increase in crystal size was noted between the rim and pore-filling cement generations, but frequently smaller pores contain more pore-filling cement than coarser grained pores. An increase in the crystal size towards the centre of a pore is not noted on Barbados, despite being cited in the literature as common in the vadose zone (Purdy, 1968; Schroeder, 1973; Tucker, 1991).

The percentage of occluded primary pores in reef associated sediments is high due to the abundance of bio-micrite. The primary pore-filling cement in this study had similar features to those noted by Steinen (1982) working on Barbados, with irregular or curved intercrystalline boundaries, an irregular crystal size distribution, a patchy development of coarse mosaic and the presence of skeletal grains floating in spar. SEM studies also indicate that the microspar is actually a cement precipitate rather than the result of aggrading neomorphism, with no evidence of an original crystal with growth bands.
Plate 6.9: Equant pore-filling cement in SP2.6 seen under the SEM
6.7 Needle fibre cement

Needle fibre cements are not a volumetrically important cement within the samples analysed from Barbados and constitute less than 1% of the total bulk rock volume in the samples in which they are found. The distribution of these randomly orientated needle fibre cements is very sporadic with individual crystals varying from a few scattered needles to more dense needle mats composed entirely of low-Mg calcite (see Plates 6.10 and 6.11). The needles vary in both size and shape with the length of the crystals appearing to be constrained by the size of the pore space. The needle fibre cements reach up to 200μm in length, with typical needles lengths of 100μm and widths ranging from 1-4μm. Straight, ropy and bladed needles are all present and identifiable under the SEM (see Plates 6.12 – 6.15).

The patches of needle fibre cement in the form of a few scattered needles are generally found in primary pores, whereas the dense needle fibre mats are generally brown in colour and found in secondary solution pores, indicating a vadose origin. Steinen (1974) reported similar needle fibre cements precipitated exclusively in the vadose zone (Christ Church) in the vicinity of rhizoliths. However, James (1972) and Harrison (1977) identified only short acicular needles ranging in length from 9-30μm and 1-2μm in width within calcretes on Barbados. James (1972) suggested that these needle fibres are precipitated inorganically, resulting from the supersaturation of vadose waters near the subaerial exposure surface. In this study sampling avoiding any palaeosols, therefore the needle fibre cements were not associated with rhizoliths and so an organic origin is therefore unlikely.
Plate 6.10: Randomly orientated needle fibre cement viewed under cross polars (MCR 2.19).

Plate 6.11: Dense mat of randomly orientated needle fibre cement viewed under cross polars (CQ 3.18).
Plate 6.12: Randomly orientated needle fibre cement development (SP2.6) viewed under the SEM.

Plate 6.13: Bladed needle fibre cement development viewed under the SEM.
Plate 6.14: Randomly orientated 'ropy' needle fibre cement development viewed under the SEM.
The distribution of needle fibre cements varies with age on Barbados. All of the exposures of Isotope Stage 5a and 5c age, and all but OI and RH in Isotope Stage 5e, contain needle fibre cements. However, volumetrically, they make up less than 1% of the total bulk rock volume. RH is subjected to surficial weathering with needle fibre cements present in the unweathered RVH (from the same exposure). This may indicate that needle fibre cements have low formation and/or preservation potential with regard to weathering. The occurrence of needle fibre cements decreases with age with only the following exposures containing minor occurrences of needle fibre cements: OQ and WR (Isotope Stage 7), HQ, WIL and EN (Isotope Stage 9), CQ (Isotope Stage 11), CD (Isotope Stage 13) and APES (Isotope Stage 15).

On Barbados needle fibre cements are found at depths of up to 5m (within the APES exposure), but were found to be restricted to the top 2m in the south coast by Steinen (1974) and only within the upper 50cm of the stratigraphic sequence within aeolianites (McLaren, 1993). There is no regional trend to the distribution of needle fibre cement on Barbados, but the decreasing abundance of needle fibre cements with age corresponds to the findings of Knox (1977) and Calvet & Julia (1983) that recent needle fibre cement is prone to early diagenetic neomorphism and therefore the preservation potential is low.

### 6.8 Secondary cement

Secondary cement on Barbados has developed in one of two ways. Firstly it may infill moulds created by the dissolution of bio-clasts or micrite (see Plate 6.15). Secondly, it occurs as an *in situ* replacement of finely crystalline carbonate mosaics by coarser, neomorphic spar where sometimes relics of the former allochem can be detected by the process of calcitisation (see Plates 6.16 and 6.17). The amount of secondary cement varied markedly between the outcrops on Barbados but with a general trend of an increase with age (see Figures 6.1-6.9) the average variation among exposures and their standard deviations are given in Appendix 3.
Figure 6.1: Mean secondary cementation in A. palmata corals

Figure 6.2: Mean secondary cementation in A. cervicornis corals

Figure 6.3: Mean secondary cementation in M. annularis corals

Figure 6.4: Mean secondary cementation in Diploria sp. corals

Secondary cementation in A. palmata corals

Secondary cementation in A. cervicornis corals

Secondary cementation in M. annularis corals

Secondary cementation in Diploria sp. corals

Legend:
- **Secondary spar**
- **Neomorphic spar**
- **Total secondary cement**
Figure 6.5: Mean secondary cementation in coral-head zone sediments

Figure 6.6: Mean secondary cementation in fore-reef sediments

Figure 6.7: Mean secondary cementation in reef-crest sediments

Figure 6.8: Mean secondary cementation in rubble sediments

Figure 6.9: Mean secondary cementation in sandy sediments
Plate 6.15: Infilling of secondary moldic pores with cement and sparitisation of the surrounding bio-micrite in DS 1.2

Plate 6.16: Neomorphic replacement of a shell fragment in ES 1.2 under plane polarised light

Plate 6.17: Neomorphic replacement of a shell fragment in ES 1.2 under crossed polars
There is very little secondary cementation within Isotope Stage 5a. However, within MCR2 cementation is more pronounced within the back reef sands at 4.1% on average compared to 1.1% in the reef-crest and fore-reef sediments. The back reef sands are situated at the top of the section, which refutes the idea of Longman (1980) that the upper vadose zone is solely a zone of dissolution. This is because the fabric of the sediment rather than position appears to be the overriding factor controlling cementation. Coral dissolution and subsequent cementation in secondary pores is limited in Isotope Stage 5a and is found in only half of the coral samples: on average, secondary cement constitutes less than 2% of the total bulk rock volume within coral heads.

In Isotope Stage 5e the amount of secondary cement is more variable than in Stage 5a, both within and amongst the outcrops. The unaltered coral samples show little increase in secondary cementation. However, in the weathered exposure RH the coral has been totally replaced with secondary cement. Within unweathered reef associated sediments secondary cementation is more pronounced; for example, in RVH secondary cementation varies from 0 to 11.6%. Secondary cementation has increased slightly from an average of 2% in Isotope Stage 5a to 6% by Isotope Stage 5e but so has the total porosity (to 9.6%). Increased secondary cementation in weathered exposures is again apparent when the high value of 13.4% for the weathered exposures of Isotope Stage 5c are brought into the discussion (all other values in the tables only relate to unweathered sites). The increase in both secondary porosity and secondary cementation which continues in Isotope Stages 7 and 9 indicates that in samples of these ages, dissolution is occurring concurrent to secondary cementation and the two processes are not separated by an hiatus. Variations are found among the fresh unaltered reef associated sediments, but these are due to local fabric differences rather than regional differences.

In Christ Church, the exposure OQ (Isotope Stage 7) is composed of fore reef, reef crest and rubble zone facies. There is some variation in the amount of cementation but point counting errors may explain the differences between the zones, rather than differences due to fabric. The fore reef sediments (OQ1) contain on average 15.7% replacement microspar (standard deviation 8.1), the reef crest (OQ2) contains 12% (standard deviation 3.3) and rubble samples (OQ3) contain 9.8% (standard deviation 8.2).
However, the standard deviations are such that actual variations between the zones are inconclusive, as the bio-micrite is undergoing sparitisation and so the actual proportion of microspar cement in relation to bio-micrite in the samples may in fact even be much higher than recorded by point counting techniques. In contrast to the reef associated sediments, the unaltered *M. annularis* and *Diploria sp.* corals in OQ1 do not contain any significant proportions of secondary cementation. The coral samples from the rubble zone (OQ3) all contain borings, mainly by burrowing bivalves, which would increase the potential for the through flow of water necessary for diagenetic processes to operate (Bathurst, 1975). However, only a single *A. palmata* coral sample from this exposure has undergone partial neomorphic replacement and that is located in the reef crest. The alteration front is noted within a single slide with replacement cements only identifiable under crossed polars, as the original coral structure has been preserved (see Plates 6.18 – 6.22).

On the West Coast, samples below the unconformity in EJ (Isotope Stage 7, see Appendix 1 for more details) are entirely composed of replacement microspar (4 – 10μm) and pseudospar (10 – 50μm) but samples above the unconformity contain both bio-clasts and quartz grains with minimal replacement cement which is, on average, 6.3%. This indicates that a former exposure surface has undergone very different processes and more rapid rates of diagenesis than the overlying sediment. It was also noted by Pingitore (1976) who suggested that alteration had proceeded the phreatic zone below the unconformity. The marked differences in the cementation within EJ, which occur over a height difference of 1.5m, highlights the need to identify and restrict sampling to samples that have only altered under vadose conditions. In the quarry WAR, both samples of *A. palmata* have been replaced with a fabric selective neomorphic spar. The reef associated sediments contain very variable amounts of secondary cement with values ranging from 0.8 - 20.4%, but with no trends noted with height. A similar picture is found within the only unweathered exposure of this age (CAR) in the Saint George’s Valley.
Plate 6.18: Unaltered A. palmata (OQ2.2) viewed under plane polarised light

Plate 6.19: Unaltered A. palmata (OQ2.2) viewed under crossed polars

(6.18)  (6.19)

Plate 6.20: Altered A. palmata (OQ2.2) viewed under plane polarised light

Plate 6.21: Altered A. palmata (OQ2.2) viewed under crossed polars

(6.20)  (6.21)
In the exposure WIL, from Christ Church (Isotope Stage 9), the *A. palmata* coral heads had not undergone any alteration; and very little dissolution or secondary cementation was noted in any of the reef associated sediments. However, on the West Coast, CNQ and EN2 are both of the same age but the nature of the type of secondary cementation varies markedly from WIL, as well as between each other: despite both exposures being located within the coral head zone. The *M. annularis* corals in CNQ have undergone dissolution and subsequent fabric selective pseudospar cementation, with none of the internal original coral structure preserved. Compare this to EN2 where the *M. annularis* corals have neomorphosed with all the internal coral structure preserved. The cement crystals are coarse and irregular in shape, reaching up to 200μm in diameter. Crystal shape appears to be controlled by the original coral structure. A sample of *Diploria sp.* coral was also collected that had only partially been replaced. In the fore-reef sediments there are also dramatic differences in the proportion of replacement cement. In CNQ replacement cements constituted on average 22.8% of the bulk rock volume with a standard deviation of 4.1%. However, in EN2 average replacement cements constitute 57.6% of the total bulk rock volume with a standard deviation of 20.5%. Increased replacement of both bio-clasts and the bio-micrite are noted in these samples.

Exposures from Isotope Stage 9 in Saint George’s Valley also display large variations between exposures in close proximity to each other. In the coral head zone sediments at LEQ and DS have on average 45% and 30.2% secondary cement respectively. This indicates that there are large variations between comparable exposures that have been exposed to similar environmental conditions. The secondary cement is both mixed with micrite in the matrix, and in the form of drusy replacement cements within moldic pores. The alteration of coral has only preserved rudimentary ghost fabrics of the original structure in LEQ and the neomorphic cements are not fabric selective in DS. In both cases the replacement cements do not exceed 100μm in size.

In exposures of Isotope Stage 11 and over there is a reduction but not a total occlusion of pores (with porosity values are in the region of 10%) and an increase in the amount of secondary cementation in the reef associated sediments. This is true of all the outcrops except CQ, which is composed of calcareous sand. Microspar is the dominant fabric replacement cement in all samples over Isotope Stage 5a in age and is intermingled with
micrite. However, in HQ, EDG, BE, CV and ES parts of the fabric are composed of pseudospar crystals and are next to patches cemented with the micrite/microspar cement (see Plate 6.22). In all other exposures larger replacement crystals are only precipitated in secondary moldic pores. Cements in moldic pores show a general trend of an increase in crystal size towards the centre of the pore, but are irregular in shape (see Plate 6.23) reaching up to 1mm in APES 1.2.

Altered corals have original coral features preserved in over 65% of the recrystallised corals in this study, but replacement can be with a fabric selective mosaic or with a non fabric selective mosaic. This was also noted on Barbados by Pingitore (1976). Where the coral is replaced with calcite with no intervening void phase, the neomorphic spar has a brownish colour. The crystal mosaic is composed of a mix of small and large calcite crystals with wavy, curved or straight intercrystalline boundaries. Steinen (1982) also found that the irregular crystal shapes are ultimately controlled by the coral structure. Hence, dense corals such as *A. palmata* have the potential for larger replacement cements than the more porous corals such as *M. annularis* and *Diploria sp.* In CV (Isotope Stage 13) the altered coral has been replaced with massive fabric selective cement crystals that reached up to 1mm in size.

Alteration need not be unidirectional. Retrogressive diagenesis may have affected the samples resulting in the loss of evidence of earlier formed vadose cements; perhaps by increased leaching at the rock/atmosphere interface. Studies of early vadose diagenesis must therefore take into account the effect of a weathering overprint before concluding that alteration has progressed in different diagenetic environments. This study has found little evidence of alteration in different diagenetic environments between freshly exposed sediments in the West Coast compared to sediments collected in Christ Church. However, samples analysed from the weathered exposures display the same characteristics that Matthews (1968) and Pingitore (1976) describe.
Plate 6.22: Irregular replacement of micrite with microspar and pseudospar crystals in HQ1.9

Plate 6.23: Secondary replacement cement crystal in APES 1.3
The importance of sampling away from surficial weathering is highlighted in the results from SH1, a weathered exposure, where the replaced coral is composed of a drusy calcite cement with no preservation of the original coral structure. However, in the fresh exposure SH2 from the same outcrop, exposed and sampled on the second field visit, the coral is replaced with neomorphic spar with the original coral structure preserved. The same pattern is also noted between weathered and freshly exposed sediments on the West Coast, in the exposure EN. The rapid 'case hardening' effect of surficial weathering is noted by Bathurst (1975) on New Providence Island where freshly exposed, poorly cemented sediments, would become lithified to a hard crust within one or two years.

6.9 Porosity Change

Within the corals and reef associated sediments on Barbados differing primary and secondary porosity values were recorded, related to the coral species, the position within the reef tract, as well as due to dissolution and secondary cementation with time. (see figures 6.10-6.18).

Porosity values within both the corals and the reef associated sediments on Barbados are low as most pores have been occluded with micritic mud prior to uplift out of the marine environment. Within both the *A. palmata* and the *A. cervicornis* corals primary porosity values decline over time and have been occluded after Isotope Stage 9. This pattern is also reflected within the *M. annularis* and *Diploria sp.* corals though the initial porosities are much higher. However, the pattern for secondary porosity development is more divergent between the massive and the more porous corals as the *A. palmata* and *A. cervicornis* corals show a trend of increasing porosity over time whereas the *M. annularis* and *Diploria sp.* corals have peak secondary porosities in Isotope Stages 7 and 9 after which they decline. Generally within all the corals the neomorphically replaced aragonite has higher porosities than the corals that have been replaced with a secondary drusy calcite.
Figure 6.10: Mean porosity change over time in A. palmata corals.

Figure 6.11: Mean porosity change over time in A. cervicornis corals.

Figure 6.12: Mean porosity change over time in M. annularis corals.

Figure 6.13: Mean porosity change over time in Diploria sp. corals.

N – neomorphic replacement
S – secondary spar replacement

A* – partially replaced coral
N – neomorphic replacement
S – secondary spar replacement
Figure 6.14: Mean porosity change over time in coral-head zone sediments

Figure 6.15: Mean porosity change over time in fore-reef sediments.

Figure 6.16: Mean porosity change over time in reef-crest sediments

Figure 6.17: Mean porosity change over time in rubble sediments

Figure 6.18: Mean porosity change over time in sandy sediments.

* - Christ Church
** - Saint George's Valley
Within the reef associated sediments there is very little primary porosity except in the sandy facies. Within the sandy facies primary pores are still evident in samples of Isotope Stage 11 in age (the oldest studied). Within all the non sandy facies there is very little difference in the secondary porosity amongst the samples. In general secondary porosity increased from Isotope Stage 5 to a peak within Isotope Stages 7 and 9, a pattern also shown in the coral samples. The total porosity is relatively constant over time regardless of position within the reef tract unlike the associated corals.

Primary pore spaces within corals are very rarely totally occluded by secondary pore-filling cements in samples of any age. However, in unaltered coral samples from Isotope Stage 5a there are marked differences in the porosity values between different coral species. In decreasing order Diploria sp. has a mean porosity value of 50.3% with a standard deviation 0.7% (MCR2) of the total bulk volume by point count, M. annularis 27.2% with a standard deviation of 10.7% (MCR2) when cut horizontal to the direction of growth (see Plate 6.24). A. palmata has 8.5% (MCR2) with a standard deviation of 1.7% (see Plate 6.25) and A. cervicornis at 8.1% with a standard deviation of 4.4%. No decrease in overall porosity is found in recrystallised corals. This is partly due to the formation of secondary pores as a result of dissolution and partly due to a lack of pore-filling cement. This concurs with the results of Harris & Matthews (1968) who calculated that the aragonite to calcite solution-reprecipitation mechanism on Barbados is operating at greater than 90% efficiency. This does little to alter the total porosity of the rock. However, Pingitore (1971) did find that though there is very little spar cement within unrecrystallised A. palmata pores, in altered samples spar cement averaged 10% of total rock volume.

