GEOCHEMICAL INVESTIGATIONS OF CENOZOIC COOL-WATER CARBONATE SEDIMENTS OF SOUTH AUSTRALIA; IMPLICATIONS FOR DIAGENESIS, PALEOENVIRONMENT AND PALEOCLIMATE

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-**Rahimpour-Bonab, H.,** Bone., Y. and Moussavi-Harami, R., 1997, Stable isotope aspects of modern molluscs, brachiopods and marine cements from cool-water carbonates, Lacepede Shelf, South Australia. Geochimica et Cosmochimica Acta, v.61, p. 207-218.

-**Rahimpour-Bonab, H.,** Bone, Y., Moussavi-Harami, R., And Turnbull, K., 1997, Geochemical comparisons of modern Cool-water calcareous biota, Lacepede Shelf, South Australia, with tropical counterparts. *In* James, N. P. and Clark, J. D. A. (eds), Cool-water Carbonates. Society of Economic Palaeontologist and Mineralogist, Special Publication No. 56, p. 77-91.

-**Rahimpour-Bonab, H.,** Bone, Y., Moussavi-Harami, R., And Turnbull, K. , 1995, Comparison of the Geochemistry of Cool-water Corals, Coralline Algae and Bryozoans from the Lacepede Shelf, South Australia with their Warm-water Counterparts, *In* Cool and Cold Water Carbonate Conference, Geelong, Victoria, Australia 14th - 19th January 1995, p. 7-8.

-Bone, Y., James, N. P., **Rahimpour-Bonab, H.** and Moussavi-Harami, R., 1996, Stable isotope Biogeochemistry of modern cool-water carbonate skeletons in southern Australia, and implications for the rock record. In Carbonates and Global Change: An interdisciplinary Approach, SEPM/IAS Conference, Wildhause, Switzerland, June 22th - 27th, 1996, p.26-27.

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ABSTRACT

Hitherto, the terms carbonate sediments and rocks were almost synonymous with the tropical area and warm climatic conditions. This misconception existed mainly due to poor comprehension of carbonate production in temperate (i.e., non-tropical) carbonate environments and insufficient studies on the carbonate producers in these environments. These deficiencies for the modern environment habitually led to overlooking of possible temperate carbonates in the rock record and even misinterpretation of their environment of formation. Consistently, contrary to the tropical/warm water carbonates, geochemical attributes, characteristics and biomineralisation in the temperate carbonate environment remained mainly unexplored.

In this study, the geochemical attributes of some carbonate producers in Holocene temperate (cool-water) carbonates have been investigated to establish a data base for further extrapolation and deduction about their ancient counterparts, and subsequent paleoenvironmental interpretation and reconstruction. Additionally, these calcareous organisms are compared with their tropical counterparts, in terms of their geochemistry and biomineralisation.

In the study of the Holocene temperate environment of the Lacepede Shelf, specimens of ahermatypic corals, coralline algae, bryozoans, bivalves, gastropods and brachiopods have been selected to scrutinise their reliability in recording their ambient environmental conditions and geochemical characteristics. Firstly, to investigate the equilibrium or non-equilibrium state of carbonate secreted by these different carbonate producers, their stable ($\delta^{18}O$ and $\delta^{13}C$) isotopic composition is compared to equilibrium isotopic values. The equilibrium isotopic values are determined by different methods. Marine cements, especially from temperate environments, usually precipitate in isotopic equilibrium with their ambient waters, so they are used as a proxy for equilibrium values of carbonate precipitated in isotopic equilibrium from seawater. To substantiate these isotopic values, the isotopic composition and temperature of seawater samples from the study area were measured. The isotopic equilibrium values for potential low-Mg calcite (LMC), high-Mg calcite (HMC) and aragonite have been calculated, using equations introduced by different researchers. The results were compared with the measured isotopic equilibrium values obtained from the marine cements, with good agreement resulting.

The isotopic composition of these modern cool-water carbonate-secreting organisms from the Lacepede Shelf of South Australia was investigated, to determine whether isotopic equilibrium or disequilibrium pertained during biogenic secretion. The causative kinetic and metabolic isotopic effects were established. Factors leading to differentiation from their tropical counterparts were determined.

Ahermatypic corals are depleted in $\delta^{18}O$ and $\delta^{13}C$ in comparison to equilibrium values, but this depletion is less than that of their tropical counterparts. The $\delta^{18}O$ values are systematically more depleted than the equilibrium values, but are adjustable for paleotemperature studies.

Coralline algae are enriched in $\delta^{18}O$, in contrast to their tropical counterparts. However, their $\delta^{13}C$ shows the same values. Both ahermatypic corals and coralline algae display a positive correlation between their isotopes, and $\delta^{13}C$ photosynthetic enrichment is prominent in the latter.

The large cheilostome bryozoan *Adeona* sp. from this area shows equilibrium isotopic values, which contrast to its tropical counterpart. In this genus (at least), skeletal $\delta^{18}O$ and water temperature are closely related over the entire temperature range of the study area. The temperature versus $\delta^{18}O$ curve is parallel to the equilibrium calcite curve.

The studied temperate gastropod and bivalves precipitate their calcareous shells in isotopic equilibrium with their ambient waters, whereas brachiopods exhibit minor $\delta^{18}O$ disequilibrium values, contrary to their tropical counterparts.

One of the major findings of this study is that cool-water taxa generally precipitate their calcareous skeleton close to equilibrium values. The explanation for this observation is that, because of the lower temperatures and consequently slower precipitation rates (of both organic and inorganic carbonates), kinetic effects have a minimum influence on the isotopic composition, resulting in many of the biogenic carbonates, such as molluscs and bryozoans, and the inorganic marine cements exhibiting equilibrium isotopic values. However, the calcareous algae and ahermatypic corals of the study area, despite their heavier isotopic values in comparison with their tropical counterparts, still exhibit large deviations from equilibrium values, induced by metabolic and kinetic effects. Therefore, some calcareous organisms living in cool-water are able to record more accurately variations in seawater temperatures and chemistry than do their tropical counterparts in their environment.

The denouements and attainments from the investigations on the Holocene temperate carbonates, and the widespread distribution of comparable fossiliferous Tertiary temperate carbonate sequences in southern Australia (specifically the

St.Vincent and Murray Basins), encouraged the author to employ these outcomes, wherever possible, for paleoenvironmental reconstruction and paleoclimatic interpretation of the Tertiary carbonate sequences. Of course, geochemical studies of such rocks are always restricted due to the possible diagenetic alterations of the skeletal carbonates. However, in many stratigraphic units of the study area, well-preserved samples are abundant, thus allowing the opportunity to employ the Holocene geochemical results to investigate the Tertiary rock records. Wherever carbonate samples were diagenetically altered, utilising the isotopic fractionation values from the Holocene organisms, the original isotopic values of the altered organism were estimated in a process called here "Backtracking Process". Results of this study show that:

1) In general, the isotopic composition of the diverse fossils from different periods of the Tertiary reflects the global variations in $\delta^{18}O$ of seawater during the different glacial-interglacial intervals.

2) The synchronous $\delta^{13}C$ variations that have been observed in the different foraminifera from diverse DSDP sites, have also been recorded by our macrofossil samples. The sea-level fluctuations initiated by the waxing and waning of ice-sheets and their associated global carbon cycles can also be deciphered from the isotopic composition of the different fossils.

3) The Monterey Event resulted in the deposition of the Cadell Marl in the earliest Middle Miocene with a conspicuous isotopic signature. The Middle/Late Miocene inception of ice-sheet growth in Antarctica led to a global sea-level fall and climatic deterioration, which itself imposed some restrictions in the Murray Basin and led to a light isotopic signature of fossil carbonate in the Upper Morgan Limestone, due to increasing fresh-water runoff.

4) The general trend in $\delta^{18}O$ value of seawater, i.e. an increase from the Early Eocene to the Holocene, is reflected in the isotopic composition of different foraminifera and is also recorded by studied macrofossils.

5) The study of stable isotope composition along the cross-section of the growth lines (in molluscs for example), showed that molluscs, when pristine and mature, are excellent recorders of short term changes in environmental conditions such as seasonal upwelling, annual temperature variations, freshwater influx and primary productivity variations.

6) Geochemical and petrographical studies have also been conducted on meteoric cements from different Tertiary stratigraphic units in the study area. The $\delta^{18}O$ values of meteoric diagenetic cements indicate the paleotemperature of their ambient environment, as well as meridional variations due to northward drifting of Australia during the Tertiary and subsequent terrestrial climatic changes. The

isotopic composition of meteoric waters sponsoring this cementation are calculated, using the isotopic composition of these cements and appropriate geochemical equations.

In conclusion, the integrated geochemical studies on the Holocene and Tertiary temperate carbonates show that these carbonate-producers are better recorders of the geochemical conditions of their ambient environments than similar carbonate-producers in warm-waters. This also demonstrates that high latitude, marginal marine carbonate environments deserve more attention regarding secular geochemical variations because they are more susceptible to glacial events and subsequent geochemical variations, than the deep sea foraminifera.

STATEMENT OF ORIGINALITY

This work contains no material which has been accepted for the award of any other degree or diploma in any university or other tertiary institution and, to the best of my knowledge and belief, contains no material previously published or written by another person, except where due reference has been made in the text.

Hossain Rahimpour-Bonab, March 1997

I give consent to this copy of my thesis, when deposited in the University Library, being available for loan and photocopying.

Hossain Rahimpour-Bonab

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DEDICATION:

"To my beloved parents, for their continuous encouragement and support during all of my career"

CHAPTER ONE

INTRODUCTION

1.1. Significance and Aims:

Many modern continental shelves are areas of carbonate-rich fauna and floral growth and subsequent sediment accumulation. These carbonate depositional environments can be subdivided into three major zones: (1) tropical/warm-water; (2) temperate/cool-water and (3) polar/cold water. Until recently research has been focused on the tropical environment, particularly in regard to the geochemistry and biomineralisation of living organisms.

The traditional conception about carbonate production is that because the precipitation of carbonate is easiest in warm, shallow seawater, most carbonate sedimentation takes place on continental shelves or banks in the tropics (James 1984). Therefore, carbonate sedimentation is primarily regarded as a tropical phenomenon that occurs mainly between about 30°N and 30°S latitudes in shallow water continental shelves (e.g., Rodgers 1957; Fairbridge 1964; Taft 1967; Wilson 1975).

Thirty years ago, Chave (1967) questioned the validity of the "warm water" carbonate concept by drawing attention to several areas of carbonate formation on modern shelves beyond the tropics. Accordingly, he suggested that temperature is not a limiting factor for carbonate production and carbonate deposition could occur on shelves at any latitude as long as the rate of dilution from terrigenous sediment was small. Nelson (1988) emphasised that "it is the overall tectonic framework and its control on the introduction and sea-floor dispersal routes of terrigenous material which is of fundamental importance in determining the location of shallow marine carbonate sediments in any climate".

After Chave (1967), many researchers attempted to present a more realistic picture of the global distribution pattern of the modern shallow marine carbonate facies and different aspects of carbonate production in non-tropical settings (e.g., Lees and Buller 1972; Lees 1975; Nelson 1978; Nelson and Bornhold 1984; Alexandersson 1978, 1979; Leonard et al. 1981; Rao 1981, 1993; James and Bone 1991; Bone and James 1993, 1997; Rahimpour-Bonab et al. 1997a, b; James and Clark 1997 and references therein).

The tropics-based models for interpretation of many ancient carbonate sequences have provided excellent information about different aspects of carbonate sedimentation and diagenesis. However, these models have ignored a great majority of the other type, i.e., cool-water carbonates. A clear distinction between tropical and non-tropical carbonate deposits is evident today because of the strong latitudinal thermal gradient between frigid polar regions and the hot equatorial latitudes (Nelson 1988).

There are major differences in the diagenetic behaviour of shallow marine carbonates between warm water and cool water environments which are related to: (1) latitudinal variations in the level of carbonate saturation of seawater; (2) mineralogical differences; (3) differences in the overall rates of sediment accumulation; and (4) differences in the geochemistry and biomineralisation processes in these environments (e.g., Alexandersson 1978; Rao 1981, 1993; Nelson 1988; Reeckmann 1988; Henrich et al. 1995; Bone and James 1993, 1997; James and Bone 1991, 1992; Rahimpour-Bonab et al. 1997a, b).

James (1995) has repeated the warning of indiscriminant use of carbonate diagenetic principles derived from well-studied Holocene tropical environments when studying ancient rocks. Based on preliminary studies of widespread temperate water Eocene-Miocene shelf limestone in southern Australia, James and Bone (1992) proposed that "... such temperate water calcite limestones are better models for the meteoric diagenesis of calcite sediments of all ages (especially calcite dominated Palaeozoic carbonate rocks) than aragonite-rich tropical sediments".

Isotopic geochemistry has the potential for assessing diagenetic, climatic and oceanographic changes throughout geological time, and for differentiating paleoenvironments by using unaltered skeletal material. The precursors for many ancient shallow water (platform) carbonate rocks were sediments similar to modern carbonate deposits which are forming today. A good example is the widespread Holocene cool-water carbonate sediments of southern Australian basins (such as the Great Australian Bight, Spencer Shelf, Lacepede Shelf and Bonney Shelf). Cenozoic counterparts of these (such as the St. Vincent and Murray Basins) are also widespread in southern Australia. These Holocene and Tertiary sediments are the subjects of this study.

Therefore, geochemical investigations on the modern and fossil skeletal and non-skeletal carbonates can provide information on the composition of marine carbonates and biomineralisation; limestone genesis and its diagenetic changes in different diagenetic settings; distinction of different sedimentary environments (cold versus warm water carbonates); paleotemperature estimations; paleoenvironmental reconstructions and paleoclimatological investigations. Accordingly, the aims of this study are:

- to determine the **isotopic fractionation** in skeletal carbonates at low bottom temperatures and comparisons of these results with those from inorganic precipitation,

- to compare the geochemical characteristics and **biomineralisation processes** of carbonate biogenic producers in cool-water environments with their tropical counterparts,

- to show the **influences** of calcification rates, mineralogy, photosynthesis and respiration on the stable isotopic composition of different biogenic carbonates, and evaluate the **kinetic/metabolic effects** on the stable isotopic composition of these organisms,

- to scrutinise the ability of **cool-water molluscs** in producing precise records of the isotopic composition of their ambient seawaters and in reflecting conditions of their environment,

- to examine the **preservation** of fossil materials of different Tertiary units and their utilisation for paleoenvironmental studies,

- to calculate the original and potential stable isotopic composition of different dissolved, recrystallised or contaminated **Tertiary fossils** of the study area by employing previous data on the isotopic composition and fractionation factors of their Holocene counterparts from the Holocene continental shelf of South Australia,

- to study the geochemical imprint of the **meteoric diagenesis** on these carbonate sequences and estimate the isotopic composition of the diagenetic fluids,

- to present the reflection of the **seawater secular isotopic variations** on the St.Vincent and Murray Basin sedimentary sequences during different Tertiary times (excluding the Pliocene),

- to establish the **$\delta^{18}O$ and $\delta^{13}C$ variation curves** for this period, based on molluscan and brachiopod samples,

- to disentangle the **regional and global seawater chemistry** changes in this area and their effects on these stable isotopic records,

- to substantiate the importance of macrofossils for such **paleoenvironmental reconstruction**,

- to estimate the amount of **sea-level fluctuations** in the Tertiary, using oxygen isotopic records from the study area,

- to evaluate **geochemical variations** in the ambient environment of Holocene and fossil molluscs which are recorded in the isotopic profiles of these organisms.

1. 2. Geological Setting and Stratigraphy

1.2.1. Holocene Cool-Water Carbonates:

Cool-water carbonate sediments are forming on the continental shelves of mid-to-high latitude area, with bottom temperatures of less than 20°C (Fig. 1.1). These cool-water carbonate platforms, due to lack of hermatypic reef building corals, are generally unrimmed open carbonate ramps, the distal parts of which are steepened (Brookfield 1988; James and Choquette 1990). These carbonate sediments also form on deep-water slopes and basin settings of low-latitude regions (James and Choquette 1990). The cool-water carbonate sediments are mainly biogenic and

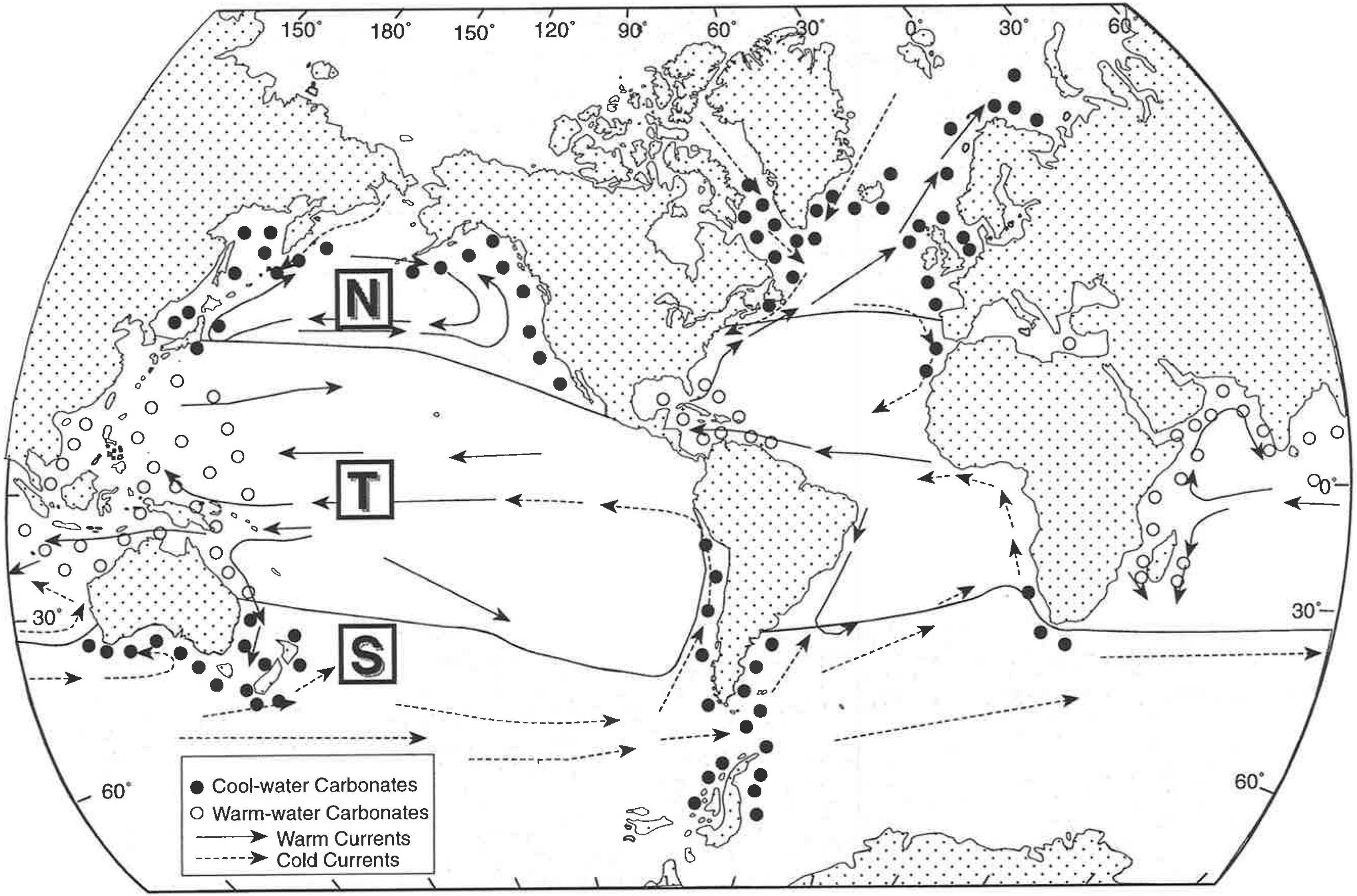


Fig. 1.1. The global distribution of modern cool-water (temperate), warm-water (tropical) carbonates and oceanic circulations. N, S = northern and southern temperate/cool-water carbonates belts; T = Tropical/warm-water carbonate belt. Modified from Henrich et al., (1995).

are dominated by aphotic skeletal associations like the foramol (Lees and Buller 1972) and bryomol (Nelson et al. 1988) assemblages. Their general assemblage is bryozoans, foraminifers, echinoids, coralline algae, bivalves, gastropods and brachiopods. Non-skeletal carbonates, such as oolites and aggregates, are absent, probably due to seawater undersaturation with respect to calcium carbonate and lower temperatures. Carbonate mud is also mainly absent. The most common carbonate mineral is calcite with varying amounts of Mg, with aragonite is much less abundant. This characteristic of cool-water carbonate sediments reduces their diagenetic potential.

The continental margin of southern Australia is the largest region of cool-water carbonate deposition on a shelf in the modern ocean. This area has been the site of almost continuous cool-water carbonate deposition since the Eocene. The Lacepede Shelf, in the continental margin of southern Australia, is one of the these extensive, open-shelf embayments, 130x190 km in area (Fig. 1.2). It is a swell-dominated region with length of the fetch and the latitudinal wind belt resulting in deep-water waves commonly being >25m high, >200m in length and >12s in period. These high energy physical attributes result in a wavebase of at least -100m (James et al. 1992).

Shelf waters are low in nutrients throughout most of the year (Schahinger 1987). Short-lived episodes of upwelling during summer are caused by stabilisation of normal eastward-tracking high-pressure systems, allowing for a reversal of flow direction and upwelling across the entire Bonney Shelf and the deep shelf edge and upper slope of the adjacent southern section of the Lacepede Shelf (Schahinger 1987; Cai Wenju et al. 1991).