Within the fore-reef and reef-crest sediments of Isotope Stage 5a age, primary porosity values on average are all low, at less than 5% with total porosity values less than 10%. The low porosity values are due to deposition of bio-micrite in the marine environment rather than due to diagenetic processes within these samples. However, within the back reef sands (MCR2) of this age, primary porosity values are higher on average at 10.8% corresponding to a reduced proportion of bio-micrite present (this was discussed in section 6.2).
Plate 6.24: Primary porosity in *M. annularis* coral.

Plate 6.25: Primary porosity in *A. palmata* coral.
Within all the reef associated sediments, porosity values were found to increase to Isotope Stage 7 though a difference was noted between the rubble zone sediments in Christ Church and Saint George’s Valley as rubble sediments from different outcrops do not have consistent fabrics. Coral-head zone sediments have porosity values that continue to increase to Isotope Stage 9, with porosity values in sandy facies being highest in sediments of Isotope Stage 11 age. These values do not correspond with the model proposed by Land et al., (1967) which found porosity values remain essentially constant at 20% on average during diagenetic alteration and the model proposed by Gavish & Friedman (1969) who proposed a consistent drop in average porosity values from 35% in Stage 1 to a total occlusion of pores by Isotope Stage 5e. In reef sediments older than Isotope Stage 7 (Isotope Stage 9 in coral-head sediments) primary porosity values fall due to cementation of the rock with essentially all pores remaining secondary in origin. The exception to this is within the sandy facies where both primary (average of 4.8%) and secondary pores (average 16.9%) remain.

6.10 Summary of the characteristic cement types

- The total degree of cementation within the carbonates on Barbados generally shows an increase with age, but there also exists a high degree of variability both within and between deposits.

- Gravity and meniscus cements types are not typically found in the reef sediments of Barbados.

- Rim cements are most common in sandy fabrics and reef associated sediments of Isotope Stage 5a age. Some pores may contain a thin rim cement whilst other pores may be devoid of rim cement and yet full of pore-filling cement.

- Syntaxial cements are uncommon and limited to a small number of echinoderm plates where there is no bio-micrite in the surrounding pores.
• In reef associated sediments total porosity values rise from Isotope Stage 5a to Isotope Stage 7 (Isotope Stage 9 in coral-head sediments and Isotope Stage 11 in sandy facies).

• In reef associated sediments secondary porosity values decrease after Isotope Stage 9, after which secondary cementation predominates over dissolution.

• Pore-filling cement mosaics are variable in distribution and are often patchy and related to the distribution of primary bio-micrite.

• Secondary cementation increases with age with older samples more lithified than younger samples.

• Microspar is the dominant cement type formed by the sparitisation of micrite.

• Aragonite bio-clasts are generally replaced with a drusy calcite mosaic especially in sediments of Isotope Stage 7 and over.

• Over 65% of recrystallised corals are replaced with a neomorphic cement with good preservation of the original coral structure.

• Within the corals and reef associated sediments on Barbados differing primary porosity values were recorded, related to the coral species, the position within the reef tract, as well as due to dissolution and secondary cementation with time.

• In decreasing order Diploria sp. has the highest porosity values, followed by M. annularis then A. palmata and A. cervicornis.

• No decrease in overall porosity is found in recrystallised corals, partly due to the formation of secondary pores as a result of dissolution and partly due to a lack of pore-filling cement.

• Within all the reef associated sediments, porosity values were found to increase from Isotope Stage 5a to Isotope Stage 7, (coral-head zone sediments rise to Isotope Stage 9 and sandy facies rise to Isotope Stage 11) after which porosity values fall due to cementation of the rock.
Chapter 7 – Progressive Diagenesis on Barbados

7.1 Progressive Vadose diagenesis

The aim of this section is to see if it is possible to identify a sequence of geochemical alteration and cementation with progressive diagenesis in the vadose zone. Current models of progressive diagenesis have been outlined in Chapter 2. In summary, two models consider alteration processes within corals (Gvirtzman & Friedman, 1977; Strasser et al., 1992, 1997), whilst other models of progressive carbonate diagenesis are restricted to aeolianites and calcareous sands (Gavish & Friedman, 1969; Reecckmann & Gill, 1981). The characteristic sequences in this thesis are termed ‘phases’ to distinguish them from the different ‘stages’ of the other models.

Due to the variations in porosity, alteration and cementation within the samples collected from Barbados, it has been necessary to construct several models of vadose diagenesis. The complexity of the diagenetic processes in relation to the fabric, as well as with age, makes the construction of a single model unfeasible. Therefore, coral samples have been separated from reef-associated sediments in the following discussion as they undergo diagenetic alteration at varying rates. Matthews (1968) has also noted that large corals were found to commonly remain as aragonite when the associated sediments (of the same age) recrystallise to calcite. This is because in the reef sediments, calcite nuclei are present from the beginning as sedimentary particles, and recrystallisation proceeds at a relatively rapid rate, whereas corals are aragonite with no calcite nuclei present.

7.2 Progressive alteration of coral

The alteration of A. palmata, A. cervicornis, M. annularis and Diploria sp. corals are outlined in the following figures.
Figure 7.1: Progressive alteration of A. palmata.

Figure 7.2: Progressive alteration of A. cervicornis.
Figure 7.3: Progressive alteration of *M. annularis*.

![Progressive alteration of *M. annularis*](image)

Figure 7.4: Progressive alteration of Diploria sp.

![Progressive alteration of Diploria sp.](image)
**Phase 1 – Isotope Stage 5**

In this study Phase 1 represented unaltered corals composed of aragonite with only minor incipient cementation in the pores. The porosity values of the corals was dependent upon the species and the presence of bio-micrite with *M. annularis* and *Diploria sp.* corals having relatively high porosity values in comparison to denser *A. palmata* and *A. cervicornis*. The bio-micrite in Phase 1 was unaltered and composed of high-Mg calcite.

It was not possible in this study to examine living corals and corals that have undergone alteration in the marine environment. However, Gvirtzman & Friedman (1977) produced a model showing how the emergent reefs, along the coast of the Red Sea in southern Sinai, have undergone progressive diagenesis. Changes in the mineral composition, fabric and porosity were traced for three families, Poritidae, Faviidae and Acroporidae, and the following 2 stages were noted that preceded Phase 1 of the Barbados model: Stage 1 - Living scleractinian coral. Stage 2 - Introduction of marine cements and decomposition of organic material in subm ergent reefs. Stage 3 of the Gvirtzman & Friedman (1977) model can be seen to be contemporaneous in part, to Phase 1 of this study with leaching of sclerodermites under subaerial conditions. Void filling and cement that may have formed at Stage 2 of the Gvirtzman & Friedman (1977) were removed and micritic envelopes and high-Mg calcite cements have altered to low-Mg calcite. However, the study by Strasser & Strohmenger (1997) also in southern Sinai found no aragonitic cements within sequences where bio-micrite was noted, which concurs with the results in this study.

**Phase 2 – Isotope Stages 7 and 9**

Phase 2 involved the alteration of high-Mg calcite to low-Mg calcite with no textural changes to the rock. Aragonite remained unaltered at this stage but secondary porosity values increased significantly in the more porous corals - *M. annularis* and *Diploria sp.* due to dissolution. Phase 2 generally involved corals of Isotope Stage 7 and 9 age. This stage was separated from the incipient cementation in the corals of Isotope Stage 5a age by time.
Phase 3 – Isotope Stages 9-13

Phase 3 involved the alteration of the coral from aragonite to low-Mg calcite. Within the corals on Barbados, this process occurred along four diagenetic pathways:

1. Dissolution occurred concurrent to reprecipitation and the coral was replaced with a fabric selective neomorphic spar with the original coral structure preserved (see Plates 7.1 and 7.2).

2. Dissolution occurred concurrent to reprecipitation and the coral was replaced with a non-fabric selective neomorphic spar with the original coral structure preserved (see Plates 7.3 and 7.4).

3. Dissolution preceded reprecipitation and a drusy calcite mosaic replaced the coral with no evidence of the original structure remaining (see Plates 7.5).

4. Dissolution proceeded to its entirety with no subsequent reprecipitation and vuggy pores remained in the rock (see Plate 7.6).
Plate 7.1: Fabric selective neomorphic replacement of A. palmata viewed under cross polars

Plate 7.2: Fabric selective neomorphic replacement of A. palmata viewed under plane polarised light
Plate 7.3: Non-fabric selective neomorphic replacement of Diploria sp. coral viewed under cross polars

Plate 7.4: Non-fabric selective neomorphic replacement of Diploria sp. viewed under plane polarised light
Plate 7.5: Secondary replacement of Diploria sp. viewed under crossed polars

Plate 7.7: Selective dissolution of A. cervicornis leaving vuggy porosity
The preservation of the original coral structure during alteration was found to be common on Barbados with over 65% of altered corals replaced with a neomorphic spar. This contrasted with the Gvirtzman & Friedman (1977) model, which found that in Stage 4 (precipitation of low-Mg calcite through meteoric fresh waters) all the corals were replaced with a low-Mg calcite drusy cement, precipitated on both sides of micritic envelopes. In the Sinai corals solution must have preceded reprecipitation, whereas on Barbados the solution-reprecipitation process was over 90% efficient (Harris & Matthews, 1968). Gvirtzman & Friedman (1977) also found that the total volume of calcite was considerably less than the original volume of aragonite with the porosity of altered faviids averaging 54%. However, a decrease in porosity following alteration within corals on Barbados indicates that calcite reprecipitation occurs adjacent to areas of dissolution with no transport away from the site, as is suggested by Gvirtzman & Friedman (1977). There are clear differences between this study and that of Gvirtzman & Friedman (1977) indicating that the model produced in Israel for diagenetic alteration within corals can not be applied on Barbados. Strasser & Strohmenger (1997), also working on corals in southern Sinai, identified a complex diagenetic history with the Isotope Stage 9 reef having been subjected to multiple sea level transgressions during Isotope Stages 7 and 5 (the oldest reef was only 30m above present sea level). Therefore the work of Strasser & Strohmenger (1997) indicates that alteration did not proceed exclusively in the vadose zone, as was the case on Barbados.

On Barbados the proportion of micrite was found to increase substantially during alteration in the *A. palmata*, *M. annularis* and *Diploria sp.* corals especially in those replaced with a drusy calcite cement. The fourth alteration pathway on Barbados was not recorded in the model as evidence was only noted in the field of large vuggy pore networks, where the coral has undergone dissolution without subsequent replacement. Vuggy pores were only noted in the fore-reef corresponding to the preferential dissolution of the *A. cervicornis* corals, generally in outcrops that had been exposed to the surface for some time (such near-surface exposures were generally avoided).

The timeframe for alteration on Barbados varies markedly between the coral species. Consequently Phase 3 could be broken down into the three subsets outlined below:
Phase 3.1 By Isotope Stage 7, *A. cervicornis* corals altered relatively quickly due to their relatively large surface areas. The lack of *A. cervicornis* corals in fore-reef outcrops of Isotope Stages 9, 11 and 15 age is the result of dissolution without replacement leaving only vuggy pores in the exposure.

Phase 3.2 By Isotope Stage 9, the massive corals *M. annularis* and *Diploria sp.* have undergone alteration (though a partially altered *Diploria sp.* coral was noted of this age)

Phase 3.3 By Isotope Stage 11, the dense coral *A. palmata* is replaced by neomorphic spar (though a partial aragonite mineralogy was noted from a sample of Isotope Stage 13 age).

**Summary**

- Phase 1 (Isotope Stages 5a to 7) represents unaltered corals composed of aragonite with only minor incipient cementation in the pores. The initial porosity values of the corals was dependent upon the species with *M. annularis* and *Diploria sp.* corals having relatively high porosity values in comparison to *A. palmata* and *A. cervicornis*. The reef system on Barbados has a high initial input of bio-micrite which is not noted in other models of progressive diagenesis and which reduces porosity values further.

- Phase 2 (Isotope Stages 7 to 9) involves the alteration of high-Mg calcite to low-Mg calcite with no textural changes to the rock.

- Phase 3 involved the alteration of the coral from aragonite to low-Mg calcite with 65% of altered corals replaced with a neomorphic spar. The timeframe for alteration varies markedly between the coral species: *A. cervicornis* has generally altered by Isotope Stage 7; this is followed by the stabilisation of *M. annularis* and *Diploria sp.* by Isotope Stage 9; and the final coral to be replaced by low-Mg calcite is *A. palmata* which typically occurs by Isotope Stage 11-13.
• Differences between this study and that of Gvirtzman & Friedman (1977) indicates that the model produced in Israel for diagenetic alteration within corals can not be applied on Barbados.

7.3 Progressive alteration of reef associated sediments

The correct identification of ‘phases’ of alteration is dependent on sediments of different ages being initially composed of similar sediments deposited in the marine environment. The coral terraces are well developed on Barbados with A. palmata corals noted in the reef crests of all the age groups studied. However, not every terrace had all the reef facies present (Mesolella et al., 1970). Therefore sediments of different ages are comparable but the identification of the position in the reef tract zonation is necessary to ensure that like sediments are compared.

The following five figures compare sediments of different ages that have come from similar positions in the reef tract in order that the trend with time could be evaluated.

Figure 7.5: Progressive alteration of reef-crest sediments.
Figure 7.6: Progressive alteration of fore-reef sediments

![Figure 7.6](image)

Figure 7.7: Progressive alteration of coral-head zone sediments.

![Figure 7.7](image)
Figure 7.8: Progressive alteration of rubble zone sediments.

Progressive alteration of rubble zone sediments

<table>
<thead>
<tr>
<th>Age (Isotope Stage)</th>
<th>5e</th>
<th>7 (a)</th>
<th>7 (b)</th>
<th>9</th>
<th>11</th>
<th>13</th>
</tr>
</thead>
<tbody>
<tr>
<td>Percentage of total bulk rock volume</td>
<td>0%</td>
<td>20%</td>
<td>40%</td>
<td>60%</td>
<td>80%</td>
<td>100%</td>
</tr>
</tbody>
</table>

- Secondary porosity
- Primary porosity
- Secondary cement
- Primary cement
- Micrite
- Micritised bio-clast
- High-Mg calcite bio-clast
- Aragonite bio-clast

Figure 7.9: Progressive alteration of sands.

Progressive alteration of sandy sediments

<table>
<thead>
<tr>
<th>Age (Isotope Stage)</th>
<th>5a - MCR2</th>
<th>5c - SP1</th>
<th>7 - DEP</th>
<th>7 - RAG</th>
<th>7 - EL</th>
<th>7 - EI</th>
<th>11 - CO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Percentage of total bulk rock volume</td>
<td>0%</td>
<td>20%</td>
<td>40%</td>
<td>60%</td>
<td>80%</td>
<td>100%</td>
<td></td>
</tr>
</tbody>
</table>

- Secondary porosity
- Primary porosity
- Secondary cement
- Primary cement
- Micrite
- Quartz
- Micritised bio-clast
- High-Mg calcite bio-clast
- Aragonite bio-clast
Phase 1 – Isotope Stage 5a

In this study Phase 1 reef rocks comprise sediments that have been exposed to vadose conditions for at least 80ka. Both aragonite and high-Mg calcite bio-clasts were abundant in all the reef-associated sediments with the exception of echinoderm fragments (which had undergone paramorphic replacement). Only a single unaltered echinoderm plate was noted within all the deposits, and that was within an exposure dated to Isotope Stage 5e. This plate was surrounded by high-Mg calcite bio-micrite, which made up over 70% of the total bulk rock volume by point count, and it is proposed that low porosity in conjunction with the large proportion of high-Mg calcite present in the matrix has retarded alteration in this case. However, other models of vadose diagenesis, including those proposed by Land et al. (1967), Gavish & Friedman (1969) and Reeckmann & Gill (1981), commence from an original, un lithified, sandy sediment in which the bio-clasts comprise high-Mg calcite and aragonite. Unconsolidated sediments were noted in the marine reef environment at the base of the core collected in Christ Church (Steinen & Matthews, 1973). These sediments showed few signs of marine cementation, but the reef-crest sediments did contain large proportions of bio-micrite in the pores. A lack of marine cement noted in this and in other studies on Barbados indicates that cementation in the outcrops studied in this research has proceeded in the vadose environment.

Preserved primary porosity values on Barbados within sediments of Isotope Stage 5a vary according to the position in the reef tract but are still much lower than the 35% proposed by Gavish & Friedman (1969) for Stage 1 sediments or the 20% porosity found by Land et al., (1967) in totally stabilised rocks. Porosity values are a function of the different types of deposits being studied. The highest porosity values were found in the sandy facies with 10.8% of the total bulk rock volume, with less than 5% noted in other reef-associated sediments. The primary porosity values have been affected to a large degree by the marine deposition of bio-micrite in pores prior to exposure to vadose conditions. Marine void fill has not been considered in other models of progressive diagenesis, which clearly do not represent the conditions or processes that operate on Barbados.
Once exposed to vadose conditions the first development of primary cementation began in the form of rim cements surrounding bio-clasts with only minor, microspar pore-filling cement development. Rim cements on Isotope Stage 5a age were chiefly limited to the sandy facies where there was little bio-micrite present and was only a minor process within other reef sediments, making up less than 1% of the total bulk rock volume. No meniscus cements were found at all in the samples examined from Barbados, despite both Gavish & Friedman (1969) and Reecckmann & Gill (1981) having proposed that by this stage both rim and meniscus cements would have been precipitated. The differences in the types of cement noted between the studies indicates that texture rather than age controls the pathways along which alteration proceeds. Models developed outside of Barbados have also stated that by this stage high-Mg calcite was lost from the system. Gavish & Friedman (1969) found that high Mg-calcite was lost within 7-10 ka in Israel, whereas Reecckmann & Gill (1981) found that high-Mg calcite persisted for 90 ka in Australia. These variations, combined with the results of this study, demonstrate the high degree of variability that exists between the models. This further questions their applicability outside of the areas for which they were developed.

**Phase 2 – Isotope Stage 5e - 7 (fore-reef, reef-crest and rubble) 9 (coral-head zone) and 11 (sands)**

The second phase of progressive alteration on Barbados saw a major phase of aragonite bio-clast dissolution. In all the reef zones, the proportion of aragonite bio-clasts fell sharply over a very short time frame with almost total dissolution occurring by Isotope Stage 7. This was accompanied by the paramorphic replacement of high-Mg calcite mineralogies and an increase in porosity. The replacement of aragonite bio-clasts was an important process in reef-crest and coral-head zone sediments of Isotope Stage 7 age but not within the fore reef, the rubble zone or the sandy facies. The exception to this was the total replacement of the sediments below an unconformity in the exposure EJ indicating possible alteration in the phreatic environment. However, in the overlying sediments, and within other sandy facies of this age replacement was only a minor process. The total replacement of the original bio-clasts and the rock matrix in exposure
EJ is not noted in other sites from the West Coast, hence this study believes the exposures sampled have been subjected to vadose conditions and not altered in the phreatic zone as suggested by Matthews (1968) and Pingitore (1976).

Other models of progressive diagenesis have the alteration of high-Mg calcite and aragonite into two stages separated by time, but this was not evident within any of the reef facies on Barbados. Gavish & Friedman (1969) and Reeckmann & Gill (1981) also suggest that porosity values decrease with time. However on Barbados, porosity values were found to increase from Isotope Stage 5a to Isotope Stage 7 (fore-reef, reef-crest and rubble), 9 (coral-head zone), and 11 (sands) indicating that dissolution and replacement were two phases operating over different timeframes (replacement discussed in Phase 3).

On Barbados rim and meniscus cements did not always occur before pore-filling cements, as some pores were totally occluded without any trace of rim cement. This suggests that rim and pore-filling cements may be contemporaneous rather than a completely separate second generation as suggested by Gavish and Friedman (1969) with different cement types developing in adjacent pores, supporting the work of McLaren (1993). Also the stabilisation of high-Mg calcite was not achieved prior to the onset of aragonite dissolution as proposed by Gavish & Friedman (1969). However, the total alteration of high-Mg calcite was achieved prior to the total stabilisation of aragonite (see Chapter 5).

**Phase 3 – Isotope Stages 9 - 13**

By Phase 3, reef-associated sediments of Isotope Stages 11 and 13 have lower porosity values and the infilling of secondary moulds with a drusy calcite mosaic was the dominant process. The exception to this was within the sandy facies where the sediments of Isotope Stage 11 age remain at Phase 2 development (without the biomicrite in the primary pores). By Phase 3 no unstable mineralologies in any of the reef-associated sediments persisted, with bio-clast replacement almost exclusively restricted to a drusy calcite mosaic. Unlike the coral samples neomorphic replacement cements were not common in any of the sediment facies, indicating that total aragonite
dissolution occurred prior to the secondary cementation phase. Despite the variations found within the initial sediments (from different parts of the reef tract) there was little variation amongst the sediments in the oldest age group studied. Though the Gavish & Friedman (1969) model proposed a comparatively rapid rate of alteration with total stabilisation attained within 125ka, the extended timeframe over which aragonitic mineralogies are retained on Barbados supports the work of Zhu et al. (1994) in Papua New Guinea, who found that aragonite was preserved for longer (up to 400ka) in areas that had been subjected to rapid tectonic uplift.

**Phase 4 – Isotope Stage 15**

In samples of Isotope Stage 15 age there was a decrease in secondary cement and an increase in micrite within the reef-crest, the fore-reef and the coral-head facies. The high micrite values indicate that both bio-clasts and cement crystals have undergone micritisation. There were still a number of mouldic pores evident within exposures from the oldest terraces sampled. It was concluded that the main phase of cement precipitation was completed by Isotope Stage 13 with little further reduction in the number of mouldic pores noted after this age. No other models of progressive diagenesis note micritisation occurring within mineralogically stabilised carbonate sediments, but there is an age difference between this project and other models, which have generally only examined sediments up to Isotope Stage 7 in age.

**Summary**

- Phase 1 (Isotope Stage 5a) both aragonite and high-Mg calcite bio-clasts were abundant in all the reef zones with the exception of echinoderm fragments (which had undergone paramorphic replacement).

- Phase 2 (Isotope Stages 5c to 7) was a phase of aragonite dissolution, paramorphic replacement of high-Mg calcite mineralogies and an increase in porosity.

- Phase 3 (Isotope Stages 11 and over) there was a reduction in porosity values and the precipitation of replacement drusy calcite cements.
• By Phase 4 (Isotope Stage 15) there was a decrease in secondary cement and an increase in micrite (retrogressive diagenesis).

7.4 Schemes of progressive alteration

A generalised scheme of progressive alteration with coral heads in the vadose zone on Barbados is given in Table 7.1 and in reef-associated sediments in Table 7.2.

Table 7.1: General trend showing alteration over time within corals

<table>
<thead>
<tr>
<th>Rock constituents</th>
<th>Age (Isotope Stage)</th>
<th>5a</th>
<th>5c</th>
<th>5e</th>
<th>7</th>
<th>9</th>
<th>11</th>
<th>13</th>
<th>15</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aragonite</td>
<td>Abundant</td>
<td>Abundant</td>
<td>Abundant</td>
<td>Abundant</td>
<td>Common</td>
<td>Negligible</td>
<td>Negligible</td>
<td>Absent</td>
<td></td>
</tr>
<tr>
<td>Primary cement</td>
<td>Negligible</td>
<td>Negligible</td>
<td>Negligible</td>
<td>Negligible</td>
<td>Absent</td>
<td>Absent</td>
<td>Absent</td>
<td>Absent</td>
<td></td>
</tr>
<tr>
<td>Secondary cement</td>
<td>Negligible</td>
<td>Negligible</td>
<td>Negligible</td>
<td>Common</td>
<td>Abundant</td>
<td>Abundant</td>
<td>Abundant</td>
<td>Absent</td>
<td></td>
</tr>
<tr>
<td>Primary porosity</td>
<td>Common</td>
<td>Common</td>
<td>Common</td>
<td>Common</td>
<td>Negligible</td>
<td>Absent</td>
<td>Absent</td>
<td>Absent</td>
<td></td>
</tr>
<tr>
<td>Secondary porosity</td>
<td>Negligible</td>
<td>Negligible</td>
<td>Negligible</td>
<td>Common</td>
<td>Common</td>
<td>Negligible</td>
<td>Negligible</td>
<td>Absent</td>
<td></td>
</tr>
<tr>
<td>Micrite</td>
<td>Negligible</td>
<td>Negligible</td>
<td>Negligible</td>
<td>Negligible</td>
<td>Common</td>
<td>Common</td>
<td>Abundant</td>
<td>Abundant</td>
<td></td>
</tr>
</tbody>
</table>

A relative scale is used for the porosity values between the coral species

Table 7.2: General trend showing alteration over time within reef-associated sediments

<table>
<thead>
<tr>
<th>Rock constituents</th>
<th>Age (Isotope Stage)</th>
<th>5a</th>
<th>5c</th>
<th>5e</th>
<th>7</th>
<th>9</th>
<th>11</th>
<th>13</th>
<th>15</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aragonite</td>
<td>Abundant</td>
<td>Common</td>
<td>Common</td>
<td>Negligible</td>
<td>Negligible</td>
<td>Absent</td>
<td>Absent</td>
<td>Absent</td>
<td>Absent</td>
</tr>
<tr>
<td>High-Mg calcite</td>
<td>Common</td>
<td>Common</td>
<td>Common</td>
<td>Negligible</td>
<td>Negligible</td>
<td>Absent</td>
<td>Absent</td>
<td>Absent</td>
<td>Absent</td>
</tr>
<tr>
<td>Primary cement</td>
<td>Negligible</td>
<td>Negligible</td>
<td>Negligible</td>
<td>Common</td>
<td>Negligible</td>
<td>Negligible</td>
<td>Negligible</td>
<td>Negligible</td>
<td></td>
</tr>
<tr>
<td>Secondary cement</td>
<td>Negligible</td>
<td>Negligible</td>
<td>Negligible</td>
<td>Common</td>
<td>Abundant</td>
<td>Abundant</td>
<td>Abundant</td>
<td>Abundant</td>
<td>Abundant</td>
</tr>
<tr>
<td>Primary porosity</td>
<td>Negligible</td>
<td>Negligible</td>
<td>Negligible</td>
<td>Absent</td>
<td>Absent</td>
<td>Absent</td>
<td>Absent</td>
<td>Absent</td>
<td>Absent</td>
</tr>
<tr>
<td>Secondary porosity</td>
<td>Negligible</td>
<td>Negligible</td>
<td>Negligible</td>
<td>Common</td>
<td>Common</td>
<td>Negligible</td>
<td>Negligible</td>
<td>Negligible</td>
<td>Negligible</td>
</tr>
<tr>
<td>Micrite</td>
<td>Abundant</td>
<td>Abundant</td>
<td>Abundant</td>
<td>Abundant</td>
<td>Abundant</td>
<td>Abundant</td>
<td>Abundant</td>
<td>Abundant</td>
<td>Abundant</td>
</tr>
</tbody>
</table>

>50% - Abundant
10-50% - Common
<10% - Negligible
0% - Absent

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The generalised schemes show that aragonite is progressively removed from the system over time, though this occurs at a much more rapid rate within reef-associated sediments when compared to corals. High-Mg calcite present in the reef-associated sediments also undergoes alteration at a rate comparable to aragonite. Primary porosity was found to decrease over time, due to cementation. Secondary pores and cements were uncommon within the youngest sediments studied, but rose in both the corals and the reef-associated sediments over time. Secondary pores reached a peak within Isotope Stages 7 and 9 after which the pores were infilled with secondary cement which increased in abundance over time. Micrite was abundant in all age groups within the reef-associated sediments due to deposition in the marine environment, micrite did undergo alteration and was replaced with cement over time but the abundance did not decrease as bioclasts underwent micritisation. Micrite was not common within unaltered corals but did not increase over time due to micritisation of the coral skeleton.

The scheme for alteration in coral heads has used a relative scale for porosity values due to the wide discrepancy between different species. For example Diploria sp. can exceed 50% of the total bulk rock volume by point count, whereas A. palmata corals have preserved primary porosity values in the order of 10%. Furthermore, in the scheme proposed for progressive alteration in reef-associated sediments sandy facies have been excluded. This is because the rate, type and nature of the alteration products were not consistent with the other reef sediments due to differences in the fabric. It is interesting to note that previous models of vadose diagenesis are based on progressive alteration of calcareous sands when this facies was found to exhibit the highest degree of variability on Barbados, with local scale processes and fabric differences largely masking trends related to time or a longer timeframe is required for stabilisation to take place.

It has not been possible to combine the coral and the reef-associated sediments as alteration not only progresses at different rates (e.g. aragonite has been lost to a large extent from reef-associated sediments by Isotope Stage 5e, but corals have generally not altered prior to Isotope Stage 9) but also different diagenetic pathways are followed. In coral heads the solution-reprecipitation process is efficient with over 65% of the corals replaced with neomorphic spar, whereas in reef-associated sediments over 99% of the
Bio-clasts are replaced with a drusy calcite mosaic with neomorphic spar restricted to selected large shell fragments which are generally over 1 cm in size.

A direct comparison of the results obtained in this study with previous models of vadose diagenesis has been hampered due to different carbonate facies being studied. The only model to examine alteration in coral heads (Gvirtzman & Friedman, 1977) only examined sediments up to Isotope Stage 7 in age (at which age all the corals were stabilised to a low-Mg calcite drusy cement). The Gvirtzman & Friedman (1977) model was also not directly comparable to this study as the exposed sediments were not restricted to the vadose zone with resubmergence noted and hence different cement types found. In the two models for which a timeframe was proposed (Gavish & Friedman, 1969 and Reckermann & Gill, 1981) stabilisation was found to occur over very different timescales (125 ka and 900 ka respectively). However, both timeframes were based on relative ages rather than on absolute dating techniques, which were employed in this study.

Diagenetic complexity exists within the reef sediments on Barbados with different cements found within adjacent pores and differences due to variations in the skeletal microstructures. This project has demonstrated that stabilisation of reef sediments is as much a function of the fabric as well as time, and supports the findings of Gardner & McLaren (1993) that models of progressive vadose diagenesis cannot be applied outside areas in which they were developed.
Chapter 8 — Conclusions

A number of uplifted coral reef tracts corresponding to interglacial high sea level conditions were studied on the island of Barbados. The outcrops ranged in age from Isotope Stage 5a to 15. Laboratory analyses allowed the diagenetic histories of the reef carbonates to be studied in relation to age and position within the reef zone.

8.1 Geochemical alteration of the reef sediments

Models of progressive diagenesis have highlighted the importance of Mg and Sr concentrations as indicators of diagenetic alteration. However, the geochemical variations within the sediments on Barbados have indicated that the rate of diagenetic alteration varies within, as well as between, bio-clasts. The analyses of Mn and Fe concentrations have been used to determine that the reef sediments on Barbados underwent alteration in the vadose zone.

Within biogenic fragments initially composed of high-Mg calcite, unaltered encrusting algae and red algae are found to Isotope Stage 9, unaltered bio-micrite is also found in samples of Isotope Stage 9 age but this is very variable. However, alteration of echinoderm plates appears to occur prior to Isotope Stage 5a. Many of the mineralogically stabilised coralline algae and echinoderm fragments appeared unaltered under the microscope, this paramorphic replacement supports the findings of Friedman (1964) who found that the identification of mineralogies only possible through the use of geochemical techniques. The proportion of Mg within coral samples was found to be very variable and did not follow a distinctive pattern of change over time or a trend related to the coral species. Higher Mg concentrations were found to be related to the presence of bio-micrite in the coral pores, with unaltered bio-micrite (containing high levels of Mg) found in samples up to Isotope Stage 9. The removal of high-Mg calcite from the system was not just dependent on the bio-clast structure but also on the composition of the sediment. Alteration was found to proceed at a faster rate where
isolated high-Mg calcite biogenic fragments were located in a porous rock. However, stabilisation had occurred in all samples by Isotope Stage 11.

The rate of alteration within aragonite bio-clasts was found to vary between different coral species with *A. palmata* preserved the longest (Isotope Stage 13) followed by *Diploria sp.* (Isotope Stage 9) and then *M. annularis* (Isotope Stage 7). This sequence is due to differences in the porosity values within the coral structures. The distribution of Sr within corals also varies with species. Higher Sr values are found in unaltered samples of *A. palmata* than in samples on *M. annularis*. Sr appears to be rapidly lost from the aragonite skeleton during inversion to low-Mg calcite as Sr values were only found to decline after Isotope Stage 7 during alteration, with no further loss from replaced corals after Isotope Stage 11. Corals were found to remain unaltered over a longer timeframe in comparison to aragonitic shell fragments. Therefore the stabilisation of aragonite cannot be viewed as a single step or confined to one period of time. Contrary to the ideas of Matthews (1968) and Pingitore (1976) no regional trend in the rate of alteration was found, with evidence of unstable mineralogies persisting for equal periods of time among exposures on the West Coast, Christ Church and Saint George’s Valley. Only weathered exposures were noted to undergo alteration at more accelerated rates regardless of location.

Evidence of mineralogical stabilisation of high-Mg calcite was found at a younger age within aragonitic corals but was contemporaneous to aragonite dissolution in reef associated sediments. Therefore, the total stabilisation of high-Mg calcite does not occur prior to the alteration of aragonite as indicated by other models of progressive diagenesis (Gavish & Friedman, 1969; Reeckmann & Gill, 1981).

### 8.2 Characteristic vadose cement types

This project is the first to examine progressive alteration in relatively well dated sediments up to Isotope Stage 15 in age. A detailed analysis of over 750 thin sections have found that the patterns of cementation vary in different parts of the reef tract and it was necessary to evaluate each coral species and their reef associated sediments
separately. The sediments were categorised according to their position within the reef tract, thereby reflecting their sedimentary characteristics. Most accounts of vadose diagenesis have forwarded the notion that cement types are a function of the diagenetic environment in which the cements are formed. Cements seen as diagnostic of alteration in the vadose zone include gravity, meniscus rim and needle-fibre cements, with secondary replacement seen as a minor process. However, McLaren (1993) demonstrated that although many of these cement types are characteristic none are unique. This study has highlighted that most previous studies have concentrated on calcarenites and the models produced are clearly inappropriate for reef deposits, particularly where there is an abundance of bio-micrite. To date this is the first attempt to model the effects of vadose diagenesis in reefs that have not been resubmerged by higher sea levels.

Gravity and meniscus cements have not been studied in reef deposits and so contrary to traditional ideas of these cement types being typical of the vadose diagenetic zone, they were not found within sediments located on Barbados. A lack of gravity cements supported the findings of McLaren (1991) who concluded that “Such a widespread absence of gravity cements in vadose cemented deposits must seriously question the idea of gravity cements being described as a typical vadose cement.” (p468). Meniscus cements were also only noted in the literature on sandy fabrics, therefore the rock fabric rather than the diagenetic environment may have been the overriding factor controlling the type of cement precipitated.