Summer shelf waters are stratified with a mixed surface layer (0-30m) averaging 18°C, a thermocline from 30 to 80m dropping to 13°C, and deep water decreasing in temperature at a rate of 1°C/100m. The thermocline is less pronounced during

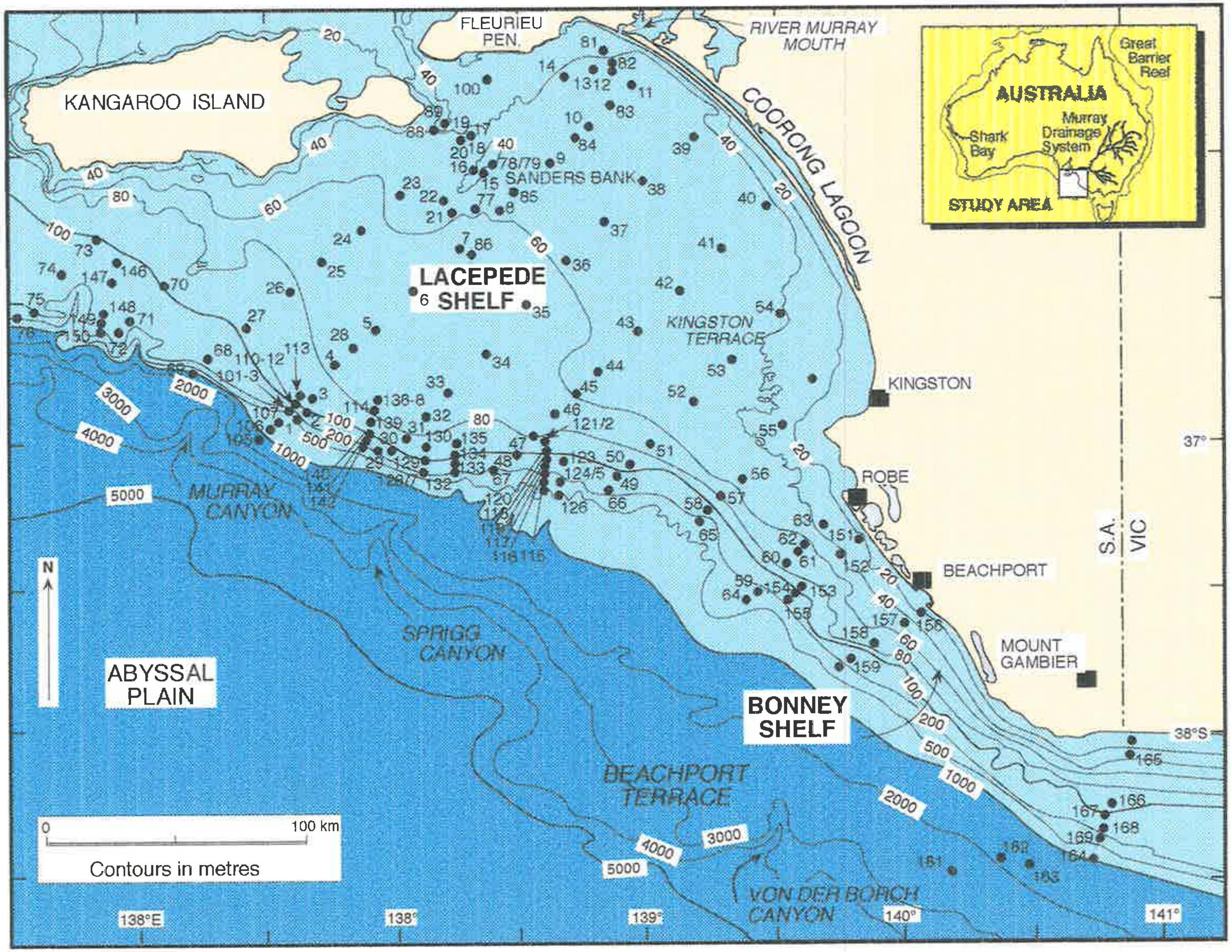


Fig. 1.2. Location map of the Lacepede Shelf, South Australia (Modified from James et al. 1992)

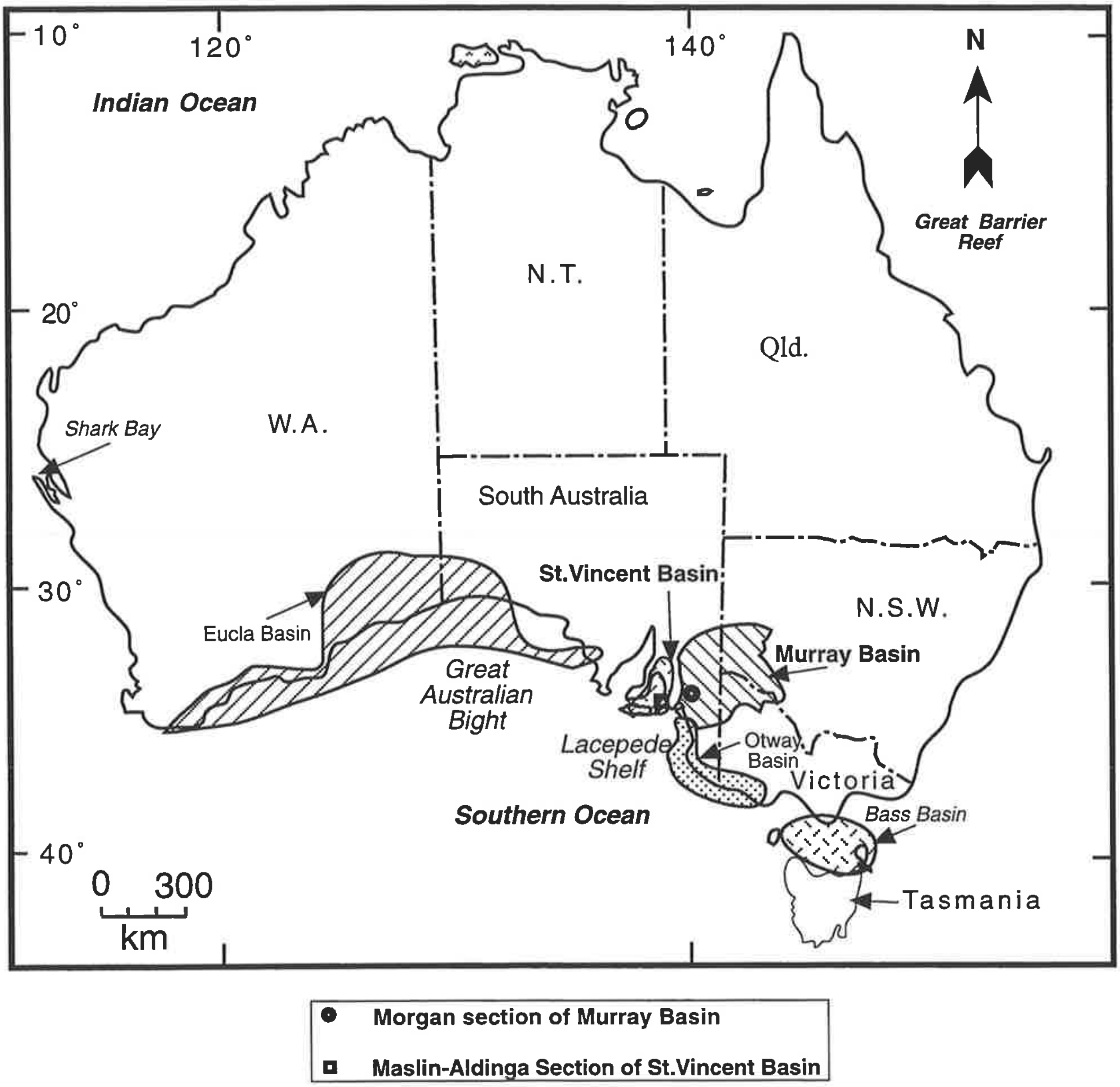


Fig. 1.3. Location map of the study area and some other Tertiary basins of southern Australia. Sampling sites in the Murray and St.Vincent basins are also shown.

winter months, with a 100m layer at 17-18°C (See Fig. 2.1 - Bone and James 1993). The River Murray does not appear to have much influence on shelf waters (James et al. 1992). In contrast, the generally eastward water movement along the shelf causes warm saline water from Gulf St.Vincent (Bye 1976) to spill through Backstairs Passage and past Kangaroo Island onto the western part of the shelf.

Summer surface salinity measurements show a SE-NW gradient (James et al. 1992) with the colder (14-15°C) waters of the Bonney Shelf being marginally less saline (35.1‰) than the slightly warmer waters of the Lacepede Shelf (35.9‰ - Bone and James 1993). This is due to a combination of the Leeuwin Current coming from the north around the south-western corner of Australia and the outflow of warmer, saline waters from Spencer Gulf and Gulf St.Vincent (Bye 1976; Fuller et al. 1993).

The most abundant benthic organisms an this shelf are sponges, foraminifera molluscs and bryozoans, and lesser significant groups are echinoids, brachiopods, ahermatypic corals and serpulids. Other groups such as crustacea, coralline algae, hydroids, gorgonians and ostracods are common in most communities but rarely make up to 5% of the living population.

1.2.2. Tertiary Carbonates:

Tertiary sediments in South Australia are mainly deposited in marginal basins as widespread thin sheets of diverse origin. Thicker sedimentary successions are accumulated in the passive continental margin basins, such as the St.Vincent and Murray Basins, where they unconformably overlie Mesozoic rift-basin sediments. A consequence of the separation of Australia from Antarctica was the initiation of marine transgressions into the southern marine basins and deposition of considerable thicknesses of marine sediments. Therefore, the Tertiary succession in southern Australia passes upwards and seawards from Early Tertiary non-marine clastic sediments into marine temperate carbonate sediments. These carbonate sediments, which are up to 1.5 km thick, contain copious macro- and microfossils, which in many cases are well-preserved. The St.Vincent Basin and Murray Basin, which together present a continuous record of most parts of the Tertiary of South Australia, contain abundant fossils, and constitute the study area.

1.2.2.1. St.Vincent Basin: The marginal St.Vincent Basin of South Australia (Fig. 1.3) in the south is largely separated from the southern continental margin and Eucala Basin by Kangaroo Island, and by a geophysically defined basement high with little Cainozoic cover across Investigator Strait. The Gulf St.Vincent has limited access to the Southern Ocean through Backstairs Passage and Investigator Strait. The nature of the sediments and fossils suggests that the basin has had similar restricted marine access through much of its history. In the Willunga-Noarlunga Embayment, the Tertiary succession ranges from Middle Eocene to Early Miocene (Fig. 1.4). The Middle Eocene in this section commences with North Maslin Sand, which comprises generally upward-fining units of crossbedded quartz sand and gravel, deposited in a braided-river system. At Maslin Bay, the first sign of marine transgression appears in the latest Middle Eocene-earliest Late Eocene, at the bioturbated top of the North Maslin Sand, after which the transgression develops slowly in the marginal marine and glauconitic South Maslin Sand (McGowran 1989, 1991). This unit contains a sparse marine fauna of bryozoan, molluscs, echinoids and foraminifera. The marine transgression continued in the Late Eocene and led to of a predominantly marine environment in the basin and deposition of different marine limestones. The Tortachilla Limestone in the southern part of the St.Vincent Basin indicates the Tortachilla Transgression (McGowran 1989, 1991). This unit contains temperate benthic foraminifera, molluscs and bryozoans. The Tortachilla Limestone is succeeded by the Late Eocene Blanche Point Formation which has

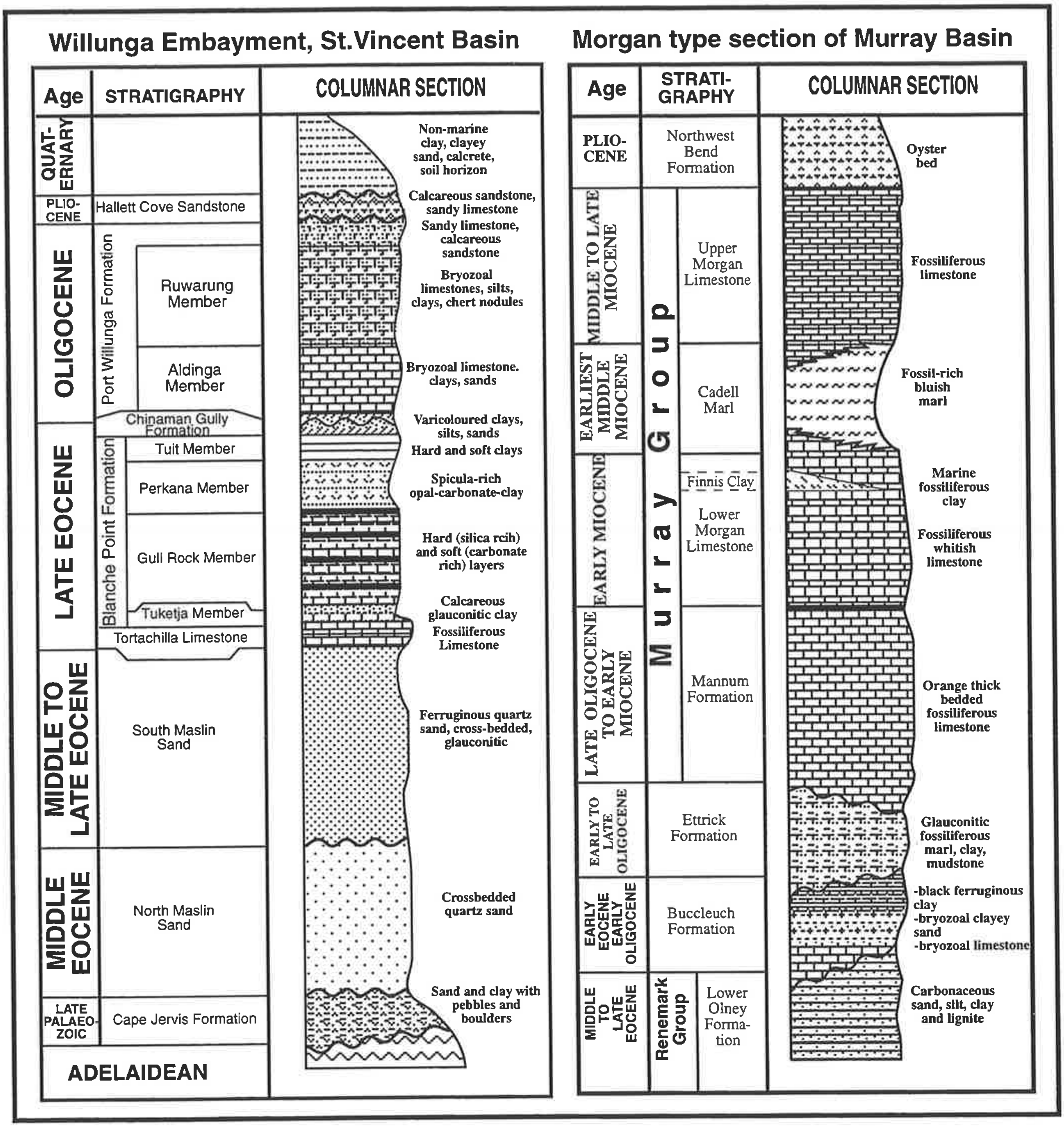


Fig. 1.4. The generalised stratigraphic columns of the Tertiary of the Maslin-Aldinga section in the St.Vincent Basin (modified from McGowran 1979), and the Morgan section of the Murray Basin (modified from Alley and Lindsay 1995) (not to scale).

been divided into four members. The lowest, the Tuketjea Member is a fossiliferous calcareous mudstone with a few thin limestone lenses. The overlying unit is the Gull Rock Member which characterised by numerous bands of spicular chert (Jenkins et al. 1982), which is widespread in the Willunga and Noarlunga embayments and beneath the City of Adelaide, and contains brachiopods and well-preserved aragonitic gastropods. The overlying Perkana Member is a massive calcareous mudstone and spongolite that is overlain by the Tuit Member. This unit contains several chert-bearing bands similar to the Gull Rock Member. The Chinaman Gully Formation which overlies the Blanche Point Formation, is a regressive sandy, silty and clayey unit of latest Eocene earliest Oligocene age. This unit represents the commencement of the major world-wide Oligocene regressive event. The Oligocene Port Willunga Formation is present throughout much of the St.Vincent Basin as bryozoan marly limestone that overlies the Chinaman Gully Formation and represents a marine transgression after the Early Oligocene dramatic sea-level fall (Fig. 1.4).

1.2.2.2. Murray Basin: The Murray Basin is the other epicratonic Tertiary basin of Australia, 300,000 km^2 area, of Palaeocene to Quaternary Age and is situated in the south-east of South Australia, the south-west of New South Wales and north of Victoria (Fig. 1.3 - Alley and Lindsay 1995). In South Australia, the basin margins are delineated by uplifted Neoproterozoic and Cambrian metasediments, and Cambro-Ordovician granites, in the west and north. The Tertiary sediments of this basin are underlain unconformably by Neoproterozoic to Early Palaeozoic basement, Late Palaeozoic glacial sediments and Early Cretaceous Monash Formation in the Berri Basin (e.g., Alley and Lindsay 1995).

The Tertiary succession is divided into three sequence sets. The Late Palaeocene to Early Oligocene unit, called the Renmark Group, consists of non-marine and marginal marine sediments. This unit consists of a massive multi-storey sand body deposited mainly in a fluvial, braided-channel environment, with minor intercalations of finer sediments of lacustrine or floodplain origin. The upper part of the Renmark Group is a widely distributed blanket of unconsolidated, thinly bedded carbonaceous sand, silt, clay, and peat coal, which extends beneath almost the entire Murray Basin, and is referred to as the Olney Formation (e.g., Brown 1985) (Fig. 1.4). This formation was mainly deposited in a fluvio-lacustrine meandering-channel, flood-plain, and extensive swamp environment which is an indication of warm temperatures and a high rainfall paleoclimate (Kemp 1978). The age of this formation ranges from Middle Eocene to Early Oligocene. The lower parts of the Olney Formation are overlain or interfingered by the Buccleach Formation, which is an indicator of a marine transgression in the Late Eocene in the south-west of the Murray Basin, with a bryozoal limestone and glauconitic limestone lithology. These marine sediments grade laterally into the marginal marine formation of the Upper Olney Formation. A unit consisting of glauconitic and fossiliferous marl, calcareous clay and mudstone, with quartz silt and sand that represents a Late Oligocene transgression phase and is referred to as the Ettrick Formation, overlies the older sediments and underlies the Murray Group.

The major but short-lived fall in sea-level in the early Late Oligocene was followed by a further progressive rise in sea-level, which resulted in a dramatic change in the sedimentation patterns in the western Murray Basin, and led to the deposition of marine sediments of the Murray Group, which include the Mannum Formation, Lower Morgan Limestone, Cadell Marl and Upper Morgan Limestone. Although deposition of non-marine (equivalent) sediments continued in the east and north (the younger component of the Olney Formation), in the west the rates of terrigenous sediment input did not initially balance the combined rates of rise in sea-level and crustal subsidence and hence the Murray Basin was partly flooded by a shallow-marine sea. This initial lack of sediment supply in combination with the marine transgression favoured development of a carbonate platform sequence

(Brown 1985). The Murray Group, which is a subject of this study includes Late Oligocene, Early Eocene to Late Eocene transgressive marine sediments. These marine carbonates are fossiliferous and are frequently well-preserved, and so are ideal for geochemical studies. This transgressive event in the shallow epicontinental sea of the Murray Basin reached its maximum in the Late Oligocene-Early Miocene and led to the deposition of the Mannum Formation which consists of coarse-grained skeletal debris of mainly echinoderms, bryozoans, molluscs and benthic foraminifera and some quartz sand. The Lower Morgan Limestone, of Early Miocene age, overlies the Mannum Formation, which has a similar lithology, denoting the continuation of marine conditions at that time. The Lower Morgan Limestone also contains different fossils such as echinoderms, bryozoans, molluscs and benthic foraminifera. In some localities thin marine clay lenses (Finnis Clay) which are fossiliferous are intercalated with Lower Morgan Limestone. The Lower Morgan Limestone is overlain in many places by blue-green marl referred to as the Cadell Marl. This is sandwiched between the Lower Morgan and the Upper Morgan limestone, and its age is earliest Middle Miocene. This marl contains copious fossils, with the aragonitic ones well-preserved. The lithology led to preservation of this generally unstable mineral. This unit contains different fossils such as ahermatypic corals, coralline algae, echinoderms, bryozoans, molluscs and benthic foraminifera. The Upper Morgan Limestone of Middle to Late Miocene time consists of alternations of fossiliferous limestone and marl. This unit is the youngest member of the Murray Group and was deposited in the regressive periods of the Middle-Late Miocene (Fig. 1.4).

1. 3. Sample Preparation and Analytical Methods Employed

1.3.1. Sample preparation:

The Holocene samples used in this study were mainly collected during the cruises FR3/89 and FR2/91 of CSIRO R.V. *Franklin* during March 1989 and January 1991 respectively. Samples were dredged using a simple Bleys Dredge, with a volume of approximately 20 litres. The closed dredge was set on the bottom and towed at a speed of 2 knots for 3-5 minutes, at which time the vessel was stopped and the dredge retrieved. All sediment samples are, therefore, a mixture of surface and subsurface materials to depths of 5-10 cm.

Preferably, samples that were living when dredged were selected for analysis. However, in many cases, these were not available. In this case, samples were selected on the basis of their fulfilling the following criteria, to ensure that they were indisputably Holocene in age: a) show living colour and or attached organic material, e.g. chitin; b) were not abraded, fragmented or bored; c) showed no alteration under either cathodoluminescence or petrographic examination (as discussed in Chapter 4).

Therefore, samples older than the modern samples were rejected following careful petrographic study and were not used in this study as they would not represent the geochemical conditions of the modern Lacepede Shelf environment.

Bathymetry was determined using a precision depth recorder. Surface temperatures were recorded every 10 minutes and vertical temperature profiles for 19 selected positions were documented by expendable bathythermography (XBT) (Bone and James 1993).

Fossil and rock samples were collected from the Tertiary sequence outcrops in the St.Vincent and Murray Basins. Prior to analysis, all Holocene and fossil samples were brushed, soaked and washed in commercial bleach (4% sodium hypochlorite concentration) by the method recommended by Love and Woronow (1991) and Gaffey and Bronnimann (1993) for removal of organic material, then rinsed several times by deionised water and dried. Samples were then powdered using a dental drill or with a pestle and mortar. In the case of cements, sampling was carried out under binocular microscope using a dental drill or scalpel. For sclerochronology, samples were obtained by grinding shallow grooves (0.5 mm depth) into the outer shell layer of each whorl or growth line.