Rim cements were found on Barbados, but were not found to be volumetrically important, generally accounting for less than 1% of the total bulk rock volume by point count. Rim cements were most common in sandy fabrics and reef associated sediments of Isotope Stage 5a age. Two types of vadose rim cement were noted, syntactical cements (restricted in their distribution to the surface of a number of echinoderm plates, where there was no bio-micrite present) and a rhombic or scalanoheletal spar surrounding bioclasts. These types of rim cement can be seen as indicative of cementation in the vadose environment, with sutured, isopachous rim cementation (noted in other studies on Barbados, in phreatically altered sediments) not being found. However, some pores contained a thin rim cement whilst other pores were devoid of rim cement and yet were
full of pore-filling cement. This is in direct comparison to the work of Land et al. (1967) and Friedman (1964) who both suggest that first generation rim and meniscus cements were followed by secondary generation pore-filling cements.

Pore-filling cements have not been discussed in detail in studies of vadose diagenesis, as they were not generally seen as a characteristic cement type prior to the study by McLaren (1993). On Barbados primary pore-filling cement mosaics are variable in distribution and are often patchy and related to the distribution of primary bio-micrite. However, secondary pore-filling cementation was found to be volumetrically very important with the total degree of cementation showing an increase with age; but, nonetheless, there also exists a high degree of variability both within and between deposits.

Secondary cementation was found to increase with age on Barbados with older samples being more lithified than younger samples. The replacement of high-Mg calcite fabrics, aragonitic bio-clasts and corals also occurred in the vadose zone within the Pleistocene timeframe represented on Barbados. Fabric cements, which have replaced bio-micrite, in sediments of Isotope Stage 9 and over were predominantly composed of microspar. This is a consequence of sparitisation. Conversely red algae and encrusting algae were increasingly replaced with micrite, through the process of micritisation. Aragonite bio-clasts in the reef associated sediments undergo dissolution in sediments of Isotope Stage 5e and over, and were generally replaced with a drusy calcite mosaic. However, over 65% of recrystallised corals were replaced with a neomorphic spar in which the original coral structure was well preserved.

The pattern of cementation on Barbados refutes the views of Longman (1980) and Land et al. (1967) that the upper vadose zone is mostly a zone of dissolution. This research has shown that extensive alteration and cementation may occur within the vadose environment and pore-filling cements are common enough to be described as a characteristic feature of the vadose zone (see Table 2.2).
8.3 Progressive vadose diagenesis on Barbados

Despite the internal variability that exists within and between corals and reef sediments on Barbados, it was possible to develop two generalised schemes of progressive vadose diagenesis. However, the progressive vadose diagenesis ‘stages’ could not be resolved within previous models of diagenesis. Limitations arose as only two models (Gvirtzman & Friedman, 1977; Strasser et al. 1992, 1997) have considered alteration processes within coral heads. Strasser et al. (1992, 1997) have demonstrated that the Gvirtzman & Friedman (1977) model of coral diagenesis in the vadose zone is inappropriate as the reefs were exposed to marine conditions after their initial exposure to subaerial conditions. Other models of progressive carbonate diagenesis are restricted to aeolianites and calcareous sands (Gavish & Friedman, 1969; Reeckmann & Gill, 1981). These models indicate that the progressive stages are mutually exclusive with very little overlap between the stages. However, a comparison of these models using data from the coral reef terraces on Barbados suggests that the sequences comprising early progressive diagenesis are far more complex and clearly the alteration of calcareous sands and coral reef deposits vary considerably.

Within corals, three stages of alteration were noted following uplift into the vadose zone, though the rate of alteration varies between each species:

Phase 1 represents unaltered corals composed of aragonite, of Isotope Stages 5a-5e age, with only minor incipient cementation in the pores. The porosity values of the corals are dependent upon the species with *M. annularis* and *Diploria sp.* corals having relatively high porosity values in comparison to *A. palmata* and *A. cervicornis*.

Phase 2 involves the alteration of high-Mg calcite bio-micrite within the coral pores to low-Mg calcite with no textural changes to the rock within Isotope Stages 7 and 9. Aragonite remains unaltered but secondary porosity values increase within *M. annularis* and *Diploria sp.* corals due to dissolution.

Phase 3 involves the alteration of the coral from aragonite to low-Mg calcite. Within the corals on Barbados, dissolution either occurred concurrent or prior to reprecipitation.
resulting in neomorphic or drusy replacement cements. This is in contrast to Gvirtzman & Friedman (1977) who found that all the corals were replaced with a low-Mg calcite drusy cement. The timeframe for alteration varied markedly between the coral species with unaltered aragonite mineralogies persisting to Isotope Stage 13 for *A. palmata*, whereas *A. cervicornis* samples and *M. annularis* samples did not persist beyond Isotope Stage 7, and Diploria sp. corals beyond Isotope Stage 9.

In comparison to coral samples the alteration of reef associated sediments varied as outlined below:

Phase 1 (Isotope Stage 5a) sediments contained abundant aragonite and high-Mg calcite bio-clasts, with the exception of echinoderm fragments, which had undergone paramorphic replacement. Initial porosity values varied according to the position in the reef tract; with porosity values ranging from 14% in the sandy facies, 13% in the fore reef (of which only 4% were primary), to 6% in the reef crest sediments. Primary cementation in the form of rim cements and minor, microspar pore-filling cement was also noted by this stage. However, rim cements were best developed in the sandy facies where there was little bio-micrite present.

Phase 2 (Isotope Stages 5c to 7) was a phase of aragonite dissolution, paramorphic replacement of high-Mg calcite mineralogies and an increase in porosity. Porosity values were found to increase from Isotope Stage 5a to Isotope Stages 7 and 9 indicating that dissolution and replacement were two phases operating over different timeframes. Unlike the reef associated sediments there was no evidence of sandy facies that have progressed beyond Stage 2. These findings differ from previous models of vadose diagenesis where high-Mg calcite undergoes alteration prior to aragonite stabilisation with no overlap between the stages.

Phase 3 (Isotope Stage 11 and over in reef associated sediments, but not in the sandy fabrics) there was a reduction in porosity values with the precipitation of replacement drusy calcite cements. By this stage no unstable mineralogies persist, and unlike corals, replacement was almost exclusively restricted to a drusy calcite mosaic. Despite the
variations in fabric found within the initial sediments there was little variation in texture between the reef associated sediments of Isotope Stage 15 age.

By Phase 4 (Isotope Stage 15) there was a decrease in secondary cement and an increase in micrite. It was believed that the micritisation was due to regressive diagenesis. The increase in micrite within sediments of Isotope Stage 15 was also noted within the coral samples. Despite the variations found within the initial sediments there was little variation between the reef associated sediments of Isotope Stage 15 age.

8.4 Concluding statement

There is no single all-encompassing model for vadose diagenesis is applicable to Barbados or anywhere else in the world. This is because variations in the textural fabric of the rock and its position within the reef tract have resulted in different rates of alteration. Clearly, distinct changes have occurred within the timeframe represented on Barbados. These changes have not been simple, and have proceeded at different rates in different settings, with many differences due to the variable nature of the deposit. The high degree of internal variability within sediments on Barbados has important implications with regard to the application of models of diagenesis. Clearly the different scales of variability (mega-, meso- and micro-scale) identified by Gardner & McLaren (1994) shows that it is difficult to identify any single variable as being the most dominant control in vadose diagenesis. Rather, a range of variables must be considered. This project has aimed to minimise the effect of many potential controls such as sea spray, plants and the groundwater table and it is a combination of the effects of time, sedimentology and reef fabric which helps to explain the diagenetic variability found in Barbadian reef rocks. The consequences of this study are that it is not appropriate to apply current models of diagenetic alteration outside of the areas in which they are developed until all factors that affect the type and rate of alteration products can be quantified. The results of this project can now be applied to uplifted coral reefs in the Pacific where purposive sampling can minimise the number of variables under consideration allowing the first directly comparable study to be established.
8.5 Suggestion for further research

- A study of the processes that occur prior to Isotope Stage 5a is required, especially within Holocene and modern day sediments.

- A refinement in dating procedures would give a more accurate chronology and a better understanding of the diagenetic history of the sediments.

- A better understanding of the diagenetic fabrics that develop related to surficial weathering and the depth to which the weathering front penetrates into sediments is needed.

- Further research into the role of bio-micrite on vadose diagenesis is required in other regions.

- Further research is needed to clarify the differences between vadose and phreatic cements.

- Further research into the geochemical alteration of the calcite lattice is required especially with respect to magnesium.

- This study has limited the number of processes investigated to fabric and time, however differences related to other environmental conditions needs to be assessed.

- This study has highlighted the variability in vadose diagenesis between different fabrics therefore a more systematic study in other geographical regions is required.

- The effects of uplift and changing environmental conditions requires study before alteration can be definitively assigned to a timeframe.
Appendix 1 – Field Descriptions

West Coast

Trents I (EG)
West Coast - Trents Road
Sheet 5 Grid ref. E2164 N7631
Land height 0 - 10m above sea level
Exposure - Road cut
Length of section - 120m
Age - Isotope stage 5a
Corresponds to Mesolella’s sample EG
Samples collected – 8

This is the youngest terrace along Trents Road and is a part of Worthing terrace
This is not a fresh face and there is evidence for wash making it difficult to distinguish
between the coral and the matrix
There is little vegetation at the base of the exposure but trees overlie it
This is a reef crest exposure and a previous worker has taken a core through an A. palmata head
Most of the coral heads are of A. cervicornis, which makes up most of the exposure and
also of Porites, there are also a small number of small heads of M. annularis and Diploria sp.
The terrace is 1.80 m tall but as it varies along the exposure between where the rock is
quite crumby and a site where the rock is hard
Two vertical transects of four samples each were taken 16m apart and at 40cm intervals
from the base
The first transect was 86m inland of the terrace edge and was within a crumby matrix
The second transect was 70m inland of the terrace edge and was within a well cemented matrix

EG Transect one
The samples are all weathered and the surface is stained green and brown, the fabric
cement is dusty and crumby in parts, but generally well cemented. The grains are
discernible from the fabric.
EG 1.3 contains finger coral branches (A. cervicornis?), the fabric cement is as the other
samples.

EG Transect two
The samples are all weathered and the surface is stained green/black, the fabric cement
is crumby in parts but generally well cemented, with no loose clay-sized particles.
There is evidence of roots and soil staining on the sample and the grains are discernible
from the fabric.
EG 2.2 and 2.3 also have some black mottling.
Coach House (CH)  
West Coast  
Sheet 5 Grid ref. E2151 N7364  
Land height 0 - 10m above sea level  
Exposure - Building site  
Length of section - 20m  
Age - Isotope stage 5a  
Corresponds to Mesolella’s sample  
Samples collected – 20

This is a very fresh site cut down into the rock in order to lay foundations for a house.  
The east-facing wall was overlain by a very thin patchy soil, which supported some small grasses.  
The height of this exposure was 1.20m and is within the reef crest as *A. palmata* was present in its life position.  
The rock was very poorly cemented; thus the samples had a tendency to break up when they were removed.  
Five samples were collected along a vertical transect at 20cm intervals from the base.  
A further 15 samples were collected at 1m intervals, along a horizontal transect, of the same face, on a second visit a year later. No further work had been carried out on the site between visits and so there was more evidence of surface wash.  
The cement was very friable on both visits.

CH Transect one  
All the samples are very crumbly and very dusty. The samples crumble easily to dust and incorporate a few, very small, discernable shell fragments.  
CH 1.5 is composed of a cross section through an *A. cervicornis* head, surrounded by fabric cement; this is dusty like the other samples from this site.

CH Transect two  
CH 2.1 + 2.3 + 2.12 + 2.14 + 2.15 are composed of cross sections through *A. cervicornis* coral branches, the coral from 2.1 contains borings and the fabric cement surrounding all the corals are very crumbly.  
CH 2.5 + 2.9 + 2.10 + 2.11 are composed of a *Sideristrea sp*. CH 2.5 has no dissolution of the polyp holes and the fabric cement is very crumbly. CH 2.9 + 2.10 and 2.11 have some dissolution of the polyp holes with dusty cement in the pores.  
CH 2.13 is composed of *A. palmata*, there is some slight iron staining, the coral surface is very dusty and there was dusty cement in the pores.  
CH 2.2 + 2.6 + 2.7 are composed of fabric cement and contain a few larger fragments and are generally better cemented than the other samples from CH transect one.  
CH 2.8 is very crumbly and very dusty, like the other samples from transect one.
This is a long variable road cut which has a maximum height of 8m
This is not a fresh face but grades from a fore reef, where A. cervicornis dominates the outcrop (to the west) to a reef crest exposure where A. palmata dominates (to the east).
Sampling was in the reef crest exposure with three cores removed from A. palmata heads by previous workers.
There are overlying trees but there is very little soil development and both the base and face of the exposure are free from vegetation.
The exposure is 5m high at the sampling point and 10 samples were collected at 20cm intervals from the base.
The rock was very well cemented making sampling difficult.
The samples are very weathered with the exposed surface having a green/black crust.
The samples are very well cemented with no loose clay-sized particles. There is solution on the cut face and a bit of iron staining. Rock allochems are difficult to distinguish but there are small colour variations with some patches a cream colour and some patches darker.
EH 1.3 is composed of A. palmata with a boring, the sample has undergone some solution and is weathered.

This is a weathered exposure of back reef sands and no coral heads were noted.
The four samples were collected at random from this 2m high exposure.
This west facing exposure is overlain by quite dense vegetation.
The samples were well cemented.
The samples are slightly weathered and very well cemented, with no chalky patches, which can be crumbled. The samples do contain loose clay-sized particles making the surface dusty and allochems difficult to identify.
Hope (HOPE)
West Coast
Sheet 1 Grid ref. E2496 N9057
Land height 20 - 30m above sea level
Exposure - Road cut
Length of section - 10m
Age - Isotope stage 5e
Samples collected – 4

This is a small, disjointed section cut within the rubble zone
This is a fairly fresh section, which has been physically weathered by the action of plant roots
This Southeast facing section is overlain by shrubs and is 1.5m high
The samples were collected at random from this chalky, very friable section which has thin bands of calcrete running through it
The cement fabric is slightly weathered and yellow coloured. The samples are covered in clay-sized particles and are very crumbly. The rock samples are light but not porous and no allochems can be seen on the sample surfaces.

Heywoods Estate (HEY)
West Coast
Sheet 3 Grid ref. E2119 N8381
Land height 20 - 30m above sea level
Exposure – Cliff face
Length of section - 20m
Age - Isotope stage 5e
Samples collected – 5

The face of this exposure is quite weathered, with small jagged peaks, like exposures that are currently affected by seaspray
This is a west-facing cut, which is overlain by trees, and there are trees at the bottom of the slope
The exposure is within the coral head zone, with massive heads of M. annularis present
Samples were collected along a horizontal section at heights of 1m, 1.5m, 0m, 1m, 1m respectively (bottom of the rock exposure is at a height of 5m above the road)
The exposure is very indurated making sampling difficult
These samples are weathered with a brown/green surface crust. There is evidence of soil and roots within the samples with the allochem grains not easily discernible. The rocks are very well cemented with evidence of some solution.
HEY 1.1 is composed of M. annularis and though the surface is stained brown there is no dissolution of the septa and no loose clay-sized particles present.
HEY 1.3 is composed of A. palmata. the surface of which is weathered brown.
This is a recently disused quarry with a maximum height of 12m.
The north facing 5m high face was studied, as the exposure was fresher.
The exposure had a sandy matrix and was a part of the back reef facies.
There is no overlying vegetation or soil.
The exposure varied with height, as it was a darker orange colour at the base up to a height of 1.5m, this colour lightened from 1.5 - 5m in height. The texture of the cement matrix also changed as the bottom facies had a rounded matrix whereas the top facies looks like mini tubes 1-2mm in length; a calcrite layer separated these two facies.
This possibly represents a back reef sand which emerged from the sea forming a calcrite band with a period of resubmergence and more sand deposition, re-emergence led to the formation of a patchy calcrite formation on the top.
Four samples were collected below the height of the calcrite layer, two were collected within the very indurated calcrite layer, a further four samples were collected above the calcrite layer.
WAR 1.1 is a bright orange cemented sand. The sample is very porous and crumbles in parts. The grains are well sorted and there is no dust in the pores.
WAR 1.2 is a dull white cemented sand. The sample is very porous with a slightly glassy appearance in between some grains. The grains are well sorted and there is no dust in the pores.
WAR 1.3 + 1.4 + 1.5 + 1.11 +1.12 are composed of an orange cemented sand similar to 1.1 with white glassy inclusions. The sand has pores and can be crumbled to a small degree, but the glassy patches are dense with no pore spaces. 1.11 contains a lot of red algae.
WAR 1.6 has a very heavy, dense, white fabric. It is glassy like the inclusions in WAR 1.3 and 1.4, without the cemented sand. It is smooth and very hard with a tendency to shatter when struck forcibly, whereas the other samples break up.
WAR 1.8 is glassy like 1.7 but with a slight yellow colouration. Unlike 1.7 the sand-sized grains can be distinguished from the cement.
WAR 1.9 + 1.10 are entirely composed of red algae and the cemented grains do not have a glassy appearance. The rocks are porous and can be crumbled to a small degree.
WAR 1.13 + 1.14 are composed of coral fragments possibly *A. cervicornis*. There is evidence for solution but not on the cut face and the coral is well cemented to the fabric. The coral is glassy in appearance and dense.
Trents III (EI)
West Coast - Trents Road
Sheet 5 Grid ref. E2217 N7651
Land height 50 - 60m above sea level
Exposure - Road cut
Length of section - 150m
Age - Isotope stage 7
Corresponds to Mesolella’s sample EI
Samples collected - 5

This is a north facing exposure where a fresh face has been exposed as a result of physical weathering by plant roots. There is a thin soil and trees overlying this 1m high exposure and the effects of vegetation are high as there is evidence of roots within the exposure that have penetrated the rock. This is a fine sand, exposure with no notable coral heads. The samples were chalky and very friable. The samples were collected at 20cm intervals from a vertical section. The rock fabric is differentially cemented with the hammered out samples breaking up into smaller, well-cemented fragments. These samples have been freshly exposed to the surface, as a result of the exposure face fracturing, probably due to plant root activity. The samples have a very large proportion of clay-sized particles and no distinguishable shell fragments. EI 1.1 is particularly well cemented and has evidence of weathering, with one face having a brown and green crust. There is evidence of roots but is otherwise similar to the other samples collected from this site.

Trents IV (EJ)
West Coast - Trents Road
Sheet 5 Grid ref. E2218 N7665
Land height 70 -80m above sea level
Exposure - Road cut
Length of section - 200m
Age - Isotope stage 7
Corresponds to Mesolella’s sample EJ
Samples collected - 15

There is a change in bedding at this site as a rubble layer is been unconformably overlain by sands at a height of 1m. of this 1.5m high exposure. This is not a fresh face and there is evidence of surface wash. This exposure is overlain with vegetation. There is a thin palaeosol along the unconformity, which is very red in colour. The rubble layer is not as well cemented as the sand layer. 6 number of samples were collected at random within the sandy layer and 9 number of samples were collected within the rubble layer. There are two very different fabrics as one set of samples were collected below an unconformity and the others above.
Samples 1.1 – 1.6 are composed of well-cemented sand sized grains that have an orange colour and no clay-sized particles. Samples 1.7 – 1.15 are composed of well-cemented allochems, but the surface features of this rubble are not distinguishable, as the rock has undergone weathering with the exposed surface having a green/brown crust.

Trents V, Blowers Quarry, (EN)  
West Coast - Trents Road  
(I) Sheet 5 Grid ref. E2347 N7723  
(II) Sheet 5 Grid ref. E2346 N7715  
Land height 120m above sea level  
Exposure - Road cut  
Length of section - 150m  
Age - Isotope stage 9  
Corresponds to Mesolella’s sample EN  
Samples collected – 20

Site I is a fresh face cut into the corners of a minor crossroads. There are some grasses above the exposure but the effects of vegetation on the exposure are very low. There was evidence of soil wash on parts of the exposure but these were avoided when sampling. The south face of the exposure was sampled where the height was 280cm; eight samples were collected at 25cm intervals from the base. As the face was fresh the rock was quite crumbly and the samples were quite easy to remove.

A previous worker has taken a core within a *M. annularis* head, from an older face along the same exposure, on the north face. The rock face was very uneven due to the cutting back of the face making the identification of corals difficult.

In a second phase of sampling a year later this site had been extended into a quarry. A fresh 4m high, east facing quarry face was sampled which had no overlying soil or vegetation. The quarry is extracting marls for house foundations. Sampling proceeded above, below and within coral heads. The rock samples were very friable with heads of *M. annularis*, *S. Sideristrea* and *Diploria sp.* noted, some of which were altered.

EN Transect one  
There is some slight weathering of the rocks and the outer surface has been stained a pale green and orange. The samples have a mottled surface and are slightly dusty. It is possible to crumble the edges of the rock, but otherwise the samples are quite well cemented.

EN 1.2 – 1.6 are less well cemented than the other samples and are easily broken up. sample 1.6 is almost totally dust. There is evidence for plant roots in these samples.
EN 1.7 is composed of the coral *M. annularis*. There has been some minor dissolution of a few of the septa, the rest are intact. There has been some mineralisation and also a chalky patch on the coral.

EN Transect two

These are fresh samples containing some large well-cemented grains. There are some loose clay-sized particles and chalky patches, but there are still a lot of open pores. EN 2.2 contains some broken *Diploria sp.*, but not on the cut face. The sample is heavier and denser than the other samples from this site. EN 2.7 + 2.12 are less well cemented and are easily broken up. EN 2.9 contains some darker, very hard, smooth bands. There is also a mineralised fragment of *Diploria sp.*. There are few loose clay-sized particles present in this sample. EN 2.2 + 2.10 are composed of *Diploria sp.*. The samples are slightly mineralised in parts and chalky in others. There is a bit of iron staining. EN 2.5 + 2.8 are composed of *M. annularis*. Sample 2.8 is mineralised with a glassy appearance in parts with chalky patches. The samples are well cemented to the surrounding fabric. Sample 2.5 is not as glassy in appearance and there is some dissolution of the septa. There are loose clay-sized particles present on the surface and in many of the pores.

Carlton Quarry (CNQ)

West Coast
Sheet 3 Grid ref. E2229 N7973
Land height 80 - 90m above sea level
Exposure - Quarry
Length of section - 15m
Age - Isotope stage 9
Corresponds to Mesolella’s sample DP
Samples collected – 10

This is a disused quarry but the exposure studied was still fresh. The rock was rubbley in nature, and overlain by small grasses and shrubs. This west facing section is 6m high. There were corals present but they were not very clear or numerous. Samples were collected at random. The samples have an orange hue and are very well cemented. The colour is slightly mottled and a few shell fragments can be seen. There is evidence for dissolution and there are few loose clay-sized particles. CNQ 1.9 + 1.10 are composed of the coral *M. annularis*. There is no dissolution of the septa pores and though the coral is intact it is chalky in places with lots of loose clay-sized particles.
Black Bess Quarry (BESS)
West Coast
(I) Sheet 3 Grid ref. E2304 N8193
(II) Sheet 3 Grid ref. E2318 N8221
Land height 120-150m above sea level
Exposure - Quarry
Length of section - 400m
Age - Isotope stage 13
Corresponds to Mesoella’s sample BB
Samples collected – 35

This 15m high, quarry is cut into the Second High Cliff on the West Coast
The matrix cements at this site are very dusty and chalky, and the rock is used to make
graded sands and gravels
The exposure is coraliferous with massive coral heads of *M. annularis* seen at the top of
the section, coral heads are present lower down in the section but are difficult to discern
and are altered
18 samples were collected from site I, which is a Northwest facing exposure
17 samples were collected from site II, which is a South facing section

BESS Transect one
The samples are composed of lots of well-cemented fragments. The shell fragments are
easily distinguished despite the surface being covered in loose clay-sized particles. The
samples are white but well cemented and not all chalky.
BESS 1.6 the whole sample is chalky and easily broken up to dust.
BESS 1.2 + 1.3 are composed of an altered head of *Diploria* sp. The coral is chalky in
part and mineralised in part, but the original structure is preserved. The samples are
covered in loose clay-sized particles, but most of the septa are not filled with sediment.
BESS 1.11 is composed of mineralised *M. annularis*. There are chalky patches in the
coral and there are lots of loose clay-sized particles. Some of the coral septa have altered
without any dissolution.

BESS Transect two
These samples are hard and dense and not as dusty as the samples from transect one.
The samples are very slightly weathered and have a grey hue and a mottled colouration.
There is evidence for dissolution of some large shell fragments and also solution. There
are crumbly patches within the samples that seem to be associated on many occasions
with bryozoa.
BESS 1.14 is composed of a mineralised head of *M. annularis*. All the septa have
altered without prior dissolution. The sample is light with only a few tiny chalky
patches.
BESS 1.21 is composed of fragments of *P. porites* and large cemented grains. The
sample has a pink hue and there is evidence of solution and dissolution.
This is the very easily identifiable Second High Cliff, which is a large exposure with a maximum height in excess of 8m.

The effects of vegetation are very pronounced at this site with grasses growing at the base of the exposure and trees growing on the top. There are also vines growing on the surface on the exposure itself.

The exposure face is not very fresh but despite the vegetation, the degree of weathering is less than for the last site.

The face is very irregular along its length with an unconformity noted at a height of 130cm above the base.

The unconformity appears as a 7cm layer of pebbles above which, is another coral layer *M. annularis* is present but is not believed to be in life position as it is broken up.

It is not possible to determine the nature of the rock in the higher portions of the exposure, but in the lower portion it is almost entirely constructed of coral and is very well cemented. Above the unconformity the rock was even more cemented making sampling very difficult.

The south face of the outcrop was sampled; nine samples were collected at 25cm intervals with sample five from within the unconformity and samples 6 and 7 immediately above the unconformity with no gap between the two.

ER 1.1 + 1.2 are composed of a totally mineralised, dense head of *M. annularis*. There has been some moderate weathering of the exposed surface but the coral structure is intact. There is evidence for some dissolution on the exposed face of the coral. There is a small patch, in the middle of the coral, where the septa are chalky with secondary pores, the rest is intact.

ER 1.3 has a dense weathered fabric. There is evidence for dissolution, associated with white chalky patches, these patches are surrounded by a more opaque fabric and grey shell fragments.

ER 1.5 is composed of altered, mineralised *M. annularis*. There is more weathering of the septa, most of which are gone or partially gone. Those partially remaining have been stained by iron and can by crumbled.

ER 1.8 is composed of altered *M. annularis*. The sample does not look glassy and the septa are whiter than the surrounding fabric is. There is evidence of solution of the coral surface. Large pebble clasts have been cemented to the coral surface, within an orange porous fabric.

ER 1.11-1.16 are composed of cemented pebbles, the pebbles are very rounded and poorly sorted. The samples are very well cemented, even though some of the cement has been dissolved out, especially from sample 1.5.

ER 1.17-1.18 are very weathered with evidence for iron staining, solution and dissolution. There are still cemented pebbles within the fabric but it is far sandier.
Apes Quarry (APES)
West Coast
Sheet 3 Grid ref. E2582 N7928
Land height 270m above sea level
Exposure - Quarry
Length of section - 50m
Age - Isotope stage 15
Corresponds to Mesolella’s sample AMA
Samples collected – 32

This is the oldest quarry on the West Coast
The fresh exposure is 15m high, and overlain by some grasses, but the effects of soil wash doesn’t come down as far as the sampling zone
The Southwest-facing slope of this active quarry was sampled
The rock from this quarry is used to make graded sands and gravel
Numerous heads of *M. annularis*, which had undergone some degree of alteration, were noted, as this site is within the coral head zone
The samples had uneven differential cementation
Samples were collected at a height of 1m along a horizontal transect
The samples are fresh and very well cemented. The rough surface has small chalky patches that can be crumbled to a small extent. The colour is pure on the cut face of sample 1.1, the rest are mottled and other than a small amount of dissolution it is difficult to make out any allochems. There are loose clay-sized particles present.
APES 1.2 + 1.29 are composed of *Diploria sp* coral. Sample 1.2 is more chalky and contains a patch of bryozoa, but both of the samples are altered. The samples are mineralised and glassy but the coral structure is very well preserved.
APES 1.17 + 1.18 + 1.19 + 1.22 are composed of the coral *M. annularis*. The corals are mineralised with evidence of borings. Most of the pores created from the dissolution of the septa remain open and only a few have been infilled and are chalky. Some of the septa have been preserved and altered without prior dissolution.

Trents VII (ES)
West Coast - Trents Road
Sheet 5 Grid ref. E2438 N7764
Land height 180 - 200m above sea level
Exposure - Road cut
Length of section - 270m
Age - Isotope stage 13
Corresponds to Mesolella’s sample ES
Samples collected – 9

This is the oldest terrace sampled along this transect
The exposure face is variable along its length and to the west of the sampling site the exposure is more weathered, with coral heads dissolved out of the exposure and not replaced.
The exposure had a 4m maximum height, but sampling took place on the north face of this road cut where the exposure height was 3m, as the effects of surface weathering were less pronounced and the exposure face was quite smooth. Nine samples were taken at 30cm vertical intervals from the base. There were patchy grasses growing at the base of the exposure and grasses and shrubs overlie it. There are a large number *M. annularis* heads present in this reef crest exposure and the rock is very well cemented making the samples difficult to collect. A previous worker has taken a *M. annularis* head a core from this site though a *M. annularis* head. These samples are very heavily weathered but the cut face is white. The samples are dense and very well cemented. The samples are glassy in appearance, in parts, with no chalky patches. There is evidence for the dissolution of some of the small shell fragments and soil and roots on the exposed face. ES 1.2 contains a large mineralised shell and the cut face has a yellow hue. ES 1.5 has a brown stained dissolution feature that can be crumbled.

**Christ Church**

Maxwell Coast Road I (MCR I)
Christchurch
Sheet 11 Grid ref. E2977 N6249
Land height 0 - 10m above sea level
Exposure - Building Site
Length of section - 20m
Age - Isotope stage 5a
Samples collected – 16

This is the youngest face sampled in the Christchurch area and belongs to the Worthing terrace. This is a fresh exposure on a building site where the rock has been cut down to lay foundations for a house. The exposure is overlain by a very thin palaeosol (less than 10cm) but no surface vegetation. The exposure is 180cm high and is situated within the reef crest with the lower 1m dominated by *A. cervicornis* and the top 80cm dominated by *A. palmata* and *M. annularis*. Samples were collected from the East face along a vertical section. The samples are composed of a well-cemented fabric, containing numerous shell fragments, and clay sized particles. MCR 1.1-1.3 contain *P. porites* in a well-cemented rock fabric, grains are discernable but there is a bit of weathering giving part of the rock a slight brown stain. MCR 1.10-13 is composed of *A. palmata* with lots of borings. MCR 1.15 is composed of *A. cervicornis* in a crumbly, dusty fabric where grains can be discerned.
Maxwell Coast Road II (MCR II)
Christchurch
Sheet 11 Grid ref. E3025 N6258
Land height 0 - 10m above sea level
Exposure - Building Site
Length of section - 5m
Age - Isotope stage 5a
Samples collected - 22

This site is slightly more inland than Maxwell Coast Road I, but part of the same terrace.
This is also a fresh exposure on a building site where the rock has been cut down to lay foundations for a house.
At the base of the section there is a storm layer of broken *A. cervicornis* heads, which is overlain by *A. palmata*, with beachrock at the top of the section.
The exposure is overlain by a very thin soil, but no vegetation.
The groundwater table is approximately 1m below the height of the section, with my lowest sample collected at an approximate height of 3m above the groundwater table.
The rock fabric is well cemented, but very dusty. The shell fragments are easily discernable on the rough surface, but not on the cut face, where the surface is slightly mottled. Some samples are slightly easier to crumble than others are.
MCR 2.1 + 2.4 + 2.5 + 2.11 + 2.17 + 2.18 contains *A. cervicornis* branches with borings and covered in loose clay-sized particles. 2.18 had beach sediment cemented to the surface.
MCR 2.6 + 2.7 is composed of *Diploria sp.* with clay sized particles in the pores.
MCR 2.10 is composed of a branch of *P. porites* not cemented to any fabric.
MCR 2.13 is composed of *M. annularis*, there is little dissolution of the septa, the rock is very light, with a shell boring, and the septa pores do contain clay-sized particles.
MCR 2.14 and MCR 2.16 are composed of *A. palmata*. 2.14 is particularly dusty, whereas 2.16 has evidence of contact with soil.
MCR 2.8 is composed of very well cemented beach sediments, with a pink hue.
MCR 2.19 + 20 are composed of poorly cemented beach sediment, there are clean shell fragments, there are clay-sized particles present, but these do not obscure the grains.
MCR 2.21 + 22 are composed of well-cemented beach sediments, though the surface grains can be crumbled. There are lots of identifiable clean shell fragments.

Garrison Savannah (GAS)
Christchurch
Sheet 8 Grid ref. E2481 N6387
Land height - 10m above sea level
Exposure - Road works
Length of section - 5m
Age - Isotope stage 5a
Corresponds to Mesolella’s sample AGA
Samples collected – 6

This is a fresh pit cut down into the side of the road.
The Northeast-facing wall was overlain by a very thin patchy soil <50cm deep.
The pit exposure was 3m and is within a mixed coral head zone at the reef crest as *A. palmata* was present in its life position, with some *M. annularis*, *Diploria sp.* and *A. cervicornis* heads scattered in this shelly section. The rock was very poorly cemented. The colour of the face varied, darkening with depth in the pit. Six samples were collected randomly, within the white coloured rock at the top of the section. GAS 1.1 + 1.4 are composed of *A. palmata*, with dust on the surfaces, 1.3 has borings into the coral. GAS 1.2 is composed of *Diploria sp.* with a few borings into the surface; the pores are filled with dust. There are a few pink fragments and shells in the fabric cement on the surface. GAS 1.6 is composed of *P. porites* within a dusty fabric.

South Point II (SP II)
Christchurch
Sheet 11 Grid ref. E3354 N6033
Land height 0 - 10m above sea level
Exposure - Building site
Length of section - 20m
Age - Isotope stage 5a
Samples collected – 3

This is a fresh exposure from a building site. The samples were collected at random from a shallow north-facing pit, which had no overlying soil or vegetation. The rock was very poorly cemented; thus the samples had a tendency to break up when they were removed. All specimens are hard, dense and heavy. There is a slight black mottling, there are no loose clay-sized particles. There are not many fragments visible on the cut face, and there are some small secondary pores. SP 2.4 is a sample of *A. palmata*, there is some weathering on the surface and some loose clay-sized particles.