1.3.2. X-Ray Diffraction:

The mineralogy of the samples was determined by X-Ray diffraction (XRD) using a Phillips PW 1050 Diffractometer. A few drop of water were added to the finely pulverised sample and about 1/3 of a spatula full of powdered quartz was also added and then mixed. The spiked quartz acts as an internal reference. This mixture was then again ground by mortar and pestle to form the required slurry. The slurry was then smeared over 1/2 a cleaned and labelled glass slide. Samples were subjected to XRD analysis under the following conditions:

Diffractometer	Phillips PW 1050
Monochromator	Graphite
Radiation source	Cobalt Ka radiation. Wavelength 1.7902 Å
2-Ø Scanning range	3° to 75° with a steep interval of 0.05°

JCPDS Manuals and an X-Plot (developed by the CSIRO Division of Soils) computer package were used in the identification of the minerals.

The following equation was used to aid in determining mineral percentages

$$R = hA.wA / hA.wA + hC.wC$$

R= carbonate mineralogy
hA= height of aragonite peak
hC= height of calcite peak
wA= width of aragonite peak
wC= width of calcite peak

These results were compared to a standard curve for aragonite determination using peak height and width analysis (Milliman 1974). In most instances the standard deviation is considerably less than 5%. Mole % $MgCO_3$ was determined by running the sample carefully using the gwbasic mgcalc program.

1.3.3. Carbon and Oxygen Stable Isotope Analysis:

Samples were analysed for their oxygen and carbon isotopes using either a Micromass Model 602E stable isotope Mass Spectrometer or an Optima Micromass Spectrometer, the latter equipped with an Isocarb autorun device for carbonate samples. The former machine requires manual gas preparation and collection, using about 15 mg of powered sample whereas the latter needs about 0.2 mg of powered sample. In the manual method of CO_2 production from a carbonate sample, the powered carbonate sample was introduced into a glass container and after evacuation it was reacted with pure phosphoric acid to produce CO_2. The container was left in the water bath at 25°C for 12 hours for complete reaction of the sample with acid. The resulting CO_2 gas was injected into the mass spectrometer for measurement of carbon and oxygen isotopes according to standard procedures. The isotope results are presented in the standard form of per mil Pee Dee Belemnite (PDB) for carbonates and per mil vs Standard Mean Ocean Water (SMOW) for water samples. Standards (NBS. 19 and NBS. 18) and duplicate samples and several blanks were used to ensure high equipment precision and appropriate corrections have been applied to the results (See Chapter Two for review). All values are reported in the standard (δ) notation where;

$$\delta^{18}O = [(^{18}O/^{16}O)\text{ sample}/(^{18}O/^{16}O)\text{ standard} - 1]\,(10^3)\text{ per mil}$$

Determination of $\delta^{13}C$ were made concurrently with $\delta^{18}O$. Average reproducibility, as evidenced by duplicate analyses and a standard run before and after sample strings, was approximately ± 0.2‰ for the Micromass Model 602E and ± 0.1‰ for Optima Micromass Spectrometer. The precision for the 602E

Mass Spectrometer is ± 0.1 for $\delta^{13}C$ and ± 0.2 for $\delta^{18}O$ while for the Optima Mass Spectrometer the precision is ± 0.05 for $\delta^{13}C$ and ± 0.1 for $\delta^{18}O$.

The dissolved inorganic carbon (DIC) in seawater samples was analysed for $\delta^{13}C$ values by methods used by most researchers (e.g., Kroopnick 1974a; Bishop 1990). The measurement of carbon isotopic composition of water requires separation of the dissolved inorganic carbon. This is usually done by direct precipitation of dissolved bicarbonate in the form of strontium (or barium) carbonate. In this method, first, $SrCl_2$-NH_4OH solution was added to the water sample with a ratio of 1:9 in a well-sealed glass bottle and the cap of the bottle was sealed with PVC tape. After shaking, the bottle it was left for 48 hours to allow precipitation. The precipitate was filtered in the air on a glass-fibre filter paper using a water jet pump and then dried in an oven at 110°C for 4 hours. The precipitate was stored in an airtight container and placed in a desiccator until analysis in a mass spectrometer.

The $\delta^{18}O$ content of water samples was determined by CO_2-H_2O equilibration at 25°C, followed by mass spectrometer analysis of CO_2 as proposed by Epstein and Mayeda (1953). Accordingly, five millilitres of seawater was introduced to a glass container and then connected to the line by means of ground joints. The water was frozen with a freezing mixture of acetone and solid carbon dioxide (temperature about -70°C) and the air in the container was evacuated. The water was then melted and warmed to room temperature to release the air dissolved and trapped in the ice during the freezing; this air was then evacuated after re-freezing the water. Then, carbon dioxide with a known isotopic composition was introduced into the sample container, at a pressure somewhat lower than atmospheric. Some water samples of known isotopic composition (laboratory standards) were prepared at the same time and served as a control of the whole preparation. The containers with the water samples were then transferred into a thermostatic bath, at a temperature of 25.0 ± 0.1°C. Isotopic exchange took place between the CO_2 and water according to the reactions:

$$CO_2\,(g) \rightleftharpoons CO_2\,(aq)$$

$$CO_2\,(g) + H_2O \rightleftharpoons HCO_3^- + H^+$$

The isotopic exchange reaction is:

$$C^{16}O_2 + H_2{}^{18}O \rightleftharpoons C^{16}O^{18}O + H_2{}^{16}O$$

After a approximately one day this exchange reaction reaches equilibrium. The CO_2 was the extracted from the container, separated from the water vapour by means of a dry ice trap, and used for mass-spectrometric analysis. The equilibrated CO_2 has an $^{18}O/^{16}O$ ratio which is related to that of the water through a fractionation factor α:

$$(^{18}O/^{16}O)_{CO2} = \alpha\,(^{18}O/^{16}O)_{H2O(liq)}$$

which at 25°C has a value of 1.0412 ± 0.0001 (e.g., Friedman and O'Neil 1977). Appropriate corrections have been made for the salts content of the water and for equilibrium with CO_2.

1.3.4. Cathodoluminescence:

Cathodoluminescence (CL) is the primary excitation of a mineral in a vacuum by a beam of electrons produced by a cathode source (Marshall 1988). Fundamentally, the process of luminescence involves the excitation of an electron from the ground state to an excited state, followed by de-excitation back to the ground state. The de-excitation process is often accompanied by the emission of a photon. Luminescence in carbonates has been shown to be correlative primarily with the presence of certain trace elements, namely manganese (Mn^{2+}). The substitution of Ca^{2+} by Mn^{2+} typically gives rise to luminescence in calcites at the orange-yellow to orange red end of the spectrum. The maximum CL intensity appears to be determined by the iron to manganese (Fe^{2+}/Mn^{2+}) ratio. After examining all of the modern and fossil samples by staining, microscopic study and XRD analysis and being assured of a lack of diagenetic alteration in the supposedly well-preserved samples, they were re-examined by CL to distinguish any diagenetic alterations. All of the samples which were here claimed to be pristine, did not show any luminescence under the CL.

Cathodoluminescence has been extremely successful for distinguishing diagenetic events, developing cement stratigraphy and establishing paragenetic sequences (e.g., Frank et al. 1995). Zonation in carbonate crystals is a direct reflection of varying crystal growth rates and pore fluid chemistry changes. Zones of calcite depleted in Fe^{2+} but enriched in Mn^{2+} are noticeably brighter under CL. Accordingly, elemental analysis of a zoned calcite crystal showed variations in Mn^{2+}/Fe^{2+} ratio between dark and light regions. The meteoric cements in carbonate rocks usually present bright luminescence due to the Mn^{2+} content, thus signifying the reducing environment of diagenesis.

CL studies were carried out in a Technosyn Cold stage Luminoscope, model 8200MkII, using a cold cathode electron gun to supply the electrons. The resultant electron beam was fixed. In the vacuum chamber of the CL stage, the electron beam is absorbed by the surface it hits. Much of the incident energy is absorbed at the atomic level by electrons. Luminescence often results. Uncovered thin sections (100 micron thick) with high quality polished surfaces were used to obtain optimal details under CL. The extra thickness is needed for heat dissipation since the standard thin sections have a tendency to crack and burn. Abnormal heating of thinner sections can alter the colour of cathodoluminescence. Thin sections were prepared using a glue/cement that is stable at the moderate temperature generated in the process. Luminescence was recorded on Ektapress PC 1600 colour film.

1.3.5. Atomic Absorption Spectrometry :

Because of the high sensivity of atomic absorption spectrometry, it has been applied for determination of trace, minor and major elements. Atomic absorption depends on the phenomenon whereby atoms of an element being able to absorb electromagnetic radiation. This occurs when the atoms are unionised and unbound to other or similar atoms. The wave-length of light at which atomic absorption proceeds is specific for the type of atom and occurs at the resonant frequencies. These correspond to the electronic transitions between the first allowable energy level and the ground state of the atoms.

In practice the sample must be brought into solution, vaporised by means of a nebulizer and then the aerosol fractionation is passed into a flame. The temperature of the flame is sufficiently high to further reduce the droplets by dehydration and dissociation into an atomic form so that the analytical elements in the vapour exist mostly, and preferably, as neutral unbound atoms in the ground state. If the flame temperature is high, atoms may be raised to excited or even to ionised states. If this happens the population density of the ground state is decreased and the lower limit of detection is accordingly decreased.

The atomic vapour is illuminated by a light source radiating the characteristic light of the target analytical element. A spectrometer is usually used to select the resonance spectral line of the element and to measure its intensity. When the solution is sprayed, the atoms of the analytical element present absorb a portion of the light at the selected wave-length; the decrease in the intensity of the analytical line is measured by the spectrometer.

The procedure for determining the relationship between absorption and atomic concentration in the solution is to measure the absorbance of a number of solutions containing known concentrations of the analytical element and then to draw an analytical graph or working curve by plotting absorbance against concentration. This graph is linear at low concentrations but may deviate from linearity at higher concentrations.

In this study, trace elements were determined by Atomic Absorption Spectrometry using a VARIAN AA6D (the wet chemical analysis method) as follows:

1- Weigh the samples: The weight ranges from 0.974 to 2.4914 gram in Teflon beakers.

2- Add the acids required for digestion: 1 ml of concentrated HCl (70%).

3- Heat the solutions for 24 hours to ensure that the solution has completely evaporated.

4- Remove beakers from hot plate and allow to cool slightly, then add 10 ml HCl and add 10 ml La/K solution.

5- Make up to final volume (100 ml).

Finally, these solutions and standard samples were analysed by Atomic Absorption to determine the concentration of different trace elements in each sample.

CHAPTER TWO

ISOTOPIC EQUILIBRIUM VALUES: REVIEW, DISCUSSION AND CALCULATIONS

2.1. Introduction:

Interpretation of geochemical data for fossil carbonate-producing organisms require a comprehensive knowledge about their modern counterparts from diverse environments and an understanding of complex chemical and biological interactions between organisms and their environment. Therefore, the researcher should be familiar with all aspects of the geochemical processes of biomineralisation, seawater chemistry and inorganic versus organic calcium carbonate precipitation. Consequently, before geochemical data can be interpreted, an understanding of geochemical theory and processes is required.

Many calcareous shells/skeletons are precipitated in or close to chemical equilibrium with the surrounding seawater, and maintain thermodynamic stability in this depositional environment (e.g., Bathurst 1975). Consistently, for utilisation of fossils for paleoenvironmental, paleoclimatic and diagenetic investigations, organisms which are precipitating calcium carbonate in chemical (isotopic) equilibrium with their ambient environment should be recognised. In this study, the strategy is to compare biogenic (organic) carbonates with non-biogenic (inorganic) carbonates (marine cements), which are in chemical equilibrium with their ambient environment, to distinguish any deviations from equilibrium values in different organisms.

2.2. Oxygen and Carbon Isotopes in Calcium Carbonate - A Review:

Three factors determine the isotopic composition of a skeletal allochem: (1) the temperature of the ambient environment, (2) the $\delta^{18}O$ of the water and the $\delta^{13}C$ of dissolved inorganic carbon (DIC) in the water from which precipitation occurs, (3) physiological processes (vital/metabolic effects) and (or) kinetic effects. Due to slightly different degrees of isotopic fractionation of aragonite, Mg-calcite and calcite, paleotemperature equations accordingly are different for each mineral. Several different equations have been given for the calculation of paleotemperature from the difference between the isotopic compositions of calcite/aragonite and water (e.g., Epstein et al. 1953; Craig 1965; Shackelton and Opdyke 1973; Friedman and O'Neil 1977; Grossman and Ku 1986; Tucker and Wright 1990; Wefer and Berger 1991).

In this study, the modified paleotemperature equation (1) from Shackelton and Opdyke (1973) and Wefer and Berger (1991), is used for calcite and equation (2), a combination of that of Tucker and Wright (1990) and Grossman and Ku (1986), for aragonite:

$$T\,(^{\circ}C) = 16.9 - 4.38\,(\delta_C - \delta_w) + 0.10\,(\delta_C - \delta_w)^2 \qquad (1)$$

$$T\,(^{\circ}C) = 20.6 - 4.34\,(\delta^{18}O_{arg} - \delta_w) \qquad (2)$$

According to equation (1), $\delta^{18}O_{calcite}$ decreases by approximately 1‰ with every 4°C increase in temperature. Grossman and Ku (1986) found similar relationships for aragonite and Tarutani et al., (1969) for Mg-calcite. Diverse calcium carbonate minerals (aragonite vs. calcite) show different fractionation coefficients. Therefore, for aragonite equation (2) should be used. Aragonitic components of carbonate rocks have invaluable advantages for use in paleotemperature and diagenetic studies, because when they are preserved in the rock record, they represent their original (marine) isotopic and geochemical composition (e.g., Tourtelot and Rye 1969, Forester et al. 1973, Brand 1982).

According to Tarutani et al., (1969), the $\delta^{18}O$ value of calcite increases by approximately 0.06‰ for each mole% $MgCO_3$. Therefore, for example, biogenic high Mg-calcite (HMC) with 12 mole% $MgCO_3$ will have 0.72‰ more $\delta^{18}O$ than pure calcite precipitated from the same water at the same temperature.

The temperature dependency of carbon isotopic fractionation is relatively minor. For example, the relationships determined by Emrich et al., (1970) imply an enrichment in the solid phase of about 1.85‰ at 25°C and that $\delta^{13}C$ calcite increases by approximately 1‰ for every 27°C increase in temperature. However, Grossman and Ku (1986), by studying molluscs and foraminifera, showed that carbon isotope fractionation between these organisms and seawater DIC have some temperature dependency up to -0.13‰ $^{-1}$°C· The relatively minor temperature dependency of the fractionation of carbon, and doubts about its certainties over the magnitude of variation, abolish the use of carbon isotopic values for temperature determination. However, stratigraphic changes in carbonate carbon values are extremely useful as indicators of changes in the composition of the marine bicarbonate reservoir. Aragonite appears to incorporate more ^{13}C relative to calcite, but this isotopic enrichment tends to diminish with faster precipitation rates (Turner 1982).

Accordingly, Turner (1982) suggested that the $\delta^{13}C$ isotopic fractionation factor in $HCO_3^- - CaCO_3$ is dependent on the rate of precipitation and mineralogy, so that the $\delta^{13}C$ value in carbonates decreases with increasing precipitation rates. He conducted detailed and comprehensive experiments on the influences of the kinetic effects on the $\delta^{13}C$ fractionation of the inorganic calcium carbonate-bicarbonate ($\delta^{13}C_{\text{inorganic calcium carbonate—bicarbonate}}$) and confirmed that a very slow precipitation rate could produce $\delta^{13}C$ enrichment in the solid carbonate phase. During these experiments, when calcium carbonate was precipitated at different rates, the calcium carbonates – bicarbonate fractionation was greatly influenced by the precipitation rates. At low rates this fractionation is up to 3.37±0.36‰, but with an increase in precipitation rates, this decreases down to 0.35±0.23‰, at 25°C. Turner (1982) demonstrated that in co-precipitating calcite and aragonite, ^{13}C enrichment in aragonite is dependent on the precipitation rates and at rapid rates, aragonite would have ^{13}C values close to those of calcite. This indicates that at rapid precipitation rates, aragonite would also be affected by kinetic effects. His results showed the importance of precipitation rates on the ^{13}C fractionation in the system aragonite, calcite and bicarbonates. Experimental work by Romanek et al., (1992) on precipitation of carbonates, contradicts Turner's results, as they stated that for the range of rates studied by them, the precipitation rate has no significant effect on the $\delta^{13}C_{calcite - HCO3^-}$ fractionation. They suggested that temperature does not effect the $\delta^{13}C$ of inorganic aragonite, and that temperature dependence of $\varepsilon\delta^{13}C_{aragonite - HCO3^-}$ in biogenic aragonite may reflect an increase in the influence of the metabolic effect with temperature. They concluded that discrepancies between measured $\delta^{13}C$ values and experimental values do not reflect temperature or precipitation rates, but rather reflect (1) the difficulty in determining experimentally the real isotopic composition of the precipitating fluid (probably because of the microenvironments), and (2) the metabolic effects and physiological microenvironments.

However, in biogenic carbonates results similar to Turner's experiments on precipitation rates and heavy carbon and oxygen isotope contents have been found. Accordingly, Land et al., (1975) and McConnaughey (1989 a, b) showed that faster growing parts of photosynthetic corals are depleted in $\delta^{18}O$ and $\delta^{13}C$ compared to slower growing parts. These phenomena have been demonstrated by many workers for diverse biogenic carbonates (Vinot-Bertowlle and Duplessy, 1973; Erez, 1977 and 1978; Weil et al. 1981; McConnaughey 1989 a, b; Wefer and

Berger 1992; Rahimpour-Bonab et al. 1995, 1997a). On the other hand, the fractionation factor and the precipitation rate, at least in most biogenic carbonates, are dependent on the temperature of the ambient waters and, as shown in cool-water carbonate environments, precipitation rate decreases with the decline in the temperature of the ambient water. Grossman and Ku (1986) found similar results in their study of biogenic aragonite. Therefore, in cool-water environments, the ^{13}C fractionation between aragonite and calcite could reach its maximum values (Rahimpour-Bonab et al. 1997b). The ^{13}C fractionation between aragonite and calcite ($\delta^{13}C_{aragonite - calcite}$) at low precipitation rates, which diminishes the influence of the kinetic fractionation effect on the ^{13}C of aragonite, is about 1.8 ± 0.2‰ (Rubinson and Clayton 1969), 1.6± 0.35‰ (Turner 1982) or 1.7± 0.4‰ (Romanek et al. 1992).

Disequilibrium precipitation both for oxygen and carbon isotopes through biological fractionations is a common phenomenon. The degree of disequilibrium is generally smaller for oxygen than for carbon, because there is a large source of oxygen (i.e., seawater) but a smaller one for carbon (mostly dissolved bicarbonate). Therefore, oxygen isotopic values in many faunal groups are close to equilibrium values, especially in the cool-water environment (Rahimpour-Bonab et al. 1995, 1997a, b). Carbon isotopic values are much more influenced by metabolic effects (e.g., McConnaughey 1989a). Early research on the isotopic geochemistry (Urey et al. 1951; Lowenstam and Epstein 1954, 1957; Weber 1964, 1967) loosely defined those biological/kinetic effects that influenced stable isotope fractionation during biogenic carbonate production as "vital/metabolic effects".

Recent progress in the field of isotopic palaeontology and paleotemperature studies is summarised by Swart (1983), McConnaughey (1989 a, b), Land (1989) and Wefer and Berger (1992). These authors have shown that isotopic disequilibrium during biogenic calcification is caused by kinetic and metabolic effects. When there is a simultaneous depletion in both ^{18}O and ^{13}C, it is attributed to kinetic effects. According to McConnaughey (1989 a), a kinetic effect is the isotopic fractionation occurring during CO_2 hydration and hydroxylation, which is an important process in biological calcification. The modifying influences of photosynthesis and respiration on the isotopic composition of the DIC of reservoir (seawater) are described as metabolic effects. Metabolic effects on the isotopic composition of biogenic carbonate manifest as deviations of $\delta^{13}C$ from equilibrium values that are not associated with $\delta^{18}O$ offset (Land et al. 1975; McConnaughey 1989 a). Thus, changes in the $\delta^{13}C$ of the DIC reservoir caused by photosynthesis and respiration, and consequent changes in the $\delta^{13}C$ of precipitated $CaCO_3$ are termed "metabolic" isotope effects.

The incorporation of isotopically negative respiratory carbon leads to isotopically lighter carbonate whereas the removal of light carbon by photosynthesis from ambient seawaters causes a heavier carbon contribution in biogenic carbonates. The extent of difference varies for different groups of organisms, so whereas brachiopods (Veizer et al. 1986; Popp et al. 1986; Brand 1989a, b; Grossman et al. 1991; Carpenter and Lohmann 1995; Rahimpour-Bonab et al. 1997b; and this study), bryozoans (Foster et al. 1973; Rao 1993; Rahimpour-Bonab et al. 1995 and 1997a; Bone and James 1997; and this study) and many molluscs (Morrison and Brand 1985; Krantz et al. 1987; Brand 1989; Land 1989; Romanek and Grossman. 1989; Wefer and Berger 1991; Rio et al. 1992; Geary et al. 1992; Mitchell et al. 1994; Israelson et al. 1994; Rahimpour-Bonab et al. 1997b; and this study) seem to precipitate their shells in or close to isotopic equilibrium, groups such as the echinoderms, some corals and calcareous algae commonly form carbonate which is far from equilibrium (Land et al. 1977; Swart 1980, 1983; Holmes 1983; Aharon and Chapell 1986; Land 1989; McConnaughey 1989a and b; Leder et al. 1990; Wefer and Berger 1991; Aharon 1991; Rahimpour-Bonab et al. 1995, and 1997a;

and this study). Weber and Woodhead (1972) suggested that with faster excretion of metabolic CO_2 to seawater, little or no metabolic carbon dioxide is incorporated in the skeleton, and accordingly organisms with more advanced and efficient respiratory systems should incorporate lesser amounts of metabolic CO_2. Grossman and Ku (1986) pointed out that due to the influence of biological and microhabitat effects on the carbon isotopic composition, interpretations of carbon isotopic data are generally more complicated. However, as shown by Rahimpour-Bonab et al., (1995, and 1997a, b), the temperature of the ambient environment has a great influence on the isotopic equilibrium precipitation of different calcareous organisms. Accordingly, a lower ambient temperature leads to a lower precipitation rate and consequently closer isotopic composition of organic, and even inorganic, carbonates to equilibrium values (next section and Chapter Three).

As emphasised before, the effects of the ambient environment on the isotopic compositions of skeletal and non-skeletal carbonate are important. Several studies have indicated that the isotopic chemistry of the water column overlying the carbonate environment can vary in response to evaporation (i.e., enrichment in $\delta^{18}O$ and $\delta^{13}C$), fresh water mixing (depletion in $\delta^{18}O$ of water); photosynthesis by planktonic algae and other photosynthetic organisms (increase in the $\delta^{13}C$ of DIC); respiration by different organisms (depletion in $\delta^{18}O$ and $\delta^{13}C$ of DIC); upwelling events; changes in pH and salinity; and, the most important factor, the temperature of the precipitation medium. Undoubtedly these isotopic changes occurring in the ambient carbonate environment leave their imprint on the skeletal carbonate which forms the basis of the isotopic record. Therefore, these variations in isotopic values of biogenic and non-biogenic calcium carbonate are extremely useful as indicators of secular changes in the seawater DIC reservoir through time and other geochemical/geological events such as biomass movement between oceans and continents due to climatic changes during glacial and interglacial periods, which are discussed in the following chapters.

2.3. Calculations of the Isotopic Equilibrium :

For the investigation of the isotopic equilibrium and disequilibrium, metabolic /kinetic effects in different carbonate producing organisms and inorganic carbonates (marine cements), the mineralogy and isotopic composition of these carbonates, as well as the temperature and isotopic composition of the ambient seawater, have been measured. These studies showed that the Lacepede Shelf HMC cements have precipitated in isotopic equilibrium with their ambient waters. Therefore, they can be used as a datum for distinguishing equilibrium versus disequilibrium in the isotopic composition of different biogenic carbonates. The values are within the range of the isotopic composition of inorganic equilibrium calcites from other areas (Morrison and Brand, 1986; Land, 1989) (See Fig. 3.1 and 3.14). The equilibrium values for the study area are confirmed by calculating the isotopic equilibrium values by measuring the seawater isotopic composition and the temperature ranges of this area. For calculation of the equilibrium isotopic fractionations in inorganic equilibrium marine calcite from the area, mean annual temperatures recorded at each sampling site, have been used (Fig. 2.1).

2.3.1. Seawater isotopic composition:

In the study area, the $\delta^{13}C_{DIC}$ of the seawater samples showed values between +0.05 to +0.7‰ (Table 2.1) which are somewhat lighter than typical values of seawater which ranges between -1 to +2‰ but are mainly about +2‰ (Deuser and Degens 1967; Deuser and Hunt 1969; Vogel et al. 1970; Weber and Woodhead 1971; Kroopnick, 1974 a, b, 1985; Land 1989). This relatively light $\delta^{13}C_{DIC}$ possibly is a reflection of the influx of the ^{13}C-depleted upwelling current in the neighbouring area of the Bonney Shelf. Thus, in the temperate environment of the Lacepede Shelf and the Great Australian Bight, the $\delta^{13}C_{DIC}$ value of seawater shows relatively lower values in comparison with world-wide average values.

Table 2.1. Isotopic composition and temperature of seawater from Lacepede Shelf• and Great Australian Bight at different depths, January 1995 and October 1995.

Depth m	Temp. °C Summer	 Winter	$\delta^{18}O$	$\delta^{13}C$
0•	18	17	0.05	0.7
0•	18	17	0.0	0.6
0•	18	17	0.04	0.6
0•	18	17	0.03	0.2
0	18	17	0.05	0.7
20	18	17	0.05	0.6
40	16	17	0.0	0.2
60	14	16.5	0.03	0.4
100	12.5	16	0.04	0.1
200	11	15	0.06	0.2

2.3.2. Inorganic Carbonates:

In the study area marine cements are HMC with an average $MgCO_3$ of 11.5 mole%. Table 2.2 shows the isotopic composition, depth, mineralogy and calculated temperature of formation of these cements. These calculated temperatures are compared with recorded temperatures. These HMC marine cements are mostly found inside and sometimes outside, bivalve and brachiopod shells, where they cemented fine quartz sand grains onto the shell.

The origin of these cements is of prime importance in an interpretation of their isotopic composition. The occurrence of these cements is presumably due to seawater supersaturation under appropriate pH conditions with slow precipitation rates (physicochemical precipitation). Since no indication of a connection between the cement precipitation and the decay of organic material has been seen under the microscope , and because of the location of the cement (which is not in micropores), the possibility of biochemical influences on the cement precipitation is ruled out. Moreover, the $\delta^{13}C$ value of these cements does not exhibit any contribution of organic materials. In fact, they are examples of cementation and lithification of marine sands by physico-chemical processes, as observed by many researchers in marine environments (for example, Shinn 1969; Alexandersson 1974) and are formed as early diagenetic the marine cement. Moreover, since the

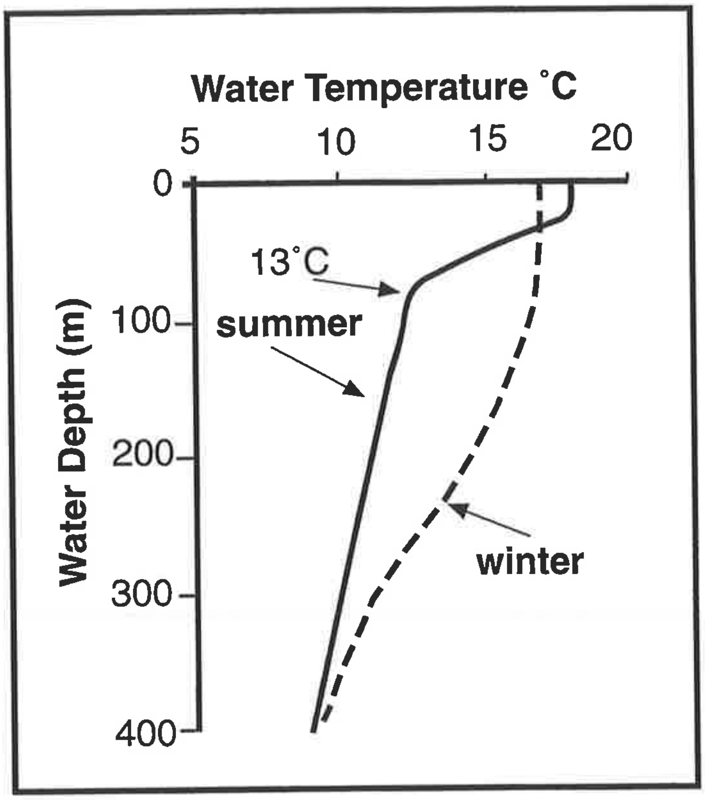


Fig. 2.1. The summer and winter temperature profiles for the Lacepede Shelf area (Modified from James et al. 1992).

process of cementation is extracellular and the cements are found on dead organisms, biological isotopic fractionation had no significant influence on their isotopic composition. As such, the isotopic composition of these cements should represent the surrounding seawater composition. This hypothesis is confirmed by the temperature of precipitation of these cements calculated from their $\delta^{18}O$ values, which is close to the average temperature in the area (Table 2.2 and Fig. 2.1).

Table 2.2. Isotopic compositions and calculated isotopic temperatures of the HMC marine cements (corrected values for $MgCO_3$ content) found in different depths of the Lacepede Shelf, compared with measured temperatures in this area.

Sample Sites	Depth m	Mg content Mole%	$\delta^{18}O$	$\delta^{13}C$	Calculated Temp.°C	Measured Temp. °C	
						summer	winter
24	65	12	1.00	2.39	15.7	14.2	16.8
34	70	12	1.20	2.42	14.8	13.5	16.8
47	80	11.5	1.35	2.40	14.0	13.0	16.8
130	90	12	1.40	2.35	13.9	12.3	16.8
111	100	12	1.75	2.86	12.4	12.0	16.4
140	100	11	1.30	2.30	13.8	12.0	16.4
30	140	12	1.40	2.34	14.0	11.8	15.3
155	180	11.5	1.60	1.80	12.8	11.0	15.0
103	300	11	1.68	1.62	10.8	10.0	11.2

2.3.3. The $\delta^{18}O$ Equilibrium Calculations:

To evaluate deviations from equilibrium values in the biogenic carbonate, potential equilibrium marine cements that could precipitate from seawater in this area have been calculated. These results were compared with the actual values of HMC marine cements (Table 2.2). The $\delta^{18}O$ of the equilibrium potential LMC marine cement (that theoretically could precipitate from seawater in this area) has been estimated by applying the seawater isotopic values and temperature records of the study area (Tables 2.1 and 2.2) to equation (1). This gives 0.25 to 1.8‰ for $\delta^{18}O$ values of potential equilibrium inorganic LMC. The $\delta^{18}O$ values of potential equilibrium inorganic HMC (11 mole% $MgCO_3$), by applying corrections for $MgCO_3$ content (Tarutani et al. 1969), is 0.94 to 2.46‰. These results are close to the actual $\delta^{18}O$ values of HMC marine cements (1.0 to 1.75‰) found in this area (Table 2.2). Therefore, isotopic values of HMC marine cement reconfirm the calculated equilibrium values for this area, and so they, as some researchers suggest, (e. g., Lohmann and Meyers, 1977; Gonzalez and Lohmann, 1985; Aharon 1991), precipitate in equilibrium with the environment. Due to the temperature prevailing in this area, however, aragonite has not precipitated as an inorganic marine cement in the area. Therefore, $\delta^{18}O$ values of potential equilibrium aragonite have been calculated from equation (2), which gives values of 0.6 to 2.7‰. Moreover, to substantiate these figures, appropriate corrections have been applied for fractionation between calcite and aragonite (Tarutani et al. 1969), giving $\delta^{18}O$ values of 1.6 to 2.35‰, which are in the range of calculated values.

2.3.4. The $\delta^{13}C$ equilibrium calculations:

In temperate carbonate environments, due to the low temperature and lower seawater saturation with respect to carbonate, precipitation rates are slow (e.g., Nelson 1988 and references therein). Therefore, kinetic effects have minimum influence on the fractionation factor of the $\delta^{13}C_{aragonite} - \delta^{13}C_{HCO3^-}$ and $\delta^{13}C_{calcite} - \delta^{13}C_{HCO3^-}$. Thus, in such environments, because of low precipitation rates, calcite-bicarbonate and aragonite-bicarbonate fractionation factors should be close to maximum values, i.e., about 2.3‰ (Bottinga 1968) or 2.26±0.32‰ to 1.83±0.32‰ (Turner 1982) for calcite, and 3.8±0.32‰ (Turner 1982) or 2.7±0.2‰ (Rubinson and Clayton 1969) for aragonite. The $\delta^{13}C$ values of the inorganic HMC cement from this area are between 1.62 to 2.86‰ (Table 2.2). Considering the fractionation factor for HCO_3^- – Calcite of about 2.26‰, and seawater DIC values of between 0.0 to +0.50‰ in this area, HMC equilibrium cement would have $\delta^{13}C$ values between 1.51 to 2.46‰. These figures are close to the $\delta^{13}C$ values of the HMC marine cements (1.62 to 2.86‰) actually found in the area.

The following equation for calculation of $\delta^{13}C$ values of equilibrium inorganic aragonite from Grossman and Ku (19860) has been used:

$$\delta^{13}C_{Aragonite} - \delta^{13}C_{DIC} = 2.66 - 0.131t\,(^{\circ}C) \qquad (3)$$

Using this equation gives $\delta^{13}C$ values between 0.57 to 1.15‰ for equilibrium aragonite, but using the correction introduced by Gonzalez and Lohmann (1985) (average $\varepsilon^{13}C_{aragonite\ -\ calcite} = 1.2$‰) values of 2.8 to 4.05‰ for $\delta^{13}C$ of equilibrium aragonite have been resulted.

No enrichment in the $\delta^{13}C$ of the HMC has been reported for $MgCO_3$ content and so its $\delta^{13}C$ is equal to LMC (See Fig. 3.14). For oxygen, the size of the equilibrium fields demonstrates the temperature range in the area and its influence on the oxygen isotopic values of precipitating carbonates. In the case of carbon, the size of the equilibrium field depicts the possible daily variations in the carbon composition that can be attributed to respiration (Weber and Woodhead 1970) or other biological effects (Gonzalez and Lohman 1985).

2.4. Conclusion:

The slow precipitation of inorganic calcite and aragonite from dissolved bicarbonates in seawater in the study area resulting from lower temperatures and seawater saturation, appears to produce an equilibrium isotope fractionation for carbon as well as oxygen, and to diminish the influence of the kinetic effects. These established equilibrium values are used in this study to recognise organisms that precipitate their calcareous skeletons in isotopic equilibrium with their ambient seawater. Then, the latter are utilised for further paleoenvironmental, paleoclimatic and diagenetic investigations of Tertiary carbonate sediments.

CHAPTER THREE

GEOCHEMISTRY AND BIOMINERALISATION OF SOME HOLOCENE COOL-WATER CARBONATE-PRODUCING ORGANISMS

3.1. Introduction:

Since 1951, when Urey et al., (1951) pointed out that the oxygen isotopic composition of carbonate minerals is controlled by the temperature and the oxygen isotopic composition of the water from which precipitation occurs, extensive analyses of carbonate secreting-organisms and limestones have been carried out primarily for determining past oceanic temperatures and secondly for distinguishing diagenetic processes (e.g., Hudson and Anderson 1988; McConnaughey 1989 a, b; Wefer and Berger 1991; Marshall 1992).

Due mainly to the diagenetic effects on the sedimentary records, and also to the possibility of initial non-equilibrium precipitation/calcification of biogenic carbonates, there are some uncertainties about the initial geochemical composition of limestones and whether they do enable the preservation of their primary environmental geochemical signature. Therefore, the composition of Holocene sedimentary components of the carbonate environments should be determined to provide a baseline for the geochemical composition of different organisms and to determine useful organisms for geochemical investigations and consequent paleoenvironmental, paleotemperature and paleoclimatic reconstructions. Moreover, utilising these data enables us to recognise any possible diagenetic alterations in diverse sedimentary components.

The geochemical and isotopic composition of various components of the carbonate sediments and rocks should be determined individually for interpretation of these sediments. As Popp et al., (1986 b) pointed out, whole rock samples are a mixture of different diagenetic and depositional phases, and therefore, their isotopic compositions do not necessarily reflect the original (depositional) values but rather the input due to the ratio of the different components. Therefore, in the study of the geochemistry of carbonate rocks and sediments it is unreasonable to presume samples are homogenous, but rather that there are a number of diverse constituents, such as corals, molluscs, brachiopods, oolites, cements, and so on, each having different isotopic and trace element values.

Hitherto, most investigations have been focused on the tropical skeletal and non-skeletal carbonates and so there is a paucity of knowledge about cold/cool water skeletal and non-skeletal carbonate isotopic compositions, equilibrium states, and calcification rates. Grossman (1984) stated that "our understanding of ^{13}C fractionation in biogenic carbonates suffers from a poor understanding of isotopic equilibrium at low temperatures due to the lack of inorganic precipitation data. Further studies should focus on this problem and also on determining accurate ε_{s-b} ($\delta^{13}C_{\text{calcium carbonate - DIC}}$ fractionation) values for other fauna (other than foraminifera) that are known to precipitate their shells in ^{18}O equilibrium with the water". As such, Romanek et al., (1992) stated that in spite of the fact that carbon isotopes are widely used in carbonates as paleoenvironmental and diagenetic tools, there are few comprehensive studies on the influences of mineralogy, temperature and precipitation rates on the isotopic fractionation of carbonates.

The isotopic composition of carbonate skeletons and cements varies in response to a wide range of environmental parameters (extrinsic factors) such as evaporation, condensation, precipitation/calcification rates, and temperature. In the case of biogenic carbonates, intrinsic factors such as metabolic fractionation and photosynthesis can also influence the isotopic compositions. The source of carbon and oxygen also have a major influence on the isotopic composition of the precipitated carbonates. Mineralogy has some effect on the isotopic composition of precipitating carbonates, as aragonite co-precipitating with calcite in the same environment is enriched in the heavier carbon and oxygen isotopes. The mineralogical enrichment itself is probably dependent on the precipitation rate which, in turn, could be influenced by the temperature of the ambient water, at least in biogenic aragonite (Grossman and Ku, 1986). Kinetic effects, the major cause of the simultaneous depletion of carbon and oxygen isotopes at high precipitation rates, are reduced by a decrease in the precipitation rates (e.g., Turner 1982). Thus, relative concentrations of the stable isotopes of carbon and oxygen in biogenic and inorganic carbonates give information about the different mechanisms of $CaCO_3$ precipitation.

Salinity does not directly affect the isotopic composition of biogenic or inorganic carbonates, but its variation from the normal values for the open seas indicates the influences of different factors such as evaporation or influx of freshwater runoff. So, freshwater dilution causes lighter isotopic values in the resulting precipitating carbonates. It seems that the small influx of River Murray waters onto the Lacepede Shelf has not had a major effect on the seawater salinity because the salinity in this area is in the normal range (James et al. 1992). In this area, evaporation is not important because of year-round low temperatures.

Disequilibrium in the isotopic composition of biogenic carbonates can be caused by either metabolic or kinetic effects. In the case of metabolic effects, respiration usually leads to ^{13}C depletion in biogenic carbonates whereas photosynthesis leads to ^{13}C enrichment. Therefore, if only the $\delta^{13}C$ is out of equilibrium, the disequilibrium could be ascribed to metabolic effects. Kinetic effects on carbonate precipitation, however, involve discrimination against both heavy isotopes, carbon and oxygen. Kinetic effects seem to be particularly effective during rapid carbonate precipitation in non-biogenic (inorganic) (Turner 1982) and biogenic carbonates (e.g., Weil et al. 1981; McConnaughey 1989a, b). On the other hand, in temperate carbonate environments the growth rates of the different calcareous organisms are slow due to low temperatures (Rahimpour-Bonab et al. 1997a, b). Moreover, at these low temperatures, inorganic carbonate cements are not common and precipitate slowly.

In temperate environments, because of the lower temperatures, growth rates tend to be slow, and similar to other oceanic environments, the $\delta^{18}O$ of seawater is constant and close to 0.0‰. Therefore, the $\delta^{18}O$ of diverse calcareous organisms are mainly dependent on the temperature of ambient waters and possible kinetic/metabolic effects. On the other hand, factors that influence the $\delta^{13}C$ values of marine biogenic carbonates include: (a) the isotopic composition of the inorganic carbon dissolved in seawater (DIC); (b) the equilibrium fractionation factors between the various forms of carbon; (c) dependency and variations of the $\delta^{13}C$ fractionation factors with temperature; (d) influx of $\delta^{13}C$-depleted upwelling currents, and (e) the possible influence of the metabolic and/or kinetic effects.

In this chapter the aims are: 1) to comprehend differences in the isotopic compositions of various organisms in different environments; 2) to prepare a data-base for the geochemistry of calcareous marine organisms from temperate environments; 3) to distinguish equilibrium and non-equilibrium carbonate production among different carbonate-producing organisms; (4) to compare the biomineralisation processes in these cool-water organisms with their warm-water counterparts and (5) to determine the potential value of different calcareous organisms for paleoenvironmental investigations.

3.2. Coralline Algae:

Coralline algae are prominent sediment producers among marine plants because of their ability to deposit large amount of calcium carbonate in their cell walls. Their mineralogy is HMC, and in fact, coralline algae are the only marine macroalgae depositing calcite, because other calcifying red algae, as well as some green algae, deposit aragonite (Johanson 1981). Today their contribution to carbonate deposition in shallow tropical waters, along with green algae, can reach levels of 61% of bulk sediments (Wefer et al. 1980), but in temperate environments only coralline algae are conspicuous. Contrary to common belief, coralline algae are not limited to shallow tropical-subtropical waters. Recently, coralline algal reefs have been discovered in the skerries of northern Norway (Henrich et al. 1995), but these reefs and build-ups are not as large as their tropical counterparts. Parameters that govern formation of the modern Arctic reef and build ups are not known (Henrich et al. 1995). Coralline algae have been important reef builders since the early Palaeozoic and usually constitute more than 20% of the reef sediments and locally more than 50% (Emery 1956).

The coralline algae (red algae) in the reef environments act predominantly as cementers and encrusters, rather than sediment contributors and photosynthesizers (Marsh 1970). Therefore, coralline algae in most benthic communities construct stable bioherms, by fixing the loose grains as hardened rocks. Because of the lack of substrate and probably low energy, coralline algae are less abundant in lagoonal environments. The rate of carbonate production by coralline algae is higher in the photic zone, but because calcification does occur in the aphotic zone too, Pearse (1972) suggested that these algae may utilise some other catalyst (other than photosynthesis) during calcification. Temperature has a significant influence on the ecology of the coralline algae, with some genera restricted to tropical-subtropical waters (Johanson 1981).

Coralline algae (Order Cryptonemiales, Family Corallinaceae) have a rigid skeletal structure formed by the precipitation of carbonate both within and between the cell walls (Johnson 1961). Calcification in some members of the Order Nemalionles (Family Chaetangiaceae) is not as complete as in the algae of the Order Cryptonemiales. Therefore these organisms are not considered significant carbonate sediment-contributors in shallow marine environments (Adey and MacIntyre 1973). Coralline algae are subdivided into three subfamilies; Lithophylloideae; Mastophorideae and Melobesoideae (Adey and Johansen 1972). Three basic morphologies are exhibited by coralline algae: (a) laminar crusts made up of basal perithallus, with sub-horizontal filaments of cells, (b) branches rising from crusts which show a central medullary zone, (c) articulating branches in which uncalcified genicalae divide calcified segments.