South Point I (SP I)
Christchurch
Sheet 11 Grid ref. E3320 N6045
Land height 10m above sea level
Exposure – cliff wall under a house
Length of section - 15m
Age - Isotope stage 5c
Corresponds to Mesolella’s sample AEG
Samples collected – 18
This is a weathered site where a wall has been cut in the past
Soil or vegetation did not overlie the north-facing wall
The height of this exposure was approximately 4m and is comprised of a *A. cervicornis*
layer which is overlain by *A. palmata*
Nine samples were collected within the *A. cervicornis* layer and nine samples were
collected within the *A. palmata* zone
The cement fabric has an orange/pink hue and is well cemented, there are a lot of loose
clay-sized particles, no allochems can be identified and the rock is slightly weathered.
SP 1.1 + 1.6 + 1.7 + 1.8 are composed of *A. cervicornis*.
SP 1.8 is weathered and not coated in clay-sized particles, the fabric is very well
cemented and there are soil and root veins within the sample.
SP 1.9 + 1.15 + 1.16 are composed of *A. palmata*, the surface of 1.9 is weathered and
coated in loose clay-sized particles. The rock has a pink hue and very well cemented.

South Point III (SP III)
Christchurch
Sheet 11 Grid ref. E3350 N6049
Land height 10m above sea level
Exposure – road cut
Length of section - 30m
Age - Isotope stage 5c
Samples collected – 14

This is a weathered Northwest facing road cut
Large shrubs overlay this exposure
The exposed face was 1m high and no coral species were noted in this sandy, bedded
deposit
The bottom of the deposit is calcretised and there was a lot of evidence of soil wash
The cement was friable in the samples that were collected at random within the
exposure
All the samples were collected above the height of the calcrete layer
The rock fabric has a grey-pink coloured fabric. The samples are weathered and there is
evidence of plant roots within the samples. The rocks are banded (some bands are grey
coloured) with no discernible shell fragments.
SP 3.1 –3.3 were collected from the same height and have an unconformably darker
pink area cemented to an orange coloured fabric, with a dark band between the two
areas. There are fragments in the rock and they seem to have a glassy appearance.

Inch Marlowe (INCH)
Christchurch
Sheet 11 Grid ref. E3379 N6060
Land height 10m above sea level
Exposure – cliff face
Length of section - 20m
Age - Isotope stage 5c
Corresponds to Mesolella's sample - AHD
Samples collected – 8

This is a weathered cliff face, which has been affected by solution processes, and the
surface of the rock face has been eroded into small jagged peaks indicating erosion by
sea spray
At the base of this site are grasses and trees but there is no overlying vegetation or soil
The height of this Southeast facing exposure was 3m
There are heads of A. palmata in the bottom 2m of the exposure but there are no corals
on the top
Samples were collected at random from the least weathered face
These samples have been weathered and the exposed outer surface has a black crust
about 1mm in depth. The samples are very well cemented and free from the dusty clay­
sized particles. The allochems are discernible but not very clear, the cut surface appears
to have a mottled colouring.
INCH 1.3 is composed of unaltered A. palmata, underneath the crust.

Club Morgan (CMO)
Christchurch
Sheet 8 Grid ref. E2685 N6443
Land height 40m above sea level
Exposure - building site
Length of section - 10m
Age - Isotope stage 5e
Corresponds to Mesolella’s sample ACH
Samples collected – 10

This is a small, fresh section cut into the First High Cliff to make the back wall of a
property
This north-facing site is located within the reef crest with abundant heads of A. palmata
present
The outcrop is 3m high and overlain with a very thin soil and a small amount of grasses
Ten samples were collected from this site following a single vertical transect. The
samples were collected in two sets of three with samples two and five collected within
coral heads with the other samples collected immediately below and above the respected
coral heads. Samples 1-3 were near the top of the section and samples 4-6 were in the
middle of the section
The samples are well cemented, but grains can be crumbled off the main body. There
are very large amounts of loose clay-sized particles, which makes the samples dusty and
any allochems difficult to distinguish. There has been a small amount of solution and
the cut face has some mottling.
CMO 1.1 + 1.2 + 1.4 + 1.8 are composed of fresh A. palmata covered in loose clay­
sized particles.
CMO 1.6 + 1.7 + 1.9 -1.10 are partially composed of fresh A. palmata.
Rendezvous Hill (RH)
Christchurch
Sheet 11 Grid ref. E2795 N6408
Land height 20 - 30m above sea level
Exposure - Road cut
Length of section - 100m
Age - Isotope stage 5e
Corresponds to Mesolella’s sample R
Samples collected – 10

This is a highly weathered exposure within the First High Cliff
This exposure graduates from a reef crest exposure in the North to a fore reef exposure in the South, and has a maximum height of 5+m
Small shrubs along the length of the exposure overlie the outcrop
Transect 1 is within the *A. palmata* zone (reef crest exposure) and five samples were collected at 40cm intervals from the base of the East face
The height of the exposure is 1.80m
Transect 2 is 25m to the south and is within the *A. cervicornis* zone (fore reef exposure) and five samples were collected at 40 cm intervals from the base
The height of the exposure at this point is 5+m

RH Transect one
The samples are weathered with evidence of surface wash and solution. The rocks are very well cemented with no loose clay-sized particles. The cut surface has mottling but no allochems are identifiable.
RH 1.2 + 1.3 is composed of weathered *A. palmata*, the surface of which is coated with a black crust.

RH transect two
The samples are weathered with evidence of surface wash and solution. The rocks are very well cemented with no loose clay-sized particles. The cut surface has mottling but no allochems are identifiable.
RH 2.1 is composed of weathered *A. cervicornis*, the surface is coated with a black crust, and there is evidence of solution and wash, with loss of some of the coral structure.

Rendezvous Hill (RVH)
Christchurch
Sheet 11 Grid ref. E2754 N6406
Land height 20m above sea level
Exposure - Quarried face
Length of section - 40m
Age - Isotope stage 5e
Near to Mesolella’s sample R
Samples collected – 22

This Northeast facing fresh section is cut into the front of the 1st High Cliff
This exposure is composed of *A. cervicornis* heads and towards the top of this 6m high section there are a few large heads of *M. annularis* within the *A. cervicornis* zone. *A. cervicornis* is very abundant in the exposure making up almost the whole of the outcrop with only a few scattered heads of *M. annularis*, thus this was determined to be a fore reef section.

The coral heads had a very fresh unaltered appearance with a chalky friable cement found between the coral heads. The coral abundance and cementation of the rock was fairly uniform along this section which was cut parallel to the reef formation.

Twenty samples were collected from this site at 2m intervals along the SE - NW face at a constant height of 1m. There was very little vegetational development at this site as above this section there is a second face which was not sampled as it has been weathered back from the new cut and is a further 6m above the height of the new face.

The rock fabric is well cemented but chalky and easily crumbled in places. There are abundant loose clay-sized particles, making the surfaces dusty and only some of the allochems can be identified.

RVH 1.1 + 1.5 + 1.6 + 1.8 + 1.14 + 1.15 + 1.16 + 1.17 + 1.18 are composed of fresh *A. cervicornis*.

RVH 1.19 + 1.22 are composed of fresh *Diploria sp.*

Oistins (01)
Christchurch
Sheet 11 Grid ref. E3127 N6243
Land height 0 - 10m above sea level
Exposure - Building site
Length of section - 25m
Age - Isotope stage 5e
Samples collected – 9

This exposure is believed to be at the base of the first high cliff. This site is behind a shopping centre and possibly cut for a building with the 2.10m high exposure overlain by a wall.

This is a fresh, reef crest exposure with some evidence of cement wash that was avoided when sampling.

The exposure contains *A. cervicornis* and *A. palmata* zone, this is also a particularly shelly deposit and believed to be a part of the rubble zone.

The Southwest facing section of the exposure was sampled.

The four samples were collected at 40cm intervals from the base.

On a second visit a year later, a further 5 samples were collected 15m northwards of the first site.

A thin soil and grasses overlay this section and there was some evidence for soil wash.

These were collected at 20cm intervals from 50cm to 100cm in height.
Of Transect one
The cement fabric is differentially cemented, with the rock samples all breaking up into smaller pieces. The allochems are covered in a large quantity of loose clay-sized particles.
Of 1.3 is composed of P. porites surrounded by a well-cemented fabric. One part of the rock has got a glassy appearance, parts of the rock are very well cemented other parts are chalky and crumble easily.
Of 1.4 is composed of Siderastrea sp. the coral is light and fresh with borings. The sample is not porous and there are no loose clay-sized particles.
Of 1.2 does have a few loose clay sized particles present, and the allochems on the cut surface have a dark band around them. There is evidence of some small-scale solution.

Of Transect two
The fabric is differentially cemented, with the rock breaking up into smaller very well cemented pieces. The allochems are covered in a large quantity of loose clay-sized particles. There is evidence of some minor weathering with the rock having a grey hue and the cut face having a slight mottled colour.
Of 2.1 + 2.3 is composed of a light chalky sample of broken A. palmata, but the structure is difficult to make out.

Ragged point (RAG)
Christchurch
Sheet 7 Grid ref. E4369 N7347
Land height 10 - 20m above sea level
Exposure – coastal cliff
Length of section - 10m
Age - Isotope stage 7
Corresponds to Mesolella’s sample ACH
Samples collected – 6

This is a north facing exposure of cemented quartz sands, which overlie marls and Tertiary bedrock.
There are no corals at this site.
The sands are well sorted and very well cemented making it difficult to collect samples.
The sands are not freshly exposed and so have undergone some minor surficial weathering.
This is a very well cemented rock composed of Tertiary sediments that have been cemented in the Quaternary. The rock is composed mainly of quartz and is orange coloured. There are no clay-sized particles present and the cemented grains are very easily distinguished from the rock matrix. The grains are well sorted with the average size smaller for sample 1.1 than the other samples.
Deebles Point (DEP)
Christchurch
Sheet 7 Grid ref. E4403 N7317
Land height 20m above sea level
Exposure – coastal cliff
Length of section - 30m
Age - Isotope stage 7
Corresponds to Mesolella’s sample ACH
Samples collected – 6

This is an east-facing exposure of cemented coral sands, which overlie marls and Tertiary bedrock.
There are no corals at this site.
The sands are well sorted and very well cemented making it difficult to collect samples.
The sands are not freshly exposed and so have undergone some minor surficial weathering.
These samples have evidence of weathering with a green/black crust on the exposed face. There has been solution of the rock that has occurred on the cut face and the rock has a mottled coloration. A few of the allochems can be distinguished from the rock fabric and there are few loose clay-sized particles.

Oldbury Quarry (OQ)
Christchurch
Sheet 12 Grid ref. E3950 N6538
Land Height 44m above sea level
Exposure - Quarry
Length of section - 20m
Age - Isotope stage 7
Near Mesolella’s YH
Samples collected – 27

This is a recently disused quarry and the face sampled was still fresh. Along this 10m high and 20m long North facing outcrop, there are three coral head zones. Starting in the east there are very abundant fore reef _M. annularis_ heads for the first three metres, overlain by rubble at a height of 6m. Between 3 and 13m moving westwards there is a wedge comprising exclusively of very abundant _A. palmata_ heads overlain again by rubble at a height of 5m. The remaining 7m towards the west of this face is a rubble zone comprising of broken coral heads.
Nine samples were collected from each zone, in sets of three, one sample was collected within a coral head and the other two samples were collected immediately above and below that coral head.
This exposure was overlain by a very thin soil and small shrubs but the maximum height sampled was at 5m, above a coral head in the _M. annularis_ zone, so the influence of vegetation should not very marked.
The degree of cementation was variable over the section, as the section itself was variable in nature.
OQ Transect one
The rock fabric is well cemented with evidence for selective dissolution of some particles, as well as solution of the rock. The rock fabric has a number of larger intact shells as well as fragments with little loose clay-sized particles.
OQ 1.2 is composed of a fresh sample of Diploria sp. with lots of loose clay-sized particles.
OQ 1.6 + 1.8 are composed of M. annularis, these samples show no dissolution of the septa, though there are a couple of borings. The samples are fresh though 1.6 does have a bit of iron staining.

OQ Transect two
The rock fabric is differentially cemented to a small degree. The samples do not break up but some parts have a chalky appearance and are easily crumbled. There is evidence for selective dissolution of some particles as well as solution of the rock but some shell fragments are still present and intact.
OQ 2.2 + 2.5 + 2.8 + 2.9 are composed of A. palmata with lots of loose clay-sized particles. Sample 2.5 is fresh. Samples 2.2, 2.8 and 2.9 have evidence of alteration as the coral surface is chalky and crumbles easily in parts.

OQ Transect three
The rock fabric is differentially cemented to a small degree. The samples do not break up but some parts have a chalky appearance and are easily crumbled, with lots of clay-sized particles. There are very few identifiable allochems in the sample. There is evidence for selective dissolution of some particles as well as solution of the rock in some samples.
OQ 3.2 is a fresh, unaltered A. palmata fragment.
OQ 3.5 is composed of a very light coral head, looks like A. palmata but not as dense as other samples of this species collected. There are lots of borings with some bivalves in situ and there is also evidence of dissolution within borings. There are some loose clay-sized particles and the coral is chalky in one part.
OQ 3.6 is also composed of a very light coral head, this time A. cervicornis. The surface is covered in loose clay-sized particles and there is a small amount of coral dissolution expanding on original pores.

A relatively fresh sample was found here in the vicinity of Mesolella's sample ADF. This is a reef crest location with large heads of A. palmata present. Two vertical transects were sampled from the South east face.
Transect 1 had a height of 2.50m and was overlain by grasses. Five samples were collected at 50 cm intervals with a change in bedding noted at a height of 1.60m. Transect 2 was 5m to the right of transect 1 and is dominated by *A. palmata* with a sandy matrix which was very crumbly so the samples collected were largely coralline as the matrix turned to dust when trying to remove the samples. Two samples were collected at each height, at 50 cm intervals from the base.

RR Transect one
These samples were collected from a fairly fresh face. The samples were hard with some small-scale evidence for dissolution. The samples are composed of hard opaque patches, which are very well cemented and small white chalky patches, which are more porous and contain loose clay-sized particles.

RR1.1 The whole of this sample can by crumbled and there are loose clay-sized particles present.
RR1.2 was collected from a layer of encrusting algae. There is no dust present and the sample is very hard and dense. The banded growth layers can be seen. There is slight weathering on the outside edge.
RR 1.5 is similar to the other samples without the chalky patches.

RR Transect two
The samples are heavy and dense with a slightly mottled colouration. There were no loose clay-sized particles and the rock was very well cemented.

RR 2.1 is composed of a coral head, possibly *A. palmata* with borings. The mud that has infilled the borings is very well cemented and there are no loose clay-sized particles.
RR 2.4 was composed of *P. porites* that is well cemented into the fabric. The fabric cement is dense and the pores are mainly restricted to the coral. There is no evidence for dissolution, though the coral had a slightly chalky appearance.
RR 2.5 is like the others but with much subtler mottling and was not as heavy and dense.

Wildey (WIL)
Christchurch
Sheet 11 Grid ref. E2753 N6530
Land height 80m above sea level
Exposure - road cut
Length of section - 40m
Age - Isotope stage 9
Near Mesolella's sample AGJ
Samples collected - 20

This is a fresh cutting that has been cut to form the back wall of a car park. This is a reef crest location composed exclusively of *A. palmata*.
The maximum height of the section is 10m and is overlain by a wall.
A horizontal section was sampled of this west facing face, with sampling occurring at a height of 1m every 2m across.
There is a calcrete layer about 4m up to the north of the section, this rises to 5m but disappears 17m along the section.
The samples are quite friable and the coral heads are very fresh and unaltered. WIL 1.2 - 1.3 are light samples with chalky patches. There is some evidence of minor dissolution and solution. The rock surfaces are slightly mottled where the sample is hard and well cemented, and white in the chalky patches. There are some loose clay-sized particles present making the rock surfaces dusty.

WIL 1.4 + 1.5 + 1.7 + 1.8 + 1.9 are dense and heavy. The surface is smooth and opaque, without the chalky patches. These samples do not contain the loose clay-sized particles, of the other samples.

WIL 1.11 + 1.12 + 1.13 + 1.14 are white but not as heavy and dense as 1.4 etc.

WIL 1.15 + 1.17 are not heavy but have a mottled surface.

WIL 1.18 + 1.19 are dense and heavy. The surface colour is not even as it varies from white to a grey. The samples are well cemented and smooth.

WIL 1.1 is composed of a fresh sample of A. palmata. This is well cemented to a very hard, opaque fabric.

WIL 1.6 + 1.10 + 1.16 + 1.20 are composed of light heads of A. palmata. The pores are open and not dusty.

St. David (STD)
Christchurch
Sheet 9 Grid ref. E3009 N6578
Land height 110m above sea level
Exposure - road cut
Length of section - 5m
Age - Isotope stage 11
Corresponds to Mesolella's sample ACZ
Samples collected - 21

This is a fresh exposure where a driveway has been cut into the Pilgrim Holy Church. This is a reef crest exposure dominated by heads of A. palmata with a few heads of M. annularis. There is no overlying vegetation. The samples were collected at random from this south facing, 1.5m high exposure. STD 1.1 - 1.5 + 1.7 - 1.9 are moderately weathered but there is no evidence for solution or dissolution. The samples are very well cemented and there are no loose clay-sized particles.

STD 1.12 - 1.16 have been moderately weathered, with evidence of shell dissolution. These samples also have chalky patches that can be crumbled.

STD 1.17 + 1.18 are weathered and very dense. There is some mottled colouration on the cut faces and evidence of dissolution on the rough face. There are no chalky patches within the samples.

STD 1.6 is composed of coral. There is some iron staining and solution on the cut face. The coral structure is more dusty and chalky than glassy.

STD 1.10 + 1.11 are composed of the coral M. annularis. The corals are mineralised and glassy in appearance with a minor amount of iron staining. The coral septa have altered and have not undergone notable dissolution.