Melobesoideae are crustose and massive, prominent carbonate sediment-contributors, and inhabit areas from high energy to quiet waters. Specific crustose and encrusting genera such as *Lithothamnium* are found in tropical to polar seas. Their diversity increases in higher latitudes relative to other species of coralline algae (Johnson 1961, Adey and MacIntyre 1973). Articulated coralline algae are generally limited to sheltered environments, with the four common genera being *Amphiroa*, *Cheilosporum*, *Corallina* and *Jania*, but in southern and eastern Australia the most important genus is *Metagoniolithon* (Johansen 1981) and the encrusting form is *Lepthophytum*. High energy in southern Australia gives rise to Rodolith pavement (Y. Bone, *pers. comm.* 1997).

The isotopic composition of benthic calcareous algae is of interest in both biological and geological studies, but in spite of their abundance in coral reefs and temperate environments, these algae have received little attention geochemically. Since they are significantly present in the geologic record and have been responsible for the build-up of enormous masses of limestone, their remains could be useful in biostratigraphy and for paleoenvironmental reconstruction. Variations in the stable isotope composition of the algae may also be useful for the analysis of calcification processes (Borowitzka and Larkum 1986). Additionally, they are commonly found in association with invertebrates, especially in marine environments. Thus they can be used for interpretation of the depositional environments. Rahimpour-Bonab et al., (1997a) reported the first detailed evidence on the systematic relationship of the isotopic composition of different types of coralline algae from the temperate carbonate environment and compared them with their warm-water counterparts.

Distribution of the $\delta^{18}O$ and $\delta^{13}C$ in skeletal carbonate of articulated and crustose algae are presented in Fig. 3.1. As demonstrated, calcitic coralline algae from tropical environment exhibit a completely different range of carbon and oxygen isotopes in comparison to equilibrium HMC and aragonitic algae from the same environment. Depleted $\delta^{18}O$ values perceived in the tropical red algae (in comparison with green algae) suggest that they incorporate metabolic and seawater-derived CO_2 at the site of calcification (Keith and Weber 1965; Craig 1953; Wefer and Berger 1981) or some of these offsets may be due to mineralogical differences. In the cool-water samples (Fig. 3.1), the $\delta^{18}O$ values are within or close to the equilibrium values and are heavier than their tropical counterparts. Another characteristic of the $\delta^{18}O$ value of tropical coralline algae is their wider range, in comparison with cool-water samples. This may be caused by greater evaporation or freshwater influx in tropical waters. The $\delta^{18}O$ values of aragonitic algae (green algae) are higher than those of calcitic ones from the same environment, which possibly is due to the higher ^{18}O incorporation in aragonite compared to calcite, as suggested by Turatani et al., (1969).

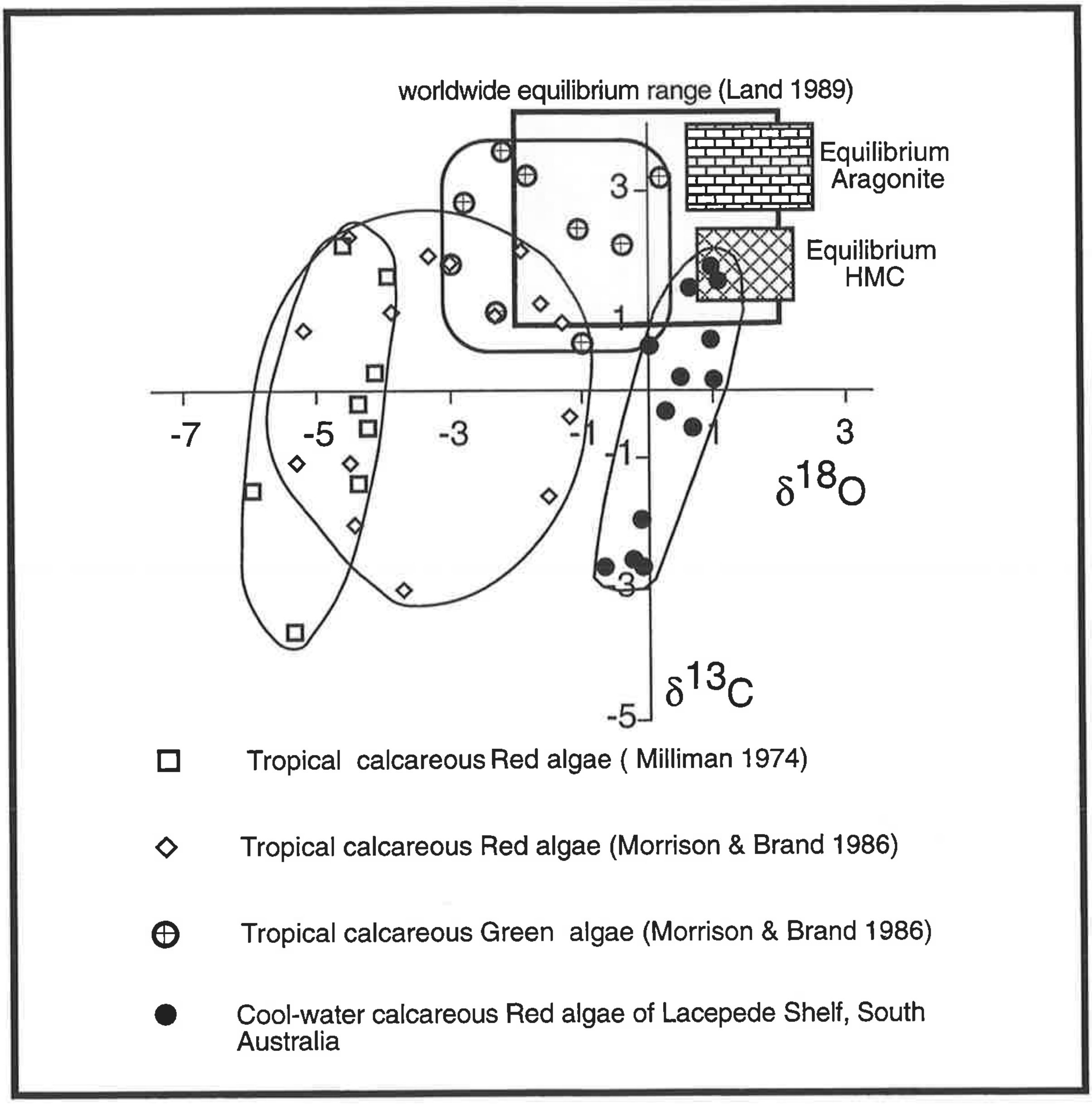


Fig. 3.1. Isotopic composition of different calcareous algae from temperate and tropical environments. Equilibrium values for aragonite and high Mg-calcite are calculated for the area.

The $\delta^{13}C$ values of Lacepede Shelf coralline algae are similar to the $\delta^{13}C$ of the tropical samples. Thus it seems that the carbon of the coralline algae from different environments has a similar origin, such as photosynthesis and respiration, and reflects the influences of similar metabolic processes, regardless of environment.

Many workers suggested that because of vital effects, the isotopic composition of both articulated and crustose algae is an unreliable indicator of seawater isotopic compositions and temperature (Craig 1953; Keith and Weber 1965; Wefer and Berger 1981, 1991; Marshall 1991). It is proposed that, in the case of the $\delta^{18}O$, the main parameter affecting the isotopic composition of coralline algae in the temperate environments is temperature, not vital/metabolic effects and that their $\delta^{18}O$ contents are within the ranges of the equilibrium values or close to it. Therefore, the $\delta^{18}O$ values of fossil coralline algae from temperate environments could be used for paleotemperature determination, provided no diagenetic overprint has occurred.

Despite evaporation effects in tropical environments causing some enrichment of $\delta^{18}O$, cool-water coralline algae are still more enriched in $\delta^{18}O$ than their warm water counterparts, thus indicating that the influence of ambient temperature on the isotopic composition of algal carbonate is far more important than the specific isotope values in the ambient seawater (reservoir effects). The lessening of intensity of metabolic processes and thus, reducing the carbonate production rate due to lower temperature of the environment, and so a lesser significance of kinetic effects, is probably the cause of higher $\delta^{18}O$ values of cool-water coralline algae. This indicates that the influence of temperature on the isotopic composition of the biogenic carbonate is far more important than the specific isotope values in the ambient seawater (reservoir effects).

3.3. Corals:

Ahermatypic corals (azooxanthellae), according to their environment, can be divided into three major groups; (a) shallow warm-water; (b) deep-sea; and (c) cool/cold-water. They calcify at lower rates than hermatypic corals (zooxanthellae) (Milliman 1974; Swart 1983; Aharon 1991; Dodd and Stanton 1990), growing approximately 1 cm/yr. in comparison to the 15 to 26 cm/yr. of hermatypic forms. The rapid precipitation of calcium carbonate by hermatypic corals is related to uptake of respiratory CO_2 by zooxanthellae (Goreau 1961). Goreau (1961) suggested that photosynthesis by these symbiotic algae consumes CO_2 and HCO_3, which accelerates the breakdown of H_2CO_3 and which increases the calcification rate.

Ahermatypic corals are widespread benthic carbonate (aragonite) producers on the deep sea floor at most latitudes, spanning the entire temperature range of the recent oceanic environments. So, if systematic variations in their isotopic compositions can be unravelled, as they have been for the hermatypes, then they too could be useful for understanding such environments. In the hermatypic reef corals, as Milliman (1974) pointed out, $\delta^{18}O$, as a function of temperature, can be determined only over a relatively narrow temperature range (20-30˚C), whereas the ahermatypic corals are distributed at all latitudes in modern oceans (Milliman 1974; Dodd and Stanton 1990). Therefore, using ahermatypic corals, the influence of temperature on the $\delta^{18}O$ content of skeletal carbonates (between approximately 0-30°C) can be extended (Milliman 1974).

It is known that corals incorporate both metabolic CO_2 and inorganic bicarbonate obtained from seawater into their skeletal carbonate (Pearse 1970). In ahermatypic corals, the $\delta^{18}O$ content is temperature-dependent but the actual relationship varies between genera (Bowen 1991). Hermatypes are usually isotopically heavier than ahermatypes, not because they eliminate metabolic CO_2 to their endosymbionts more efficiently than ahermatypes do to seawater, but because of the higher uptake rate of isotopically heavy seawater bicarbonate to meet the carbon demands of the zooxanthellae (Goreau 1977).

Little is known about the isotopic composition of ahermatypes from the deep-sea and especially from temperate environments. The lower temperature of this area compared to tropical environments, which is associated with low calcification rates in these corals, could provide coral samples with isotopic composition close to equilibrium values. The isotopic values of the ahermatypic corals (Fig. 3.2) are the heaviest isotopic compositions in this group that have been reported so far, confirming their lower calcification rates. However, even the studied coral samples that show the highest values of $\delta^{18}O$ and $\delta^{13}C$ in ahermatypic corals, are only partly in equilibrium with their ambient environments. This is mainly due to kinetic effects (on the isotopic composition of these corals), causing simultaneous depletion in both $\delta^{18}O$ and $\delta^{13}C$. However, as shown in Table 3.1, the ambient water temperatures determined by $\delta^{18}O$ content of the ahermatypic coral *Cullicia tenella* for the study area, are constantly about 2.05 to 2.6°C higher than the recorded mean annual temperature. Therefore, although the $\delta^{18}O$ value of these corals is not in equilibrium with their ambient water, but shows systematic variations (about 0.5 to 0.65‰ constant offset compared to equilibrium values), and allows a mean calibration of 0.58‰ for these coral samples, giving water temperature estimates with reasonable precision (Table 3.1, Figs 3.3 and 3.4).

The $\delta^{18}O$ offset of coral aragonite is related to the equilibrium isotopic partitioning, by the following relation (Weber and Woodhead 1972):

$$\delta^{18}O_{coral} = \delta^{18}O_{equil.} + \delta^{18}O_{offset}$$

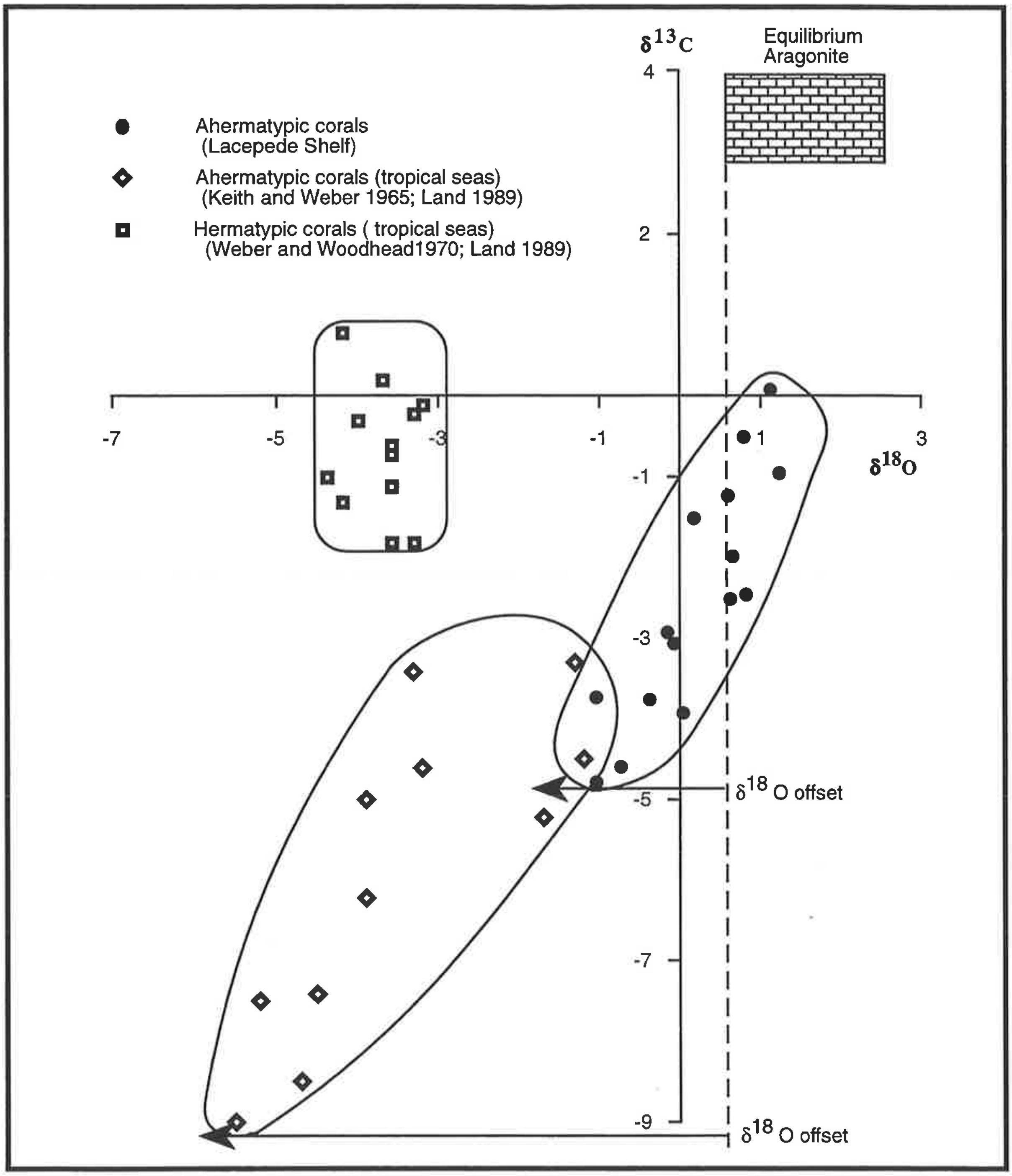


Fig. 3.2. Relationships between isotopic compositions of hermatypic and ahermatypic corals from tropical and temperate environments. The δ^{18} O isotopic values of tropical samples exhibit more offset than their temperate counterparts. Tropical ahermatypic corals are more depleted in δ^{13}C in comparison with their temperate counterparts and with hermatypic corals.

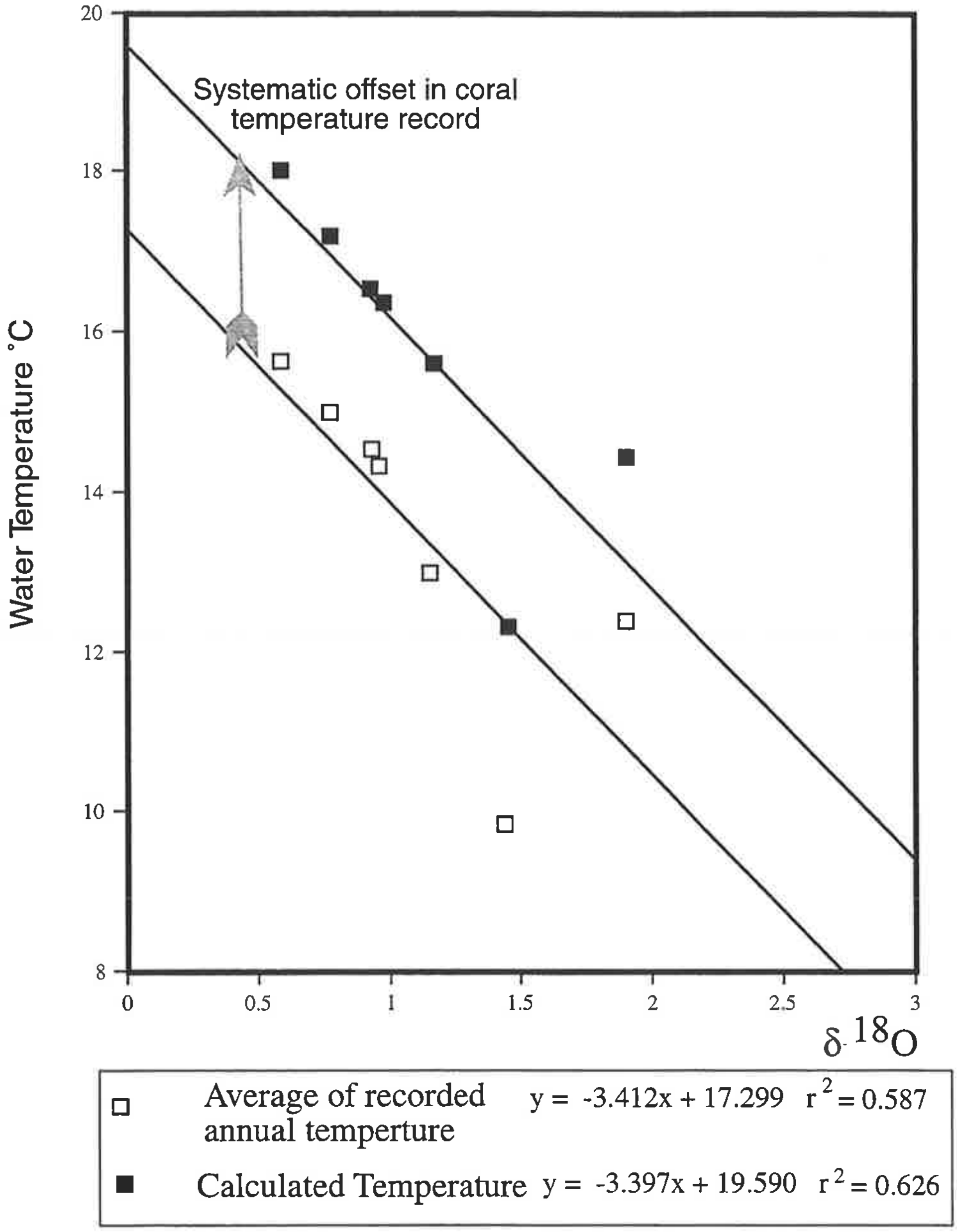
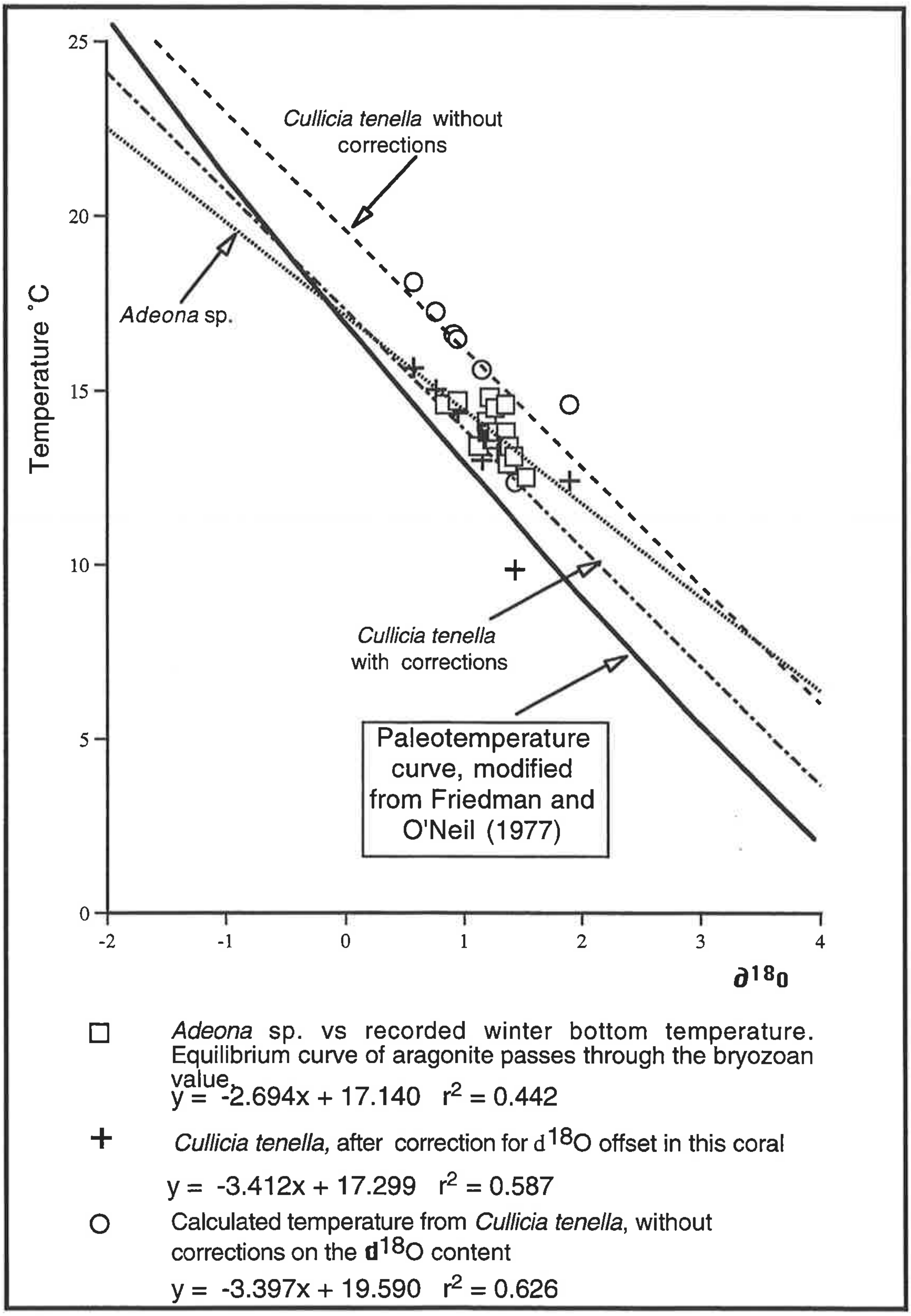


Fig. 3.3. Oxygen isotope variations with temperature in ahermatypic coral *Cullicia tenella.* Average offset in temperature extracted by this coral from mean annual recorded temperature is shown. This offset is systematic and variations in temperature have been recorded in the oxygen isotope signature of this coral. Therefore, with some correction of $\delta^{18}O$ values, this coral can be used for paleotemperature studies.



□ *Adeona* sp. vs recorded winter bottom temperature. Equilibrium curve of aragonite passes through the bryozoan value.
$y = -2.694x + 17.140 \quad r^2 = 0.442$

+ *Cullicia tenella,* after correction for $d^{18}O$ offset in this coral
$y = -3.412x + 17.299 \quad r^2 = 0.587$

○ Calculated temperature from *Cullicia tenella*, without corrections on the $d^{18}O$ content
$y = -3.397x + 19.590 \quad r^2 = 0.626$

Fig. 3.4. Comparison of the paleotemperature curve of Friedman and O'Neil (1977) with the ahermatypic corals *Cullicia tenella* (with and without corrections) and bryozoan *Adeona* sp. from the study area.

This offset is constant in respect to temperature but varies among different taxa. *Cullicia tenella* shows a constant offset in respect to recorded average annual temperature, with the average offset about 0.58‰ in a temperature range of 9.5 to 16.9°C. The relationship between the temperature and $\delta^{18}O$ content of coral suggests that unlike many organisms that secrete their calcareous skeleton during warmer seasons, presumably this coral precipitates its aragonitic skeleton all year-round, and therefore, has the capability to record its ambient water temperature during all seasons. So, although few investigators treat corals as equilibrium precipitates, stating that they are generally depleted in $\delta^{18}O$ compared to apparent equilibrium values (McConnaughey 1988 a), the results of this study show that ahermatypic corals can be used in paleoecological and paleoenvironmental interpretation, if certain precautions are taken.

Table 3.1. The isotopic composition and comparison of the recorded and calculated temperature by the ahermatypic coral *Cullicia tenella* from the Lacepede Shelf. T_{RA} is the recorded average annual bottom water temperature, and T_{Cal} is the calculated temperature from the $\delta^{18}O$ values of this coral.

Sample sites	Depth m	$\delta^{18}O$ ‰	$\delta^{13}C$ ‰	Recorded Temp. °C summer	Recorded Temp. °C winter	Average Annual Temp. °C	Calculated Temp.°C	$\Delta T = T_{RA} - T_{Cal}$
45	60	0.58	-1.21	14.5	16.9	15.65	18.1	2.45
136	75	0.77	-0.50	13.25	16.8	15.02	17.25	2.23
135	90	0.92	-0.2	12.3	16.8	14.55	16.6	2.05
57	95	0.95	-0.09	12.2	16.5	14.35	16.47	2.13
168	180	1.15	0.50	11	15	13	15.6	2.6
59	220	1.43	1.1	10.8	14	12.4	14.6	2.2
64	350	1.9	0.80	9.5	10.2	9.85	12.35	2.5

The carbon in the corals is derived from different sources: 1) total dissolved inorganic carbon in the seawater (DIC), either within the coral tissue or surrounding the coral, 2) organic carbon ingested as particulate food by the polyp, and (3) by photosynthesis of zooxanthellae within the coral's tissue (Weil et al. 1981). Obviously the latter is not relevant in the case of ahermatypic corals.

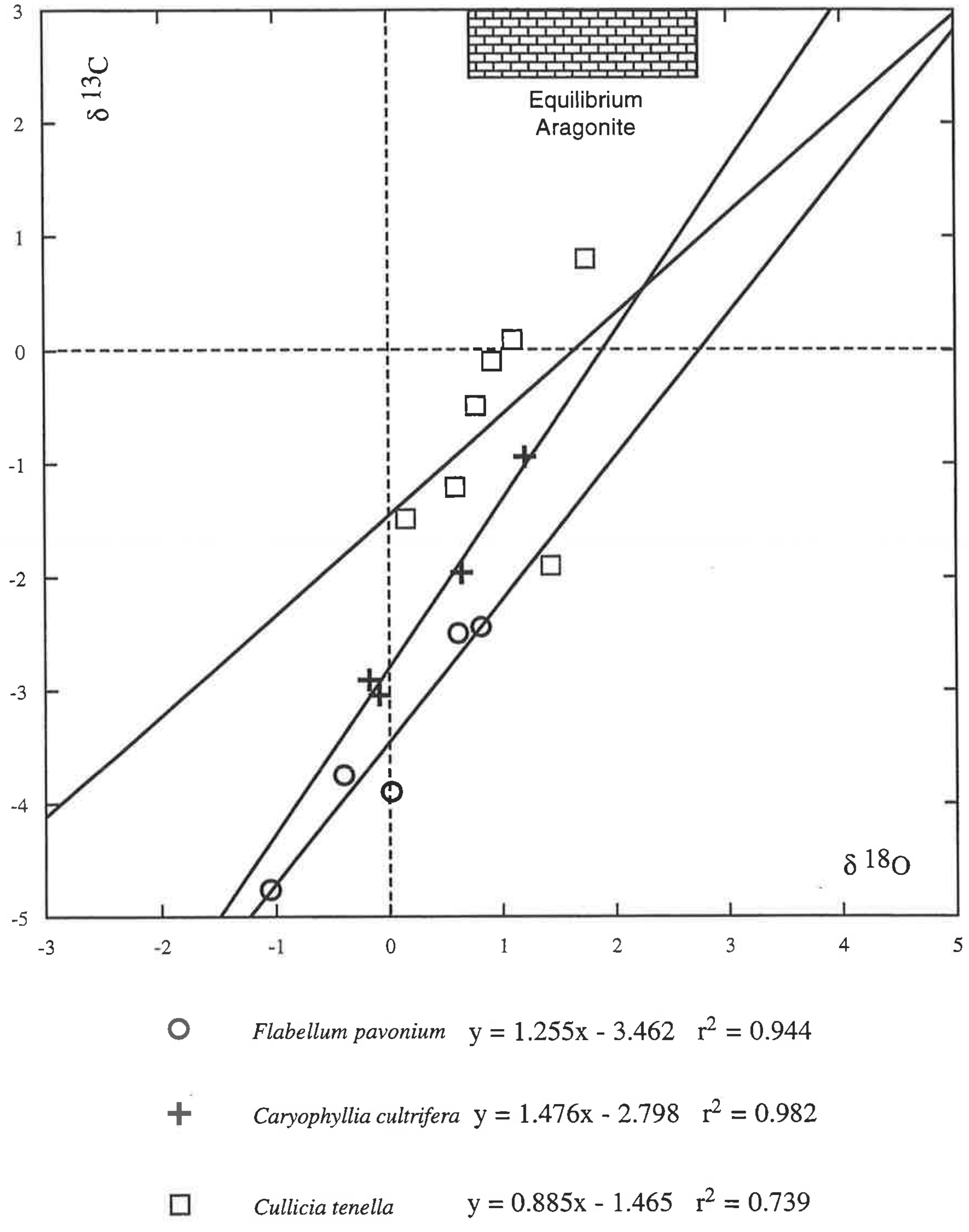


Fig. 3.5. Close, positive correlations of carbon and oxygen isotopes, typical of ahermatypic corals aragonite, on the Lacepede Shelf.

Respiratory CO_2 is enriched in the lighter isotopes with respect to bicarbonate dissolved in seawater. Both $^{18}O/^{16}O$ and $^{13}C/^{12}C$ ratios are invariably lower in biogenic $CO_3^=$ than in $CaCO_3$ in isotopic equilibrium with the ambient seawater system under the same environmental conditions (Weber 1973; McConnaughey 1988a), because skeletal aragonite contains a mixture of carbon and oxygen derived from these two different sources (metabolic and seawater). The degrees of these deviations are dependent on the amount of incorporation from these different sources.

Weber and Woodhead (1970) and Wefer and Berger (1991) state that ahermatypic corals have lower $\delta^{13}C$ values than the hermatypic ones, because zooxanthellae algae preferentially use the respiratory ^{12}C produced by hermatypes during photosynthesis, and this process leads to higher ^{13}C values in hermatypic aragonite skeletons. However, ahermatypic corals from the Lacepede Shelf in most cases have higher $\delta^{13}C$ values than ahermatypic corals from tropical areas, and in fact their $\delta^{13}C$ is almost equal to that of tropical hermatypic corals (Fig. 3.2, i.e., there is a marked environmental difference). Ascribing differences in $\delta^{13}C$ of hermatypic and ahermatypic corals entirely to the utilisation of respiratory ^{12}C by zooxanthellae during photosynthesis is doubtful. It is likely that another factor is influencing the $\delta^{13}C$ of ahermatypic corals, and only ahermatypic corals. These light $\delta^{13}C$ values of ahermatypic corals of the tropical environments could be attributed to strong influences of both kinetic and metabolic effects on their isotopic compositions. In contrast, studied ahermatypic corals show simultaneous depletions in both isotopes, in a systematic manner (Fig. 3.5, Table 3.1), indicating the likelihood of kinetic effects.

Organisms which are strongly depleted in ^{18}O usually are also strongly depleted in the ^{13}C, and vice versa. This correlation in non-reef corals is positive (Weber 1973, McConnaughey 1988 a) and may be due to the mixing and utilisation at the calcification site, of both carbon and oxygen from different sources or metabolic pathways (e.g., Keith and Weber 1965; Aharon 1991). Non-photosynthetic organisms, such as ahermatypic corals *Flabellum pavoninum, Caryophyllia cultrifera,* and *Culicia tenella*, display nearly linear correlation between skeletal $\delta^{18}O$ and $\delta^{13}C$ (Fig. 3.5). This strong correlation between the skeletal $\delta^{18}O$ and $\delta^{13}C$ demonstrates that there is a functional linkage between these two isotopes and indicates the influence of kinetic effects on the carbonate secretion of studied corals. Metabolic effects on these processes are not likely because any such contribution would cause more deviation and depletion in the $\delta^{13}C$ contents of coral samples, as it does in tropical ahermatypes. Hence, linear correlation between skeletal $\delta^{18}O$ and $\delta^{13}C$ of the non-photosynthetic corals apparently results from partial equilibration (incomplete isotopic equilibrium) of this isotopically light kinetic endpoint (McConnaughey 1989a, b). Generally, the ahermatypic corals show a strong correlation between $\delta^{18}O$ and $\delta^{13}C$ values in many specimens or species, or even between species. In coral samples, within a given genus, $\delta^{18}O$ and $\delta^{13}C$ are closely correlated, and the correlation is positive, indicating that higher $^{13}C/^{12}C$ ratios are associated with higher $^{18}O/^{16}O$ ratios. Accordingly, as mentioned earlier, despite the fact that aragonite deposited by the ahermatypic coral *Cullicia tenella* exhibits lower $^{13}C/^{12}C$ and $^{18}O/^{16}O$ ratios than aragonite in isotopic equilibrium with seawater, due to systematic (regular) variations in its isotopic composition, it can be used for paleotemperature studies.

The similarity in the isotopic compositions of the ahermatypic coral genus *Caryophyllia* from the temperate environment of Scotland (Weber 1973), and from the Lacepede Shelf, are shown on Fig. 3.6. Thus, it is possible that similar processes were responsible for producing such similar isotopic values at these geographically distant sites.

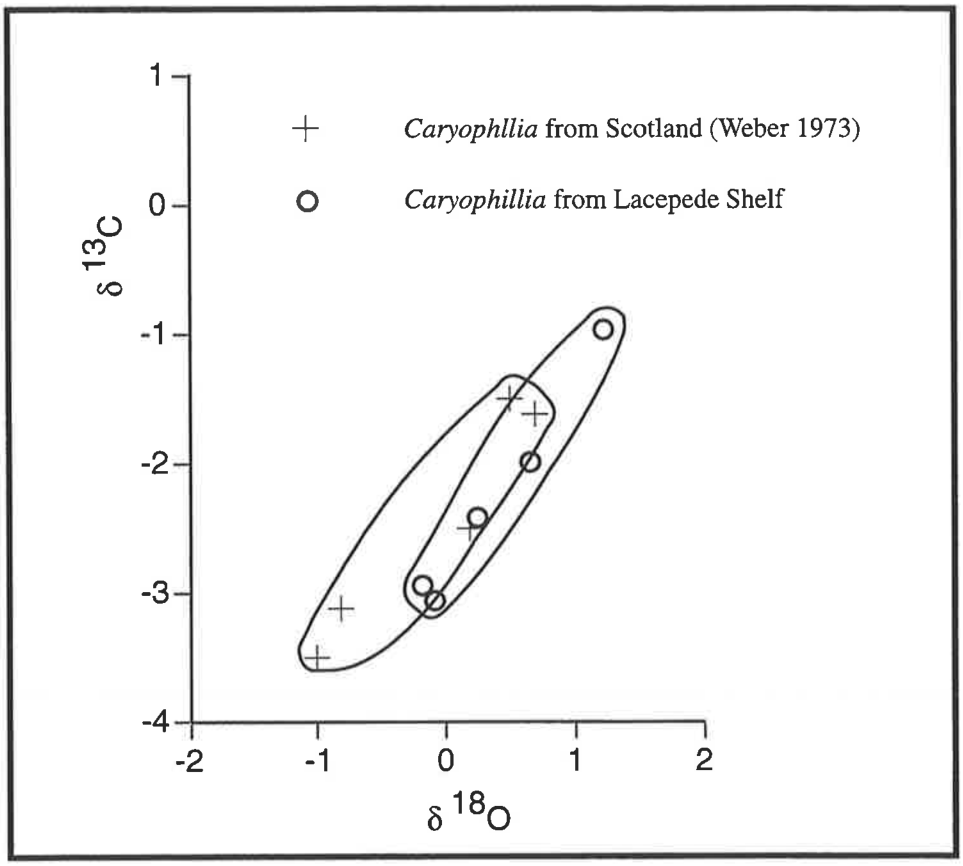


Fig. 3.6. Isotopic compositions of the ahermatypic coral genus *Caryophyllia* from two temperate carbonate environments, Lacepede Shelf of South Australia and Scotland (from Forester et al. 1973).

3.4. Bryozoans:

Bryozoans are often inconspicuous but nonetheless ubiquitous members of the benthic fauna of all modern seas. They are strictly colonial and individuals within the colony (zooids) are commonly less than 0.5 mm in size. The colony (zooarium) may reach several centimetres in maximum dimensions. Bryozoans feed, with a lophophore, on phytoplanktons and detrital organic matter. A few species contain zooxanthellae in their tissue and probably receive some of their nutrition from these algae. Many species require a hard substrate for attachment, with others preferring marine algae or sea grasses as a substrate and yet others root themselves in unconsolidated sediments. On the Lacepede Shelf, bryozoans are dominant sediment-producer in most facies, contributing particles to all grain sizes (Bone and James 1993). Bryozoans also attach to other biota (both living and dead) and can be important constituents of reefs (Cuffey 1977). Bryozoans show a range of skeletal mineralogy, consisting of LMC, IMC, aragonite and various mixtures of these. The degree of calcification is more significant in advanced and complex superfamilies. Some workers believe that calcification is strongly dependent upon water temperature (Smith and Haderlie 1969).

Bryozoans occur across a broad temperature range from the tropics to polar climates. Many species are stenothermal and thus can potentially be used as paleoclimatic indicators (Dodd and Stanton 1990; Bone and Wass 1990). Bryozoans are found under salinity conditions ranging from fresh water to hypersaline lagoons. According to early studies (e.g., Forester et al. 1973; Dodd and Stanton 1981) they are most abundant and diverse on the continental shelf from 20 m to 80 m. However, recent studies show that they are commonly the most abundant carbonate particles on cool-water carbonate shelves up to deeper waters. They have been found at all depths in the ocean from intertidal to depths of 8300 m (Ryland 1970). Therefore, although of usually minor significance in tropical reef environments, bryozoans are major components of temperate shelf carbonate sediments. They are dominant producers of carbonate on the Australian (e.g., Wass 1970; James et al. 1992; Bone and James 1993) and New Zealand (e.g., Nelson 1988) shelves. North Pacific sediments also contain bryozoan carbonate (e.g., Smith 1970; Nelson and Bornhold 1984). In the North Atlantic both the North American and the European (e.g., Dobson et al. 1972; Bouysse et al. 1979; Scoffin et al. 1980) shelves include bryozoan-rich carbonates. Even in the Antarctic (Domack 1988) bryozoan are sub-dominant producers of carbonate sediments. Nelson et al., (1981,1988) have termed such sediments "bryomol" indicating the importance of both bryozoans and molluscs (together with ubiquitous foraminifera). Dominance of a fauna by bryozoans along with the presence of other temperate organisms, indicates a non-tropical setting (Smith 1995).

Most bryozoans are sensitive to suspended sediments in the water, and hence are not common in areas of high sedimentation rates (Schopf 1969). This is probably because their feeding mechanism is readily clogged by sediment. Their small sizes also make them more easily buried than larger animals. Therefore, bryozoans would have higher diversity in lower sedimentation rates (Kelly and Horowitz 1987). Many bryozoans are adapted to live in very turbulent waters.

On the Lacepede Shelf of southern Australia, sponges, molluscs, bryozoans and foraminifera are the most abundant organisms. In this study, one of the most important and conspicuous bryozoan morphotypes, *Adeona* sp. is selected for geochemical studies. *Adeona* sp. is an aragonitic, large, robust fenestrate form. On the southern Australian continental shelf this Cheilostome bryozoan is so distinctive and useful as a paleoecological indicator that it warrants being treated as a distinct morphotype (Bone and James 1993), and is best used in studying Cenozoic faunas (e.g., Smith 1995). Under-water photography shows that *Adeona* sp. is common in areas where the seafloor is highly mobile, and particularly in the subaqueous dune fields above the shelf break (James et al. 1992).

Little attention has been paid to the geochemistry of bryozoans, probably because they are relatively unimportant in Holocene tropical environments, and have not been considered a tool for paleotemperature studies. However, recent studies show that some of them are valid for paleotemperature interpretations, as they secrete their skeleton at approximately equilibrium conditions with their ambient seawater (Rahimpour-Bonab et al. 1995, 1997a; Bone and James 1997).

In this study, isotopic composition, mineralogy and trace elements of *Adeona sp.* have been considered. The observed $\delta^{18}O$ values of *Adeona* sp. lie between 0.84‰ and 1.52‰. These $\delta^{18}O$ variations appear to be due to temperature variations with depth (Fig. 3.4; i.e., they record environmental temperature variations). Kinetic and metabolic effects do not influence the ^{18}O content of this bryozoan, as most $\delta^{18}O$ values plot within the equilibrium area and there are no significant variations of the $\delta^{18}O$ from equilibrium area (Fig. 3.7).