STD 1.19 - 1.21 have been weathered and have an orange hue. There is evidence of plant roots and hard dense bands in the rock. There are slightly chalky features within the fabric.
Saint George's Valley

Carrington Quarry (CAR)
ST. George’s Valley
Sheet 10 Grid ref. E3659 N6864
Land Height 50m above sea level
Exposure - Quarry
Length of section - 110m
Age - Isotope stage 7
Corresponds to Mesolella’s sample AJN
Samples collected – 15

This is an active quarry and the face sampled was fresh
The quarry was over 15m high with some overlying grasses and a few shrubs but they
were at a much greater height than the samples collected
At the bottom of the section upto 1m up the exposure heads of M. annularis and
Diploria sp. were noted
Above this was a well sorted sand upto a height of 2.5-3m, this was overlain by a
differentially cemented sand
The matrix was shelly and predominantly sandy and differentially cemented, but mainly
very friable
There was iron staining on the exposure that was associated with coral heads
Four samples were collected from the three bands within this exposure
CAR 1.1 + 1.2 + 1.3 + 1.6 + 1.7 + 1.8 + 1.9 The cement fabric has an orange hue and is
composed of lots of tiny cemented grains. The rock is well cemented in places and
easily crumbled in others. There is evidence of solution but the sandy grains and a few
shell fragments can be distinguished, as the samples do not have a large quantity of
loose clay-sized particles within them.
CAR 1.4 + 1.5 + 1.10 + 1.11 + 1.12 + 1.13 + 1.14 + 1.15 have a white colour and are
composed of the same material except that the samples are far easier to crumble and
have a large proportion of clay-sized particles.

Lower Estate Heights
St George’s Valley Transect 2
Sheet 8 E2685 N69823
Land Height 60 - 70m above sea level
Exposure - Road cut
Length of section - 180m
Age - Isotope stage 7
Corresponds to Mesolella’s sample OV
Samples collected – 10

This terrace goes around a bend in the road, and is overlain by small grasses and some
newly built houses on the North face.
Sampling proceeded on the North face in the reef crest. A. palmata is present and there
are a number of large scattered Montastrea and Diploria sp.
The exposure is about 2m high and the rock face is highly weathered
The samples were collected along a vertical transect from this weathered well cemented section.
These samples have undergone weathering with the exposed outer surface covered in soot, from car exhausts. The rock is very well cemented with the cut face showing evidence of solution and black mottling. There is evidence of plant roots with the cement fabric containing hard veins interlaced with chalky, more easily crumbled parts, with no allochems identifiable.
LEH 1.3 is composed of \textit{A. palmata}, which has been weathered on the exposed surface, with some clay-sized particles in the pores.

Waterford Road (WR)
St George’s Valley Transect 2
(I) Sheet 8 E2533 N6798
(II) Sheet 8 E2534 N6817
Land Height 30-40m above sea level
Exposure - Road cut
Length of section - 350m
Age - Isotope stage 7
Corresponds to Mesolella’s sample HG
Samples collected – 18

Small trees and shrubs overlie this long road cut
For site (I) the Southeast face of this 2m high exposure was sampled in the \textit{A. cervicornis} (fore reef zone)
Nine samples were collected along a vertical transect at 25cm intervals from the base
The exposure face is not fresh and the rock was very consolidated making the removal of the samples difficult
On a second visit a year later a second site was sampled
A north facing road cut was sampled at a point where recent road works had cleared a fresher face
The exposure was 1.3m high and still within the \textit{A. cervicornis} zone
Samples were collected along a horizontal transect the first three at a height of 0.5m, the remaining 6 at a height of 0.8m
The exposure was chalky and quite friable

WR Transect one
These samples are weathered and the exposed surface is covered in a dark grey crust so allochems can not be identified. The samples are very dense and well cemented. There is evidence for plant roots and some minor solution.
WR 1.1 + 1.2 + 1.7 – 1.8 are composed of weathered \textit{A. palmata} that has a black crust on the exposed surface. There are very few loose clay-sized particles present.

WR Transect two
These samples are very dusty and only moderately cemented as the rocks can by broken up fairly easily. The rock is very light and no allochems are visible on the rough surface.
Samples 2.4 – 2.9 are composed of *A. palmata*. The samples are very light with open pores but no evidence for solution. The samples are slightly yellowed and dusty on the surface.

Dayrells (DS)
St George’s Valley Transect 2
Sheet 9 Grid ref. E2743 N7056
Land height 80 - 100m above sea level
Exposure - road cut
Length of section - 220m
Age - Isotope stage 9
Corresponds to Mesolella’s sample D
Samples collected – 13

This is a freshly cut road exposure located by some crossroads with only small grasses growing on the top of this 8+m high exposure. Thirteen samples were collected from the North face of this site, at 20cm intervals from the base.

This is a freshly cut face with little to no weathering on the face of this fore reef exposure and the samples were not very well cemented and thus proved very crumbly and easy to remove.

This was a very coraliferous site with large coral heads of *M. annularis* and *Diploria sp.* present. The samples are from a relatively fresh face and there is only evidence for very slight weathering. The samples are heavy and dense and very well cemented. There are some chalky patches in the samples that can be crumbled, but on the whole the samples are not particularly dusty. There is evidence for some minor solution and dissolution which seems to be more marked in samples 1.8 + 1.11 + 1.13. Sample 1.10 is lighter and not as dense as the other samples.

DS is composed of a fresh head of *Diploria sp.* coral with open pores. The coral is glassy in appearance.

DS 1.3 + 1.4 are composed of *M. annularis* coral. The coral is chalky in parts and very well cemented to the surrounding fabric. Allochems are cemented to the coral.

DS 1.5 + 1.6 contain *Diploria sp.* coral. The coral is partially mineralised but there are a lot of loose clay-sized particles present, and the samples can be crumbled. The sample are very light with evidence for solution.

Lears Quarry (LEQ)
St George’s Valley
Sheet 8 Grid ref. E2698 N7123
Land height 80 - 90m above sea level
Exposure - Quarry
Length of section - 100m
Age - Isotope stage 9
Near Mesolella’s sample AFB
Samples collected – 16

This is an active quarry composed of sands and graded pebbles used for construction. This quarry is over 30m deep and the west-facing slope was sampled.

Sample 1 was collected at a height of 2m above the ground and each successive sample was 3m above the last, along a horizontal section.

At the bottom of the quarry is a coral head zone which grades upward into a *A. palmata* zone, which grades up into sands (sample 15).

Sample 16 is altered and is from another face higher up than this one.

There is evidence of some soil wash, and the exposure is overlain by a small amount of grasses.

LEQ 1.1 +1.2 + 1.3 + 1.7 + 1.8 + 1.9 are in the main smooth, hard and dense with no pores, though there are some chalky patches. The samples are fresh with some mottling, with some fragments in the samples that are glassy in appearance. There is evidence for the dissolution of some shell fragments and a few small solution pores.

LEQ 1.4 is a sample of *Siderastrea sp.* There has been some dissolution of the septa, a few of which have been subsequently cemented, most are open. The coral is mineralised and glassy in appearance.

LEQ 1.5 contains a moldic pore of *P. porites,* the pore outline is mineralised, with the glassy cement also expending into what would have been the pores. The cut face is similar to the other samples.

LEQ 1.6 contains some borings, which have been filled with sand-sized cemented fragments.

LEQ 1.10 is a slightly weathered head of *M. annularis,* which has been mineralised.

LEQ 1.11 + 1.12 are in the main smooth, hard and dense with no pores, though there are some chalky patches. The samples are slightly weathered with some mottling. There is evidence for some minor solution.

LEQ 1.13 + 1.14 + 1.15 all have evidence for shell dissolution and the rocks have a yellow hue. The cemented grains are porous with inclusions of hard opaque bands.

LEQ 1.16 is a very light, mineralised, coral head. There are no loose clay-sized particles present.

Edgecumbe (EDG)
St George’s Valley
Sheet 9 Grid ref. E3564 N6890
Land height 60m above sea level
Exposure – Quarried face
Length of section - 10m
Age - Isotope stage 9
Corresponds to Mesolella’s sample RW
Samples collected – 15

This is a small 3m high, freshly quarried face composed of sands and rubble. The sands are differentially cemented with patchy colour varying between orange and white.

The west facing exposure is overlain in part by soil and going back away from the exposure there is a sugar cane field.
This was a coraliferous site with *M. annularis* heads and broken heads of *A. cervicornis* noted. The samples were collected at random and were friable and not very well cemented. The samples are composed of a well-cemented sand. The cement is glassy in patches in these parts there are no pores, other parts of the sample are more open and it is possible to crumble grains off the edges. Samples 1.2 + 1.4 + 1.9 + 1.10 are a bright orange colour. Sample 1.2 is white with more loose clay-sized particles than the others, whereas the remaining samples are an intermediate colour. EDG 1.1 is composed of a *M. annularis* coral head. There has been some minor dissolution of some of the septa, some of the septa are intact, some are open and some have been filled with loose clay-sized particles. The coral surface is dusty with part of the coral mineralised.

Ebenezer (EBZ)
St George’s Valley
Sheet 9 Grid ref. E3542 N6964
Land height 70m above sea level
Exposure - road cut
Length of section - 80m
Age - Isotope stage 9
Corresponds to Mesolella’s sample AMU
Samples collected - 11

This is a freshly cut, 1-1.5m high, road exposure. The matrix was white and sandy, containing some heads of *M. annularis*. Grasses overlie the road cut. Samples were collected along a horizontal transect at a height of 1m. These samples were from a fresh face and very light. The samples are moderately well cemented and can be broken up. There are lots of loose clay-sized particles, both on the surface and in the pores. Allochems are not readily identifiable. EBZ 1.3 + 1.4 contain *M. annularis* coral heads. There has been some minor dissolution of the septa, which have subsequently been filled with loose clay-sized particles. The coral surfaces are dusty with a little iron staining and is partially glassy in appearance.

Hampton Quarry (HQ)
St George’s Valley Transect 1
Sheet 10 Grid ref. E3734 N6893
Land height 50m above sea level
Exposure - Quarry
Length of section - 150m
Age – Isotope stage 9
Corresponds to Mesolella’s sample AIZ
Samples collected – 20
There are two disused quarries at this site with only the second, older quarry is accessible for sampling.
This exposure is a deep fore reef section, composed of sandy rubble.
Small sparse grasses overlay the section.
The deposit is fairly uniform with occasional isolated coral heads of *M. annularis*.
Ten samples were collected at 20cm intervals from the base of the East face.
On a second visit one year later, a further ten samples were collected from the same face at 50cm intervals beginning at 3m up from the base of the face.

**HQ Transect one**
These samples have undergone very slight weathering. There is evidence for some minor solution and dissolution. Though the samples are differentially cemented - they can be easily crumbled away in parts and well cemented generally, there are few loose clay-sized particles. The samples contain lots of small pores and the grains are distinguishable but not identifiable.
HQ 1.7 + 1.8 were less well cemented than the other samples and easily broke up into small pieces.

**HQ Transect two**
These samples have undergone very slight weathering. There is evidence for some minor solution and dissolution. Though the samples are differentially cemented - they can be easily crumbled away in parts and well cemented generally, there are few loose clay-sized particles. The samples contain lots of small pores and the grains are distinguishable but not identifiable.

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**Chapel Quarry (CQ)**
St George’s Valley Transect 1
Sheet Grid ref. E3721 N7009
Land height 70 - 80m above sea level
Exposure - Quarry
Length of section - 50m
Age - Isotope stage 11
Corresponds to Mesolella’s sample U
Samples collected - 42

This active quarry is younger than the second high Cliff, which can be seen behind the rear of the quarry.
The rock from this quarry has been cut into bricks for building purposes.
The quarry is 12+m high but a small 2.50m section in the centre of the quarry was sampled, as this is a very fresh cutting with no surface vegetation.
The rock has quite a sandy matrix with a quite uniform course, well-sorted fossiliferous material and there are no large discernible coral heads present.
Twenty samples were collected from two vertical transects 15m apart from a east facing exposure.
The sampling was carried out at 25cm intervals, as the rock face was very uniform.
On a second visit, one year later, a further 22 samples were collected following a horizontal transect at a height of 1m above the base of the transect along the same face as the previous visit, samples were collected at 1m intervals along the face.

CQ Transect one
These fresh samples are composed of well sorted sand-sized grains. The samples are relatively well cemented, as it is possible to crumble allochems away from the edges of the samples. There are lots of loose clay-sized particles. The allochems are too small to identify any of components.
CQ 1.5 + 1.6 are a faint grey and have a slightly mottled colouration caused by iron staining.

CQ Transect two
These fresh samples are composed of well sorted sand-sized grains. The samples are relatively well cemented, as it is possible to crumble allochems away from the edges of the samples. There are lots of loose clay-sized particles. The allochems are too small to identify any of components.

CQ Transect three
These fresh samples are composed of well sorted sand-sized grains. The samples are relatively well cemented, as it is possible to crumble allochems away from the edges of the samples. There are lots of loose clay-sized particles. The allochems are too small to identify any of components.
CQ 3.5 + 3.13 are a faint grey and have a slightly mottled colouration caused by iron staining.
CQ 3.7 + 3.22 have evidence for some slight weathering, and some mottling caused by iron staining.
CQ 3.8 + 3.9 + 3.16 are a faint grey.
CQ 3.15 has less loose clay-sized particles, and the sand-sized grains are very clear. There is a slight mottling of the rock surface.

Bourne (BE)
St George’s Valley Transect 2
Sheet 9 Grid ref. E2821 N7178
Land height 130 - 140m above sea level
Exposure - road cut
Length of section - 110m
Age - Isotope stage 11
Corresponds to Mesolella’s sample OU
Samples collected – 12

This terrace has a maximum height at 6+m with heavy vegetation growing on the top, on the base and even on the face of the exposure. This is an old weathered face within the reef crest, which has had a core removed by a previous worker. The South face of this sheer faced exposure was sampled.
Four samples were collected at 50cm intervals, along a vertical transect with the first sample collected at 0cm above the road height, more samples were not taken due to the extensive weathering and the large influence of the vegetation on the sampling surface. The exposure was within the *A. palmata* zone with a great deal of the coral dissolved out of the exposure face, without replacement, leaving large holes in the rock. The rock was extremely well consolidated making the removal of samples very difficult. These samples are weathered and the exposed face is a dark grey/green colour. The samples are very heavy and dense. The samples are exceptionally well cemented and there are no loose clay-sized particles. The face is smooth and looks glassy in parts and is an opaque white colour. There is evidence of solution and dissolution. BE 1.6 – 1.9 are composed of weathered, very heavy and dense *A. palmata*. The coral is mineralised and looks glassy. There is evidence for some of dissolution.

Cliff Den (CD)
St George’s Valley Transect 1
Sheet 10 Grid ref. E3734 N7169
Land height 150m above sea level
Exposure - Road cut
Length of section - 50m
Age - Isotope stage 13
Corresponds to Mesolella’s sample VA
Samples collected – 22

This is the first terrace encountered inland of the Second High Cliff. This 1.80m high exposure is overlain with grasses and has a fairly old face. This is the top of a reef crest exposure with abundant heads of *A. palmata, M. annularis* and *Diploria sp.*
A core has been collected within an *A. palmata* head by previous workers, on the South facing exposure but on this occasion the North facing exposure as the face was fresher. Samples were collected along two vertical transects, the first is 1.75m high and contains an *A. palmata* head near the top of the section. The second section was 5m to the east of transect 1, it is 1.80m high and contains *M. annularis* within the section.

CD Transect one
The samples are weathered with glassy fragments. The samples are hard and well cemented with chalky patches that can be crumbled. In sample 1.2 the chalky patch can be associated with bryoza. There is also evidence for dissolution. CD 1.3 + 1.4 are composed of weathered *A. palmata* coral. The coral has alternating white and brown bands, both of which are mineralised. The white bands are very hard and dense, the brown bands can be crumbled. There is evidence for soil within the sample.
CD 1.5 is a coral sample that can not be identified in hand specimen. This sample also contains hard white bands but is not as weathered as 1.3.
CD 1.6 – 1.8 are composed of *A. palmata* coral. The coral is mineralised and cemented to encrusting algae, which can be seen as a white band. The underside of the coral (away from the encrusting algae) can be crumbled.
CD Transect two
The samples are weathered with an orange hue. The samples can be crumbled, but there are no loose clay-sized particles. There is evidence for solution and dissolution within the chalky patches, thin, hard, opaque bands surround these.
CD 2.1 + 2.2 are a very hard dense coral. There is a hard dense white band that can be identified as encrusting algae. There are chalky patches within the sample. There is evidence for solution and dissolution.

Cottage Vale (CV)
St George’s Valley Transect 1
Sheet 10 Grid ref. E3699 N7093
Land height 120-130m above sea level
Exposure - Building site
Length of section - 35m
Age – Isotope stage 13
Corresponds to Mesolella’s sample VH
Samples collected – 20

Cottage Vale is the nearest town but this is exposure is part of the Second High Cliff exposure and not the Cottage Vale Terrace
This is a very fresh face created behind a new house being built
Eight samples were collected from a North-facing cutting
Samples 1-10 were collected at 10cm intervals from the base with sample 10 at the top of the section
Sampling proceeded in the hardest areas, as the rock was very crumby
Samples 11-20 were collected from an older outcrop 30m to the east of samples 1-10
This is also a fresh face and appears to be harder, but there is evidence of wash on the rock surface
This exposure has a predominantly sandy matrix with a small number of isolated coral heads no larger than 10cm across
CV Transect one
The rock samples fresh, well cemented and covered in loose clay-sized particles. The rock has been partially mineralised and is dense and hard. The outlines of some grains can be seen on the cut face. There is evidence for dissolution, associated with chalky patches. 1.1 and 1.9 are dense, whereas the other samples are lighter and more chalky.
CV 1.6 + 1.7 are composed of A. palmata. There are no pores in the coral or chalky patches.