Hitherto, the $\delta^{18}O$ as a function of temperature in bryozoans has not been investigated as much as it has in other taxa. Fig. 3.4 shows that $\delta^{18}O$ in bryozoans is temperature dependent, and the relationship is well-defined. Based on Fig. 3.4, it can be concluded that : (1) $\delta^{18}O$ and water temperature are closely correlated over the cool-water temperature spectrum in which this bryozoan lives; (2) the relationship is apparently linear and inverse (negative slope); (3) the equilibrium line relating $\delta^{18}O$ and temperature for equilibrium aragonite passes through the bryozoan, and is roughly parallel to the paleotemperature curve which expresses the relationship between $\delta^{18}O$ and temperature for CaCO3 in isotopic equilibrium with the ambient seawater system. However, the bryozoan $\delta^{18}O$-temperature curve is displaced toward higher $\delta^{18}O$ values with respect to the paleotemperature curve, because of the lower temperature of the temperate

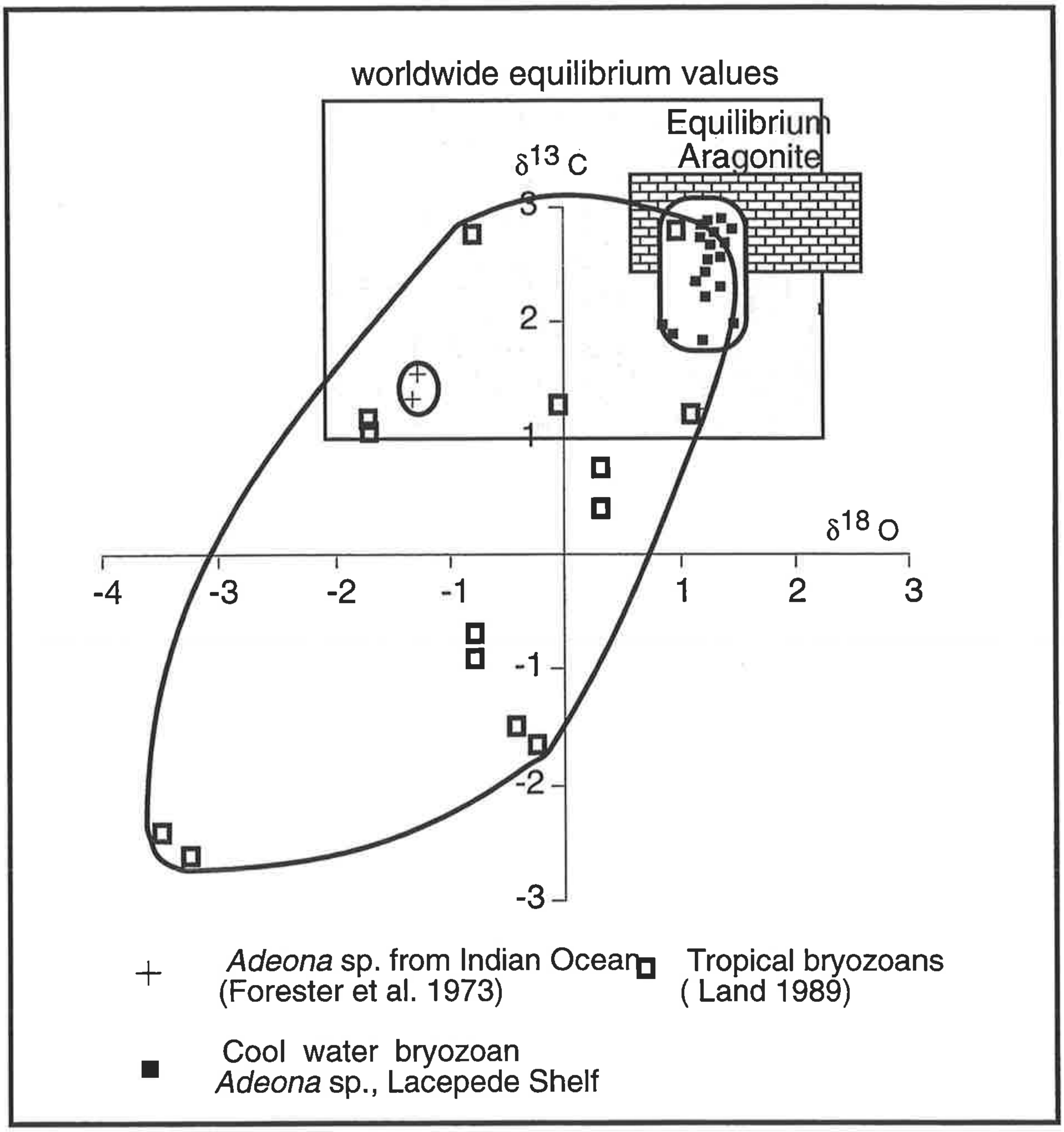


Fig. 3.7. Comparison between isotopic composition of the cool-water bryozoan *Adeona* sp. with its tropical counterparts. The equilibrium aragonite is calculated for the Lacepede Shelf and worldwide equilibrium values from Land (1989).

environment in comparison to the tropical environment, which is the basis for this paleotemperature curve (Friedman and O'Neil 1977). Moreover, the paleotemperature curve introduced by Friedman and O'Neil (1977) is based on calcitic organisms, and so the higher $\delta^{18}O$ values of the studied bryozoan can be attributed to its aragonitic mineralogy.

The $\delta^{13}C$ of this bryozoan is between 1.9‰ and 3.2‰, close to the range of equilibrium values for $\delta^{13}C$ of equilibrium aragonite calculated for their ambient seawater (2.11 to 3.17‰) (Fig. 3.7). A few samples show some offset in their $\delta^{13}C$ content which could be ascribed to local variations in the $\delta^{13}C$ values of HCO_3^- because of different processes such as organic material decay (reservoir effects), or microhabitat effects.

Comparisons between *Adeona* sp. samples from the Lacepede Shelf and from the Indian Ocean (Forester et al. 1973) show differences in the $\delta^{18}O$ and $\delta^{13}C$ (Fig. 3.7). For $\delta^{18}O$ values, this difference can be explained by temperature differences. Many authors (e.g., Wefer and Berger 1991, Marshall 1992) have pointed out that for every 4C° increase in temperature, there is a 1‰ depletion in the $\delta^{18}O$. Thus with the 14°C differences in average temperature of these two areas, a 2.5‰ difference in $\delta^{18}O$ of *Adeona* sp. is expected. Clearly, *Adeona* sp. reflects variations in the temperature of modern environments. This observation reconfirms the utility of bryozoans in paleotemperature determination and support the hypothesis of isotopic equilibrium secretion in bryozoans.

In the case of $\delta^{13}C$ (Fig. 3.7), the Lacepede Shelf samples are enriched in comparison with their tropical counterparts by about 1‰, but are still in equilibrium with their ambient environment. The differences in the $\delta^{13}C$ content may reflect a different food source in the two environments, or possibly a different seawater $\delta^{13}C_{DIC}$ value.

Rapid skeletal growth under higher temperatures (e.g., Land et al. 1975; Erez 1977,1978; Weil et al. 1981) is associated with depletion in $\delta^{13}C$ in different organisms. On the other hand, despite the fact that ^{13}C-depleted upwelling currents lead to an offset in the $\delta^{13}C$ content of biogenic carbonates (reservoir effects), the low temperature of these currents causes lower precipitation rates (lower kinetic effects) and so, some enrichment in $\delta^{13}C$ values of the studied bryozoan compared to its tropical counterpart. Temperature effects on the $^{13}C/^{12}C$ equilibrium fractionation of aragonite have been observed by Turner (1982) in inorganic aragonite, and reconfirmed by similar observations by several researchers on biogenic carbonates (for example Weil et al. 1981; Grossman and Ku 1986). Consequently, differences in the growth rate of bryozoans in the temperate and tropical environments can be responsible for such differences observed in their isotopic compositions. Furthermore, the concentration of respired carbon within the site of calcification in the ambient seawater (greater in warm-seawater and thus lighter $\delta^{13}C$ values of DIC) could be responsible for such an offset in $\delta^{13}C$ of tropical bryozoans. Moreover, in tropical *Adeona* sp., some of the $\delta^{13}C$ from equilibrium values not associated with $\delta^{18}O$ offset, could be attributed to metabolic effects from modifications of the dissolved inorganic carbon (DIC) by respiratory CO_2.

The $\delta^{18}O$ content of *Adeona* sp. exhibit unimodal distribution, whereas $\delta^{13}C$ values are more scattered (Fig. 3.7). For $\delta^{18}O$ this is due to the narrow range of the ambient temperature in the area, whereas the $\delta^{13}C$ could be influenced by several factors such as food source, DIC variations, microhabitat and temperature effect on the $\delta^{13}C_{carbonate\text{-}bicarbonate}$ fractionation. Nevertheless, the influence is minimal as $\delta^{13}C$ values are still around aragonite equilibrium values.

3.5. Trace Element Content of Diverse Taxa:

The Mg content in different groups of coralline algae varies. For example, Corallinaceae have Mg contents ranging from 2.94 to 7.0% and *Melobesia* contain between 1.74 and 7.2% Mg in their carbonate skeleton. The Lacepede Shelf samples range between 1.27 to 3.13% for *Lepthophytum* and 2.81 to 3.31% for *Metagoniolithon* (Fig. 3.8). Their Mg-calcite range is well within the limits set for HMC (Chave 1954 a, b; Milliman 1974). However, the variable and relatively large range in Mg content are probably related to factors such as nutrient level, salinity and/or ambient temperature, growth rate of skeletal material, or some other factor at the biological level (i.e., biological fractionation or metabolic effects). Kolsar (1978) found a systematic variation of the Mg content in some coralline algae and determined that the growth rate, and thus the Mg uptake of these algae, is temperature dependent. The ranges of Mg concentration in the studied samples are marginally lower than their tropical counterparts, due to the lower temperature. Moberly (1968) also found a wide range of Mg concentrations throughout coralline algal skeletons. He suggested that these variations are the result of periodic fluctuations in the ambient environment and corresponding changes in the organism's metabolism. In temperate areas, seasonal variations in the temperature may control Mg incorporation and other trace elements such as Mn, Fe, Sr, and Na. The Mg content of ahermatypic corals is lower than their tropical counterparts, but is closer to equilibrium values (Fig. 3.8).

The Mg content of the studied bryozoan is higher than expected equilibrium aragonite, perhaps indicating some metabolic enrichment. No trace element data have been presented in literature for bryozoans from tropical environments.

The high Sr (0.95%) contents of some algal genera reflect their aragonite mineralogy (e.g., *Peysonnelids*), demonstrating that these algae incorporate Sr into carbonate in equilibrium with their ambient seawater (Kinsman 1969; Milliman

1974, Veizer 1983 a, b; Fig. 3.9). In the studied branching and crustose algae, variations in the absolute Sr content are possibly related to growth rate, water temperature or other factors such as metabolic effects, or the higher level of Mg and lower level of Sr is merely a result of ionic size. The Sr content of the samples are almost the same as their tropical counterparts (Fig. 3.9) and are in the range of equilibrium values.

All scleractinian corals are aragonitic, so their Sr contents are high, generally between 0.75 and 0.90% in tropical samples, with similar values in the cool-water samples from the Lacepede Shelf (Fig. 3.9). Lowenstam (1964) and Kinsman (1969) suggested that the higher amounts of Sr contained in deep sea corals (ahermatype) are related to the higher distribution coefficient of Sr in colder waters, but Thompson and Livingston (1970) stated that the Sr concentration is not temperature-dependent, and that the higher Sr content in deep-sea corals is due to the lack of symbiotic algae rather than to low temperature. Ahermatypic corals in this study show higher contents of Sr compared to their tropical counterparts, thus supporting Thompson and Livingston's (1970) hypothesis. Overall Sr values of ahermatypic corals are close to those expected for aragonite precipitated in equilibrium with normal seawater (Fig. 3.9).

The Sr content of *Adeona* sp. shows greater ranges than the equilibrium aragonite (Fig. 3.9).

The Fe content of organic and inorganic carbonates are strongly dependent on the Eh and the chemistry of ambient water. The observed Fe and Mn levels in branching and crustose algae are somewhat higher than predicted values from theoretical considerations of biogenically precipitated carbonates (Figs 3.10 and 3.11). Growth rate, metabolic effect or some other factors may account for this higher Fe and Mn content. A converse relationship between temperature of formation and Fe and Mn content could be postulated, but Fe and Mn contents

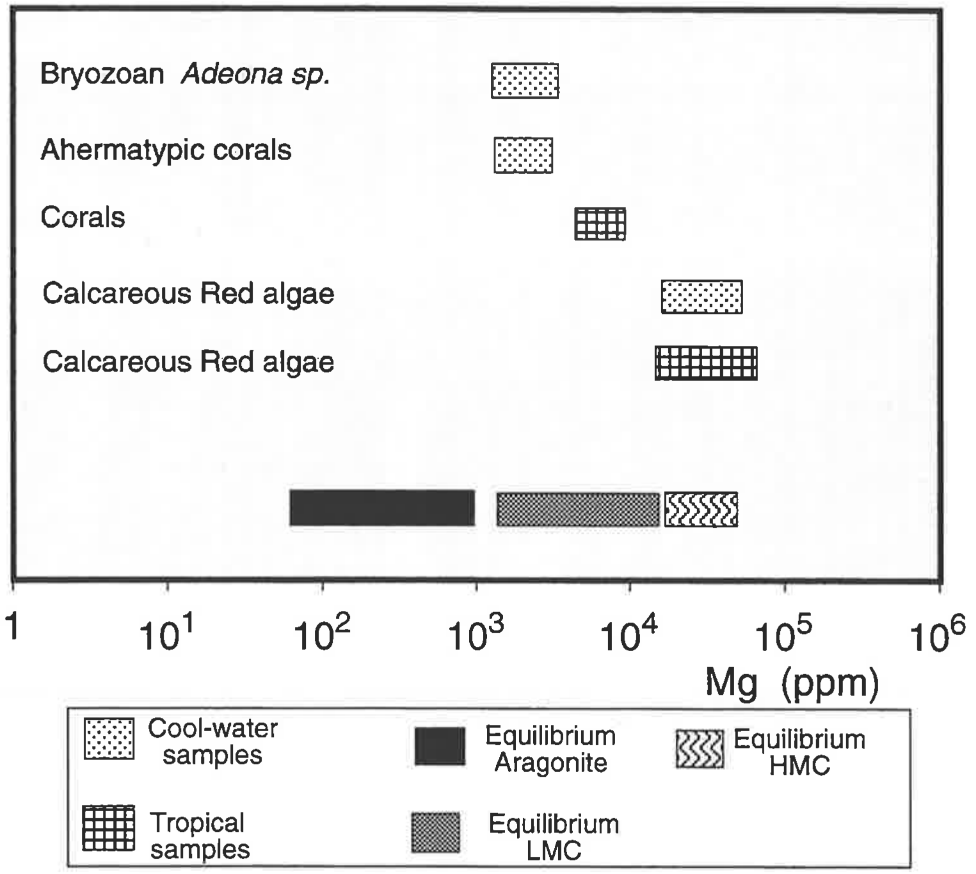


Fig. 3.8. Variations in Mg content for some carbonate secreting organisms from the temperate environment of Lacepede Shelf and their tropical counterparts. There are no data for trace element content of tropical bryozoans. Tropical data for trace elements and equilibrium values for different mineralogy (in Figs 3.8, 3.9, 3.10 and 3. 11) are from Morrison and Brand (1986).

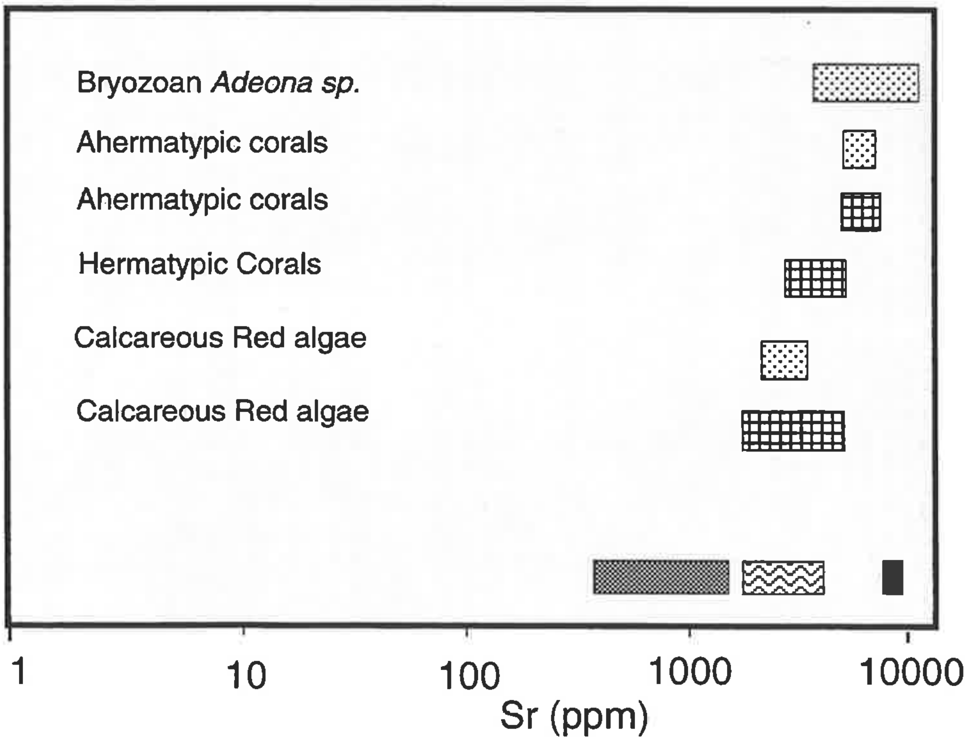


Fig. 3.9. Sr variations in different organisms from diverse environments. Hermatypic and ahermatypic corals from Thompson and Livingstone (1970). See Fig. 3.8 for legend.

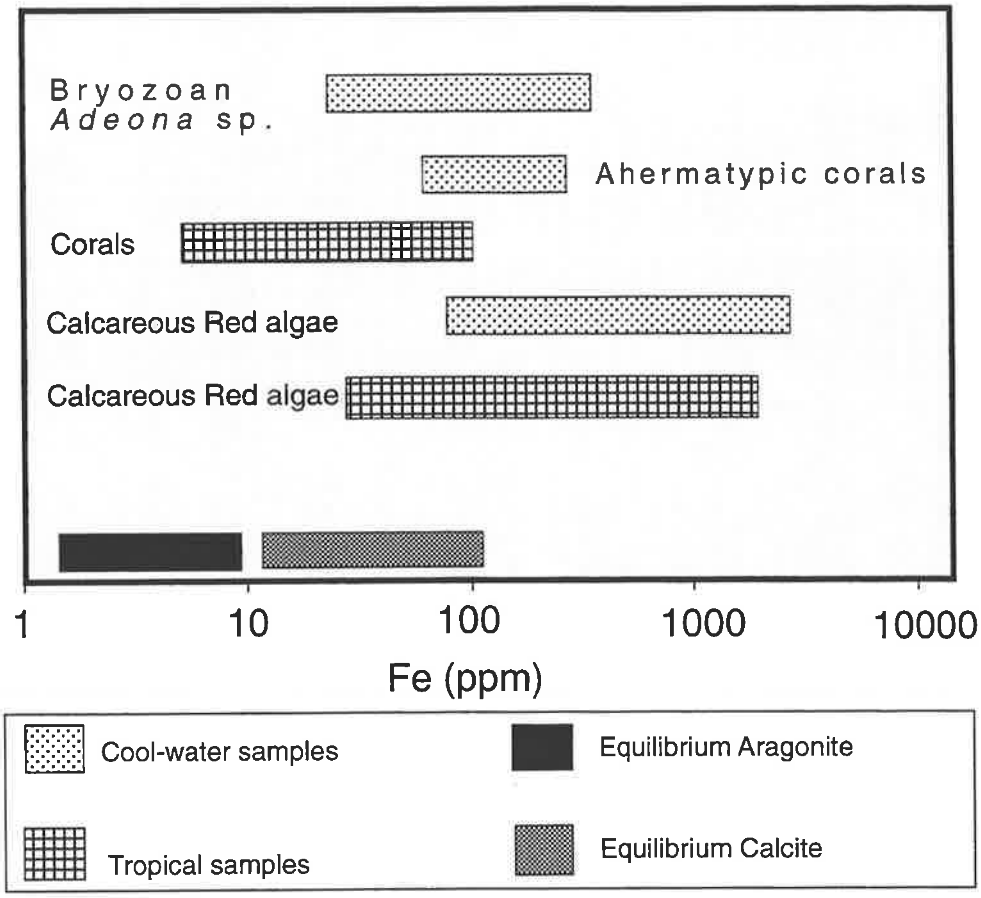


Fig. 3.10. Fe variations in different organisms from diverse environments.

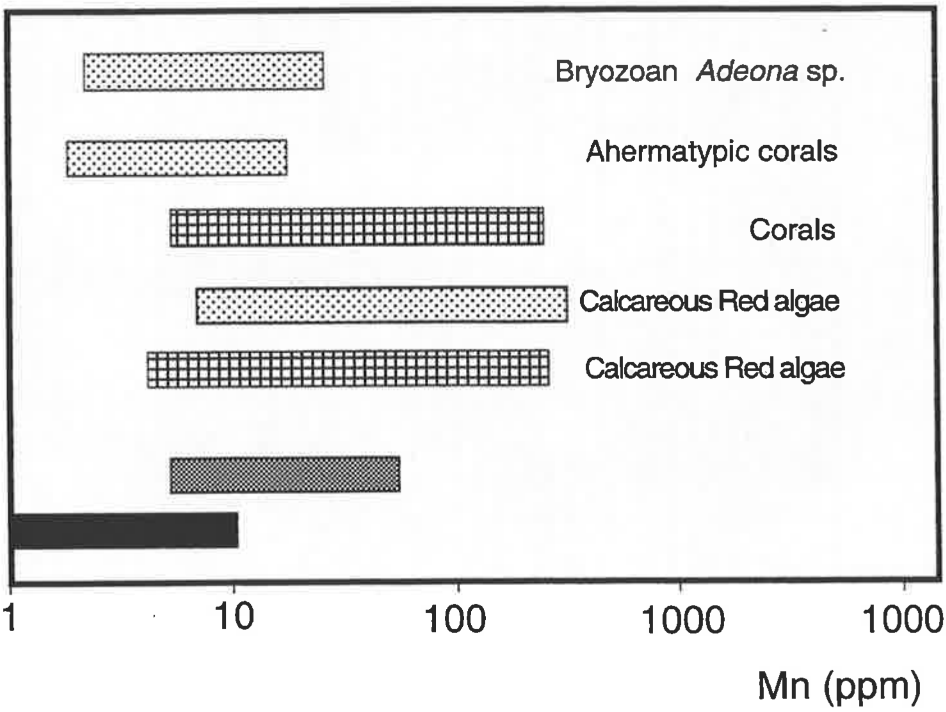


Fig. 3.11. Mn variations in different organisms from diverse environments. See Fig. 3.10 for legend.

of ahermatypic corals are similar to their tropical counterparts (Figs. 3.10 and 3.11). Mn behaves similarly. The Fe and Mn content of studied bryozoans is in the range of, and sometimes higher than, the equilibrium values.

Kolsar (1978) and Lorens (1981) suggested that higher water temperatures may influence the growth rate and thus calcification rate, which can result in variations of the minor and trace element concentrations of biogenic carbonate. However, despite lower temperatures in the study area there are some variations in trace element content of different samples, which probably signify that temperature alone, is not the only controlling factor on the trace and minor element content of biogenic carbonates.