CV Transect two
The samples are slightly weathered and pale grey in colour. The samples are relatively well cemented with evidence of plant roots.
CV 1.12 is broken up and not as dense as the other samples.
CV 1.14 is exceptionally light, but well cemented.
Locust Hall Terrace (LHT)
St George’s Valley Transect 2
Sheet 9 Grid ref. E2836 N7181
Land height 140 - 150m above sea level
Exposure - road cut
Length of section - 150m
Age - Isotope stage 13
Corresponds to Mesolella’s sample OT
Samples collected – 15

Southward of Locust Hall the road cuts through a terrace, which is covered by dense vegetation, consisting of large shrubs and trees on the West side and grasses on the East side.

Sampling took place on the West side of this 2m high, fore reef exposure.

The rock face is highly weathered, the structure is matrix supported with a few small scattered coral heads of *M. annularis* present, the coral Acropora cervicornis has been dissolved out in places and not replaced leaving large finger like secondary pores about 3cm in diameter.

Taking the base sample as 0cm where one sample was collected a further 14 samples were collected along a single vertical transect, two at each point, at 25cm intervals.

In the exposure there is a change in bedding at a height of 50 cm above the exposed base of the rock. Below this point the rock is very hard, above this the samples were not crumbly but were easier to hammer out.

The samples are very weathered and contain mineralised grains that are grey in colour. The samples are heavy and dense. The fabric is grey in part and white preserving the grain outlines. There is evidence for solution and dissolution. The dissolution is associated with chalky patches.

LHT 1.4 – 1.6 are composed of the coral *A. palmata*. The coral structure is not easily identifiable. The samples contain hard opaque bands with bands of a yellow hue, with both bands equally well cemented.

Locust Hall (LH)
St George’s Valley Transect 2
Sheet 9 Grid ref. E2888 N7198
Land height 150-170m above sea level
Exposure - Road cut
Length of section - 150m
Age - Isotope stage 15
Corresponds to Mesolella’s sample QU
Samples collected – 8

This is a very steep sided road cut that pertains to the very consolidated nature of the rock.
This old rock face is overlain by grasses with grasses also growing at the base of this exposure.
Sampling took place on the West side of this reef crest exposure along a single vertical transect, midway between two coring locations, the samples of which were removed by previous workers. The base sample was taken at 0cm above the road height and in all, eight samples were collected at 30cm intervals of this 3m high exposure. It is difficult to make out the coral species at this site due to the weathering that had taken place, with evidence of wash also present. The coral species *A. palmata* and *M. annularis* however, were noted. The samples are heavily weathered. The samples are heavy and dense, with a grey mineralised fabric, there are also small white chalky patches that are slightly crumbly. There is evidence for solution and dissolution. LH 1.4 contains some altered coral but it is difficult to distinguish due to the high degree of weathering. The coral is not glassy in appearance. There are some small pores that look like dissolved out *Halimeda* sp. The sample is very well cemented with some small chalky patches. LH 1.5 + 1.6 contain some coral but it is difficult to distinguish due to the high degree of weathering. The corals are mineralised with dust in the pores and evidence of solution.

St. Helens (SH)
St George’s Valley Transect 2
Sheet 6 Grid ref. E2937 N7216
Land height 170-180m above sea level
Exposure - Road cut
Length of section - 310m
Age - Isotope stage 15
Corresponds to Mesolella’s sample QV
Samples collected – 14

This exposure does not have a fresh face but is not as weathered as the previous terrace sampled (ABS)
This site is overlain with shrubs and grasses with some vegetation growth on the exposure face itself
Ten samples were collected from the East face, along a single vertical transect at 25cm intervals from the base
The rock is quite well cemented with the samples proving not too difficult to remove
This exposure is in the back reef section of the terrace, as it is dominated by *A. cervicornis* with a few scattered, small coral heads within a sandy matrix
The exposure is variable along its length and does grade into the reef crest, which is dominated by *A. palmata* but this, was at a point that was less suitable for sampling.
On a second visit a year later a further four samples were collected opposite the first site, on the west face, where part of the face had been cleared for a telegraph pole, exposing a fresher face
SH Transect one
These samples are heavily weathered and very well cemented. There is evidence for solution and dissolution and plant roots within the samples. The shells within the samples are mineralised and the fabric is mottled but generally a cream colour. SH 1.2 is not as heavily weathered. SH 1.8 is composed of a mineralised head of *M. annularis*. The coral is glassy and not as heavily weathered as some of the samples collected from this location.

SH Transect two
SH 2.1 is from a fresher face and so is only moderately weathered, but is still very well cemented. The shells within the samples are mineralised and the fabric is mottled but generally a cream colour. There is evidence for solution and dissolution. SH 2.3 + 2.4 are composed of *Diploria sp.* coral. The coral structure is preserved but stained a brown colour. The coral is mineralised and glassy in places.

St. Augustine’s Boys School (ABS)
St George’s Valley Transect 2
Sheet 6 Grid ref. E2977 N7251
Land height  180-200m above sea level
Exposure - Road cut
Length of section - 220m
Age - Isotope stage 15
Corresponds to Mesolella’s sample QW
Samples collected – 7

This terrace has lots of vegetation growing up the side of this 5m high exposure making this quite a poor site
The nature of this terrace is variable with evidence of wash, and sampling took place at the maximum possible distance away from vegetation growing on the exposure. The terrace at this point has a height of 230cm.
The North west face of this highly weathered exposure was sampled and 7 samples were collected from a single vertical transect at 35cm intervals from the base.
The rock was very consolidated and contained *A. cervicornis* with large heads of Montastrea and Diploria also present which pertains to a fore reef exposure
These samples are heavily weathered and very well cemented. There is evidence for some large solution pores and lots of very small pores can be seen on the cut face. There is evidence of soil on the exposed face.
ABS 1.2 + 1.3 are composed of a weathered and altered head of *M. annularis*. There is evidence for solution and the pores created from the dissolution of the septa seem to have the main concentration of iron staining.
ABS 1.4 + 1.5 contain a weathered fragment of *Diploria sp.* that has been iron stained, unlike the surrounding fabric. There is evidence for solution, pores are concentrated within the coral, not the fabric.
Market Hill (MH)
St George’s Valley Transect 2
Sheet 6 Grid ref. E2990 N7277
Land height 200-210 m above sea level
Exposure - Road cut
Length of section - 100m
Age - Isotope stage 15
Corresponds to Mesolella’s sample QQ
Samples collected – 10

This is the oldest terrace sampled along this transect and is located opposite an old windmill just below some crossroads.
There is a strong influence exerted on this weathered exposure, by the overlying trees which grow on this site.
The 2.50m maximum height of the Northwest face of this road cut was sampled.
Samples were taken at 25cm vertical intervals from the base.
There are a large number of small, flattened heads of *M. annularis* present and the rock is very well cemented making the samples difficult to collect.
These samples are heavily weathered and very well cemented. The exposed surface has a green/black crust and some iron staining.
The cut face is white with some mottles.
There is evidence of dissolution but otherwise the samples are not very porous.
MH 1.6 is composed of a weathered head of *M. annularis*. The sample is dense and discoloured.

Guinea Quarry (GQ)
St George’s Valley Transect 1
Sheet 6 Grid ref. E3661 N7378
Land height 180-190m above sea level
Exposure - Quarry
Length of section - 100m
Age – Isotope stage 15
Corresponds to Mesolella’s sample AMA
Samples collected – 37

This is an active quarry where graded pebbles are being produced.
This is a very deep section with large scattered heads of *M. annularis* and shells, within a silty matrix.
There is evidence for a change in the bedding at a height of 1m from the base and at the top of the section there is evidence for burrowing suggesting a former surface.
There are abundant *A. cervicornis* heads at the top of the section most of which are dissolved out.
This is a fresh face with some discolouration towards the top.
The 10+m thick deposit is about half the total pit depth.
The North facing exposure was sampled.
Four transects were followed at differing heights, with samples collected at 20cm intervals.
Sample 0.0 – 0.7 were collected from a higher section not in situ.
Sample 1.1 was at a height of 0cm from the base with sample 1.7 on the unconformity.
Sample 2.1 was at a height of 80cm from the base
Sample 3.1 was at a height of 140cm from the base (at the same height as 1.8)
The samples below the unconformity are very well cemented, above the unconformity
the rock is much more powdery

GQ loose samples
These samples were collected from rocks which have fallen from the top of the quarry.
The samples contain *P. porites* and *A. palmata* coral. Some of the *P. porites* coral has
been dissolved out leaving just the fabric outlining its former position.

GQ Transect one
GQ 1.1 + 1.2 are fresh and very well cemented. The samples contain filled borings
which are white in colour. The surrounding fabric is mottled and glassy in appearance.
GQ 1.3 is composed of altered *M. annularis*. The coral is dense and glassy, with the
features are difficult to discern. The surface is not particularly dusty and the surface has
some black mottling.
GQ 1.4 + 1.5 + 1.6 +1.7 + 1.8 is very well cemented and strongly mottled. The samples
are mineralised and glassy in appearance. There is evidence of solution and dissolution
and the few allochems that can be seen have a slightly grey appearance against a creamy
background. The samples have pores in the shape of ticks due to the dissolution of
*Halimeda sp.*

GQ Transect two
GQ 2.1 + 2.2 + 2.3 + 2.4 + 2.5 are very well cemented and not mottled. The samples are
cream in colour. There is evidence of solution and dissolution and the few allochems
that can be seen have a slightly grey appearance against a creamy background. The
samples have pores in the shape of ticks due to the dissolution of *Halimeda sp.*
GQ 2.6 is composed of the coral *A. palmata*. The coral is part mineralised and part
chalky and consequently very dusty with lots of loose clay-sized particles. The sample
contains lots of borings.
GQ 2.7 contains some mineralised encrusting algae, all pores in this sample are
confined to this feature.
GQ 2.8 has two large dissolution features, these contain some chalky fabric.

GQ Transect three
These samples are very well cemented and not mottled. The samples are cream in
colour. There is evidence of solution and dissolution and the few allochems that can be
seen have a slightly grey appearance against a creamy background. The samples have
pores in the shape of ticks due to the dissolution of *Halimeda sp.*
GQ 3.3 + 3.5 are composed of the coral *M. annularis*. There is lots of dissolution with
most of the septa gone, most are open but a few are infilled. The corals are altered but
cream coloured and not particularly glassy in appearance. Sample 3.5 has mineralised
borings in the coral, which are white in colour.
GQ 3.4 is composed of the altered coral *A. palmata*, but it is creamy rather than glassy
in appearance. This is cemented to the surrounding fabric.
Guinea Plantation (GP)
St George’s Valley Transect 1
Sheet 6 Grid ref. E3715 N7280
Land height 160m above sea level
Exposure - Road cut
Length of section - 30m
Age – Isotope stage 15
Corresponds to Mesolella’s sample VC
Samples collected – 8

This outcrop is very small with a maximum height of 1.10m
This small road cut is overlain by large bushes and soil, consequently a horizontal rather than a vertical transect was sampled
This reef crest exposure has a highly weathered face but abundant heads of *A. palmata* were discernible
Eight samples were collected from the centre of the west face of the exposure at 4m intervals
Previous workers have taken cores within the *A. palmata* heads
The samples are very weathered and very well cemented. The exposed face is stained green/black and the cut face is mottled. There is evidence for solution and dissolution. GP 1.4 is not as weathered as the other samples. Allochems can be seen on the cut face as they are pure white surrounded by a grey mineralised outline. There are two dusty chalky patches that are undergoing dissolution.
Appendix 2 — Laboratory Techniques

Fiegl’s solution

The Fiegl’s solution stain developed by Fiegl (1937), was made in the following way:

1. 11.8g MnSO₄·7H₂O was added to 100 ml distilled water and was heated until the solution was boiling.
2. 1g of commercial grade Ag₂SO₄ was added to the boiling solution.
3. The suspension was cooled and filtered.
4. 2 drops of 10% sodium hydroxide were added.
5. This was left to stand for 2 hours before being filtered into a dark storage bottle.

The thin section was immersed in Fiegl’s solution for 10 minutes at 20°C after which time the aragonite is stained black while calcite remains unstained.

Titan Yellow

The Titan yellow stain developed by Choquette and Trusell (1978) was made in the following way:

1. A reagent was made using 1g of Titan yellow powder, 8g NaOH and 4g diNaEDTA dissolved in 1 litre distilled water at room temperature and stored in a dark bottle.
2. A fixer was made by slowly dissolving 200g NaOH pellets in 1 litre distilled water. This procedure must be carried out in a fume cupboard, wearing surgical gloves. The resulting solution was stored in a polythene bottle.
3. The epoxy mounted thin sections were etched for 30 s in 5% acetic acid solution before being dried in a stream of warm air.
4. The thin section was then immersed in the Titan yellow stain solution for 20 minutes, before again being dried in a stream of warm air.
5. Without touching the surface of the stained slide, the fixer was added for 30 seconds, and the slide was again air dried.

Calcite with 5-8% MgCO₃ is stained a pink to pale red colour, which intensifies to a deep red colour for high Mg-calcite.
Alizarin red S

Alizarin red S developed by Dickson (1965, 1966) was made in the following way:

1. The stain was made in two parts: part 1 was composed of 0.2g Alizarin red S dissolved in 100 ml 1.5% HCl solution.
2. Part 2 was composed of 2g potassium ferricyanide crystals dissolved in 100 ml 1.5% HCl solution, this solution was made fresh for each staining session.
3. The two solutions were combined in the ratio three parts Alizarin red S dye to two parts ferricyanide solution, which lasted for one staining session.
4. The thin section was etched for 10-15 seconds at 20°C, using 15 ml of 36% HCl dissolved in 500ml distilled water, then topped up to 1000ml with distilled water.
5. Warm the slide in a dish of hot water before applying the dye solution for 30-45 seconds, whilst wearing rubber gloves.
6. Gently wash the specimens in two changes of distilled water, for only a few seconds at a time.
7. Dry the stain surface in a stream of warm air and handle the thin section carefully.

The stain dyes calcite pale pink to red, whereas dolomite does not stain at all.

Peels

Peels were made in the following way:

1. The impregnated rock sample was ground and polished, prior to being stained as outlined above.
2. The specimen was held using plasticene and tilted a few degrees to the horizontal.
3. A piece of acetate film was cut allowing a 1cm overlap around the specimen edge.
4. The specimens were refrigerated before the surface was flooded with acetone.
5. The acetate film was placed along the lower edge and unrolled over the specimen.
6. The specimen was left for at least half an hour before the film was gently lifted off.
7. Excess film was removed from the peel, before it was mounted between two slides.

Scanning electron microscope

In this study a Hitachi S-520 scanning electron microscope was employed in the following way:

1. The sample was adhered to the stub using araldite and coated with carbon.
2. The coated sample was placed in the sample chamber, and evacuated to a high vacuum.
The SEM image was formed by an internally generated electron beam, created by heating a tungsten filament in the electron gun.

Features seen were noted and photographed.

Microprobe

The microprobe specifications for analysing carbonate samples in this study are outlined below:

**Instrument**

JEOL JXA-8600S

**Beam conditions**

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<tr>
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**Analysed Elements (Carbonates – Condition file 149)**

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<th>X-ray line</th>
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The precision and detection limits of the microprobe analyses were calculated for BESS 1.11 an altered *M. annularis* coral, CH 2.9 an unaltered sample of *Siderastrea sp.*. MCR 2.13 an unaltered sample of *M. annularis* and EI composed of cemented red algae using the following tables.
Electron microprobe precision and detection limits

The samples were prepared for analysis using the XRD in the following way:

1. A fine-grained rock powder was produced using an agate swing-mill.
2. Samples were packed into a powder holder and placed in the X-ray diffractometer.
3. The percentages of the carbonate minerals were calculated from X-ray peaks.

X-ray diffraction (XRD)
The X-ray peak heights were measured and from this it was possible to determine the various percentages of aragonite and calcite using the reference intensity ratio method. (a computer programme based on the work of Chung, 1974).

**X-ray fluorescence (XRF)**

The samples were prepared for analysis using the XRF in the following way:

1. A fine-grained rock powder was produced using an agate swing-mill.
2. Approximately 15g of powder were weighed into a small beaker. Ten drops of Moviol 88 solution (this is a solution of polyvinyl alcohol in a 1:6 mix of methanol and distilled deionised H₂O) was added to bind the powder.
3. This mixture was then placed in the die and hydraulically pressed.
4. The dried pellet was then placed in the XRF and the concentration of an element was calculated from a measurement of the intensity of the radiation produced.

The X-ray emissions from international reference materials were measured to produce a calibration curve, against which the coral samples in this study were compared.

**Inductively Coupled Plasma Spectrometry (ICP)**

The samples were prepared for analysis using the ICP-OES in the following way:

1. A fine-grained rock powder was produced using an agate swing-mill.
2. 10mg of coral sample was dissolved in 10ml 10% HCl overnight.
3. The ICP source was produced by a two-turn induction coil, which carried a high frequency current generating a rapidly varying magnetic field and an ionised gas passing through this field generated the ICP flame.
4. The sample solution was carried in an aerosol in argon to the centre of the plasma flame and a photon of light energy was emitted, at a characteristic wavelength.
5. Using calibration lines, which relate elemental concentration with intensity of light emitted, the electrical signal was converted into a concentration measurement.
6. The final results are determined by using the standard solutions as controls.
### Appendix 3 - Point counting Summaries

#### Rock components within *A. pulchra* coral samples

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#### Rock components within *A. cervicornis* coral samples

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Rock components within *A. variabilis* sp. coral samples

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### Rock components within coral head zone sediments

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### Rock components within core reef sediments

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*Table entries represent percentages.*
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Senn, A. 1946. Geological investigations of the ground water resources of Barbados, B.W.I. British Union Oil Company, Ltd. 171pp.