3.6. Comparisons between Isotopic Composition of Photosynthetic and Non-Photosynthetic Organisms:

Photosynthetic and non-photosynthetic corals have approximately similar $\delta^{18}O$ ranges, so it seems photosynthesis has little effect (McConnaughey 1988a). Apparently, photosynthesis does not directly affect the ^{18}O fractionation between water and skeletal carbonate. Similar ^{18}O depletion occurs in the coralline algae (photosynthetic plants) and non-photosynthetic corals (Fig. 3.12). Whereas, amongst samples having similar skeletal $\delta^{18}O$ from the same environment, photosynthetic corals always have heavier $\delta^{13}C$ than non-photosynthetic corals (Keith and Weber 1965, Land et al. 1977, McConnaughey 1988 a, Aharon 1991). Consequently, for any $\delta^{18}O$ value, the photosynthetic organisms have heavier $\delta^{13}C$ values, suggesting that photosynthesis elevates the skeletal $\delta^{13}C$ (a metabolic effect, Swart 1983; Fig. 3.13). Comparisons of photosyntethic organisms such as coralline algae and non-photosynthetic

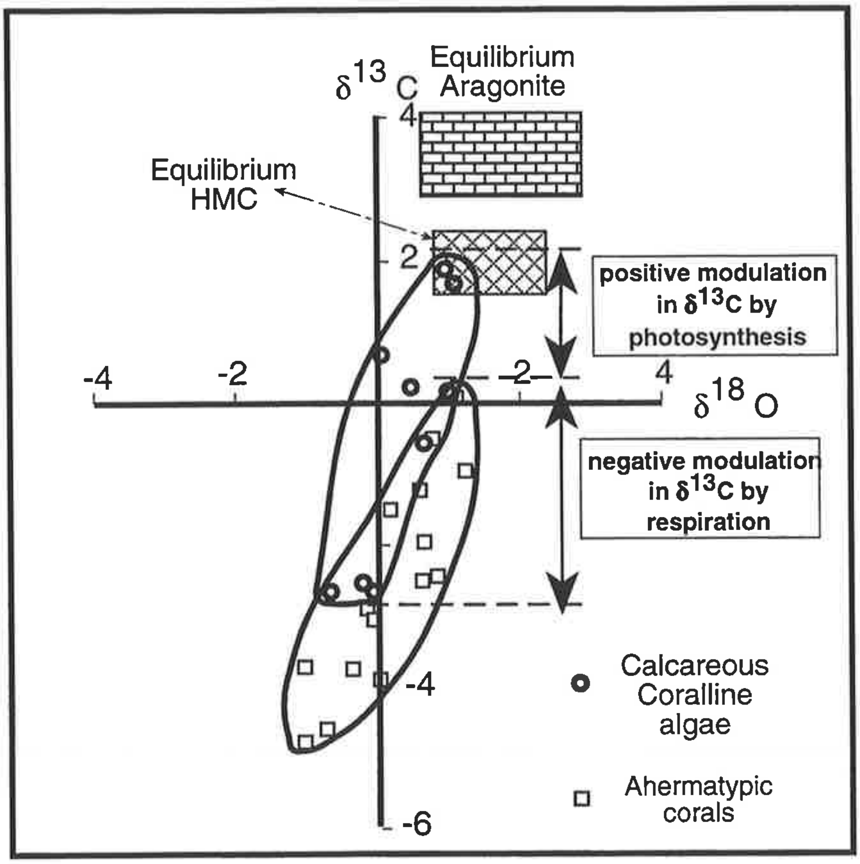


Fig. 3.12. Comparison of the isotopic compositions of coralline algae and ahermatypic corals from study area. Some of the $\delta^{13}C$ enrichment in the algae in comparison to ahermatypic corals is due to positive modulation of carbon by photosynthesis. The $\delta^{13}C$ offset from equilibrium values in algae is due to negative modulation of carbon by respiration. As a whole, ahermatypic corals show depletion in carbon relative to algae, but they show close $\delta^{18}O$ values.

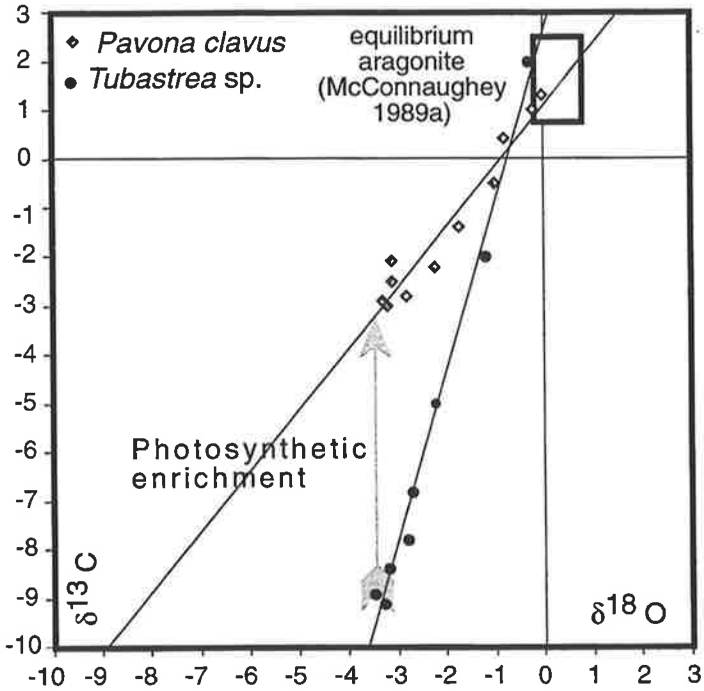


Fig. 3.13. Isotopic comparisons between the photosynthetic coral *Pavona clavus* and the non-photosynthetic coral *Tubastrea* sp. (Modified from McConnaughey 1989a). Photosynthesis caused some enrichment in $\delta^{13}C$ of corals.

organisms such as ahermatypic corals display these higher $\delta^{13}C$ values, even at the same sampling sites (Fig. 3.12).

These observations support the theory of positive modulation of skeletal $\delta^{13}C$ by photosynthesis (Weber and Woodhead 1970; Goreau 1977; Swart 1983; McConnaughey 1989). When the importance of kinetic effects is ignored, the opposite conclusion is drawn (e.g., Erez 1978; Erez and Honjo 1981; Williams et al. 1981). In comparing the isotopic composition of studied ahermatypic corals and of coralline algae, the former provide a striking example of simultaneous ^{13}C and ^{18}O depletion attributed to kinetic effects, whereas coralline algae exhibit a good example of positive modulation of skeletal $\delta^{13}C$ by photosynthesis and negative modulation by respiration. The positive modulation in these organisms caused some ^{13}C enrichment compared to equilibrium values, whereas, negative modulation is responsible for some ^{13}C depletion (Fig. 3.12).

Equilibrium fractionation predicts that a calcite precipitating under the ambient conditions of the Lacepede Shelf seawater would have a $\delta^{13}C$ value of 0.51 to 1.57‰ (Chapter Two). Under the same conditions (slow precipitation rates and similar temperature ranges) an equilibrium aragonite would have $\delta^{13}C$ values of 2.81 to 4.05‰. But studied coral aragonite has a mean $\delta^{13}C$ value of -2.40±1.3, which exhibits offset from both calcite and aragonite equilibrium values by 4.0‰ and 6.45‰, respectively. Comparing coral results with $\delta^{13}C$ values of coralline algae (average $\delta^{13}C$ values of -0.53±3.5‰), indicates that the $\delta^{13}C$ value of the coralline algae, regardless of its calcitic mineralogy, on average, is higher than the ahermatypic corals (Fig. 3.12). This is due to positive modulation of $\delta^{13}C$ content during photosynthesis in this plant, which gives rise to higher $\delta^{13}C$ values. So, it appears that photosynthetic $\delta^{13}C$ enrichment overshadows the mineralogical fractionation effects on the $^{13}C/^{12}C$ fractionation during carbonate precipitation.

In the Lacepede Shelf samples, apparently, photosynthesis does not directly affect the ^{18}O fractionation between water and the skeleton as the $\delta^{18}O$ values of corals and coralline algae are very close. However, photosynthesis may influence physiology in ways which do affect $\delta^{18}O$ value (i.e., by influencing calcification rates).

3.7. Molluscs:

Three major classes of molluscs, the bivalves, cephalopods and gastropods, are among the major carbonate producers in recent and ancient marine environments. Molluscs were the subject of the very first studies of isotopes in calcareous shells (e.g., Epstein et al. 1951, 1953; Epstein and Lowenstam 1953). They have been studied from diverse marine and terrestrial Holocene (mainly tropical) environments and from fossil samples from different geologic times. These studies are mainly focused on different aspects such as mineralogy, microstructures and geochemistry (e.g., Gross 1964; Keith and Parker 1965; Fritz and Poplawski 1974; Milliman 1974; Bathurst 1975; Killingley and Berger 1979; Arthur et al. 1983; Abell 1985; Grossman and Ku 1986; Morrison and Brand 1986; Wefer and Berger 1991; Israelson et al. 1994; Jones et al. 1995; Bemis and Geary 1996; Rahimpour-Bonab et al. 1997b).

Molluscs live in different marine environments from warm tropical seas to subfreezing Arctic and Antarctic waters. They are epifaunal or infaunal and live as vagile or sessile organisms, with some of them nektonic. Calcification rates in molluscs are dependent on environmental factors such as temperature, energy, and substrate and on some biological factors. Bivalves are aragonitic or calcitic and some of them have mixed layered shells. Their mineralogy and shell structure remain constant within any super-family. *Pecten* (*Chlamys* sp., super Family

Pectinidae), one of the subjects of this study, is mainly calcitic with some (up to 5%) aragonite, as shown by XRD analysis. This bivalve is widespread on the Lacepede Shelf. Gastropods are mainly aragonitic and, similar to bivalves, they secrete thinner shells in cooler and calmer waters and thicker shells in turbulent (agitated) waters. They inhabit diverse environments and most of them are epifaunal but a few are infaunal. *Turritella* sp. (Family Turritellidae) which has been studied in this research, is an aragonitic gastropod which lives in sands and silts, especially among the roots of sea grasses or algae. Ecological, environmental and growth rates of these molluscs are discussed with more detail in Chapter nine, where, in an integrated approach, the isotopic data versus growth lines have been used for investigations of the environmental conditions recorded in shell carbonates. In this section the ability of cool-water mollusc to produce precise records of isotopic composition of their ambient seawaters and to reflect their environmental conditions, is scrutinised.

The isotopic compositions of *Pecten* sp. and *Turritella* sp. are shown on Fig. 3.14. The aragonitic gastropod *Turritella* sp. shows some enrichment in its ^{13}C and ^{18}O compared to the calcitic bivalve *Pecten* sp. (Fig. 3.14). This isotopic enrichment in aragonite over calcite is about 1.5‰ in $\delta^{13}C$ and 0.8‰ in $\delta^{18}O$ and is in the range or close to the $\delta^{18}O_{calcite - aragonite}$ and $\delta^{13}C_{calcite - aragonite}$ enrichment values that are suggested by the many workers mentioned earlier(Tables 1 to 4).

The $\delta^{13}C$ value of the biogenic aragonite could be influenced by other factors besides temperature. Metabolic effects, as seen in corals and coralline algae, and some other taxa, can lead to either positive or negative deviations of the $\delta^{13}C$ from equilibrium values. In *Turritella* sp., however, as the results of this study show, there is no significant biogenic fractionation and its isotopic composition is within the range of equilibrium inorganic aragonite (Fig. 3.14). Therefore, it is concluded that these minor variations in the $\delta^{13}C$ values of *Turritella* sp. are

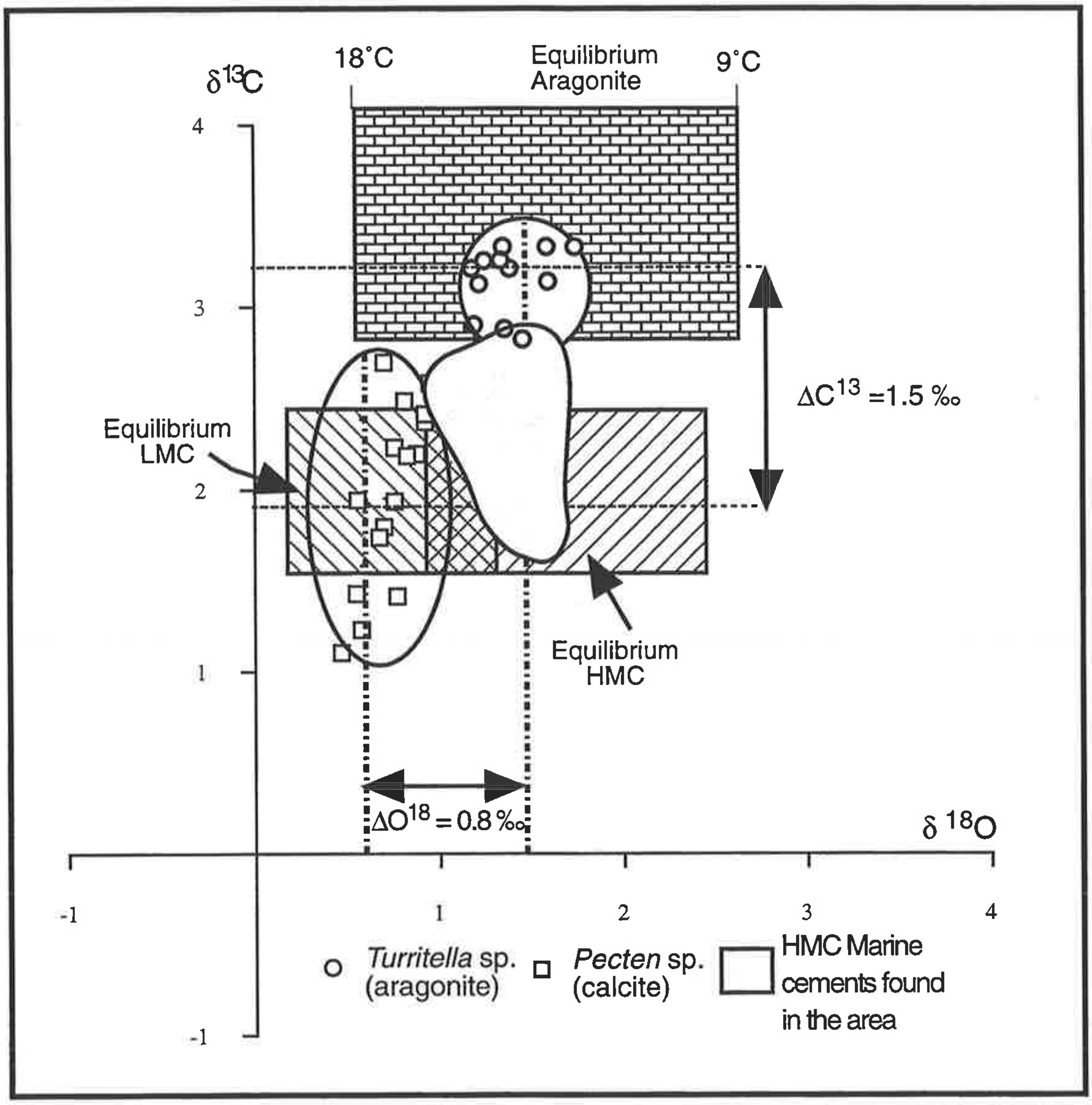


Fig. 3.14. Comparison between the isotopic composition of the aragonitic gastropod (*Turritella* sp.) and calcitic bivalve (*Pecten* sp.) of the Lacepede Shelf. The Δ shows differences in $\delta^{18}O$ and $\delta^{13}C$ between biogenic aragonite and calcite. These are within the range of values for fractionation in these minerals in inorganic precipitates, as suggested by Rubinson and Clayton (1969), Turner (1982), Gonzalez and Lohmann (1985) and Romanek et al. (1992).

possibly caused by the temperature effect on the aragonite-seawater DIC fractionation ($\delta^{13}C_{\text{biogenic aragonite - DIC}}$) and DIC isotopic variations with depth. *Turritella* sp. has an average $\delta^{13}C$ enrichment factor of 2.75‰ relative to $\delta^{13}C_{DIC}$, which is close to estimated equilibrium values introduced by Rubinson and Clayton (1969) and Grossman (1984).

Unlike the calcitic foraminifera examined by Grossman (1984), the calcitic bivalve *Pecten* sp. is not depleted in $\delta^{13}C$, but is actually enriched in $\delta^{13}C$ relative to the $\delta^{13}C_{DIC}$ (Fig. 3.14). This $\delta^{13}C$ enrichment is possibly because of the low precipitation rates of carbonates in this temperate environment, enabling maximum fractionation between dissolved bicarbonates and aragonite/calcite systems. *Pecten* sp. has an average $\delta^{13}C$ enrichment factor of 1.5‰ relative to $\delta^{13}C_{DIC}$. This contradicts Morse and Mackenzie's opinion (1990) that the $\delta^{13}C$ values of calcitic shells usually do not even show the 0.5‰ enrichment relative to bicarbonate. Results of this study show that the temperate calcitic and aragonitic molluscs of the Lacepede Shelf, have an average $\delta^{13}C_{\text{calcite - DIC}}$ and $\delta^{13}C_{\text{aragonite - DIC}}$ of about 1.5‰ and 2.75‰, respectively. The $\varepsilon\delta^{13}C_{\text{aragonite - calcite}}$ in these biogenic carbonates is, therefore, about 1.5 ± 0.3‰, which is comparable with inorganic values of 1.8 ± 0.2‰ (Rubinson and Clayton 1969), 1.6± 0.35‰ (Turner 1982) and 1.7± 0.4‰ (Romanek et al. 1992). This indicates that the $\delta^{13}C$ of the molluscs in this environment is precipitated in equilibrium with ambient seawater, and testifies that because of lower temperatures, and thus slower calcification rates, biogenic carbonates can reach equilibrium values.

These observations show that there is no major metabolic (vital) effect in the studied molluscs and the differences in the carbon isotope values are due to the different mineralogy, and consequently different fractionation rates, and thus, are not due to metabolic effects. Differences in $\delta^{18}O$ of *Pecten* sp. (LMC calcite) and *Turritella* sp. (aragonite) is about 0.8‰ which is in the range of the difference in fractionation values of inorganic calcite and aragonite (Fig. 3.14). Accordingly, this study shows that *Pecten* sp. and *Turritella* sp. from this temperate carbonate environment are precipitating their carbonate shells in isotopic equilibrium with their ambient seawater. Thus, they do not exert significant metabolic effects over the isotopic composition of their calcareous shells and so diagenetically unaltered samples could be used for paleoenvironmental studies with great precision. Table 3.2 shows measured temperatures, both summer and winter, and temperatures calculated from the $\delta^{18}O$ values of the calcitic and aragonitic molluscs.

Table 3.2. Isotopic temperature calculated from aragonitic and calcitic molluscs of the Lacepede Shelf area from the same sampling sites, and comparisons with the recorded summer and winter bottom water temperatures.

Depth	Measured Temp.°C		Calcitic Mollusc		*Pecten* sp.	Aragonitic Mollusc		*Turritella*
m	Summer	Winter	$\delta^{18}O$	$\delta^{13}C$	Temp.Cal. °C	$\delta^{18}O$	$\delta^{13}C$	Temp.Cal. °C
55	15.1	16.9	0.46	1.21	14.9	1.25	3.26	14.6
70	13.5	16.8	0.76	1.43	13.6	1.20	2.75	14.8
80	13	16.8	0.57	1.50	14.4	1.20	2.54	14.8
90	12.3	16.8	0.69	1.80	13.8	1.23	3.13	14.7
100	12	16.4	0.56	1.98	14.4	1.49	2.77	13.6
180	11	15	0.85	2.20	13.1	1.50	3.20	13.5
300	10	11.2	0.98	2.42	12.6	1.59	3.34	13.1

The calcitic and aragonitic mollusc temperatures are similar and fall within the range of measured temperatures. Thus, the molluscs are probably precipitating their calcareous shells in both summer and winter, since the temperature of formation (the average temperature of carbonate secretion) is similar to the average temperature experienced throughout the year.

Land (1989) using data from e.g., Clayton and Degens (1959), Eichler and Ristedt (1966), Eisma et al., (1976), Gross (1964), Keith and Parker (1965), Mook (1971), Teys and Naydin (1975), Zhirmunskey et al., (1967), and Wefer and Killingley

(1980), stated that the oxygen isotopic values of molluscs are almost in equilibrium with ambient seawater, but that carbon values are considerably out of equilibrium (Fig. 3.15). These authors also observed that lower $\delta^{13}C$ values were associated with rapid growth rates in the aragonitic gastropods *Strombus gigas* and *S. costatus*. Results from the Lacepede Shelf, however, have shown that both oxygen and carbon isotopes in *Pecten* sp. and *Turritella* sp. are in equilibrium with their environment (Figs 3.14 and 3.15). Land (1989), based on the works of Lloyd (1964), Bandal and Hoefs (1975) and Wefer and Killingley (1980), stated that greater vital effects have been observed in gastropods than in bivalves, and concluded that they are less reliable for paleoenvironmental interpretation. In addition, Wefer and Berger (1991), considering isotopic information on gastropods from different sources (e.g., Deuser and Degens 1969; Hoefs and Sarthein 1971; Bernal, 1980; Winter et al. 1983; Price et al. 1985; Grossman et al. 1986; Meinecke and Wefer 1990), suggested that in the gastropods $\delta^{18}O$ is precipitated in equilibrium, whereas $\delta^{13}C$ is depleted, relative to equilibrium values. However, results of this study reveal that both bivalves and gastropod show no significant metabolic (vital) effects and so both are equally useful for paleoenvironmental studies. These differing results may arise from the fact that most previous isotopic data for molluscs are from tropical environments that are geochemically different from temperate ones (Rahimpour-Bonab et al. 1997b).

The oxygen isotopic composition of *Pecten* sp. shows almost unimodal distribution, whereas $\delta^{13}C$ values are more scattered (Fig. 3.14). In equilibrium biogenic carbonates, such as molluscs that do not exert significant metabolic effects, $\delta^{18}O$ is controlled by temperature which varies within a narrow range in this environment, whereas the $\delta^{13}C$ value is probably a function of several factors, such as food sources, temperature effects on $\delta^{13}C_{\text{carbonate - bicarbonate}}$ fractionation, DIC variations and so on. However, these effects on the $\delta^{13}C$ of *Pecten* sp. are not significant, so that $\delta^{13}C$ values are still close to the equilibrium

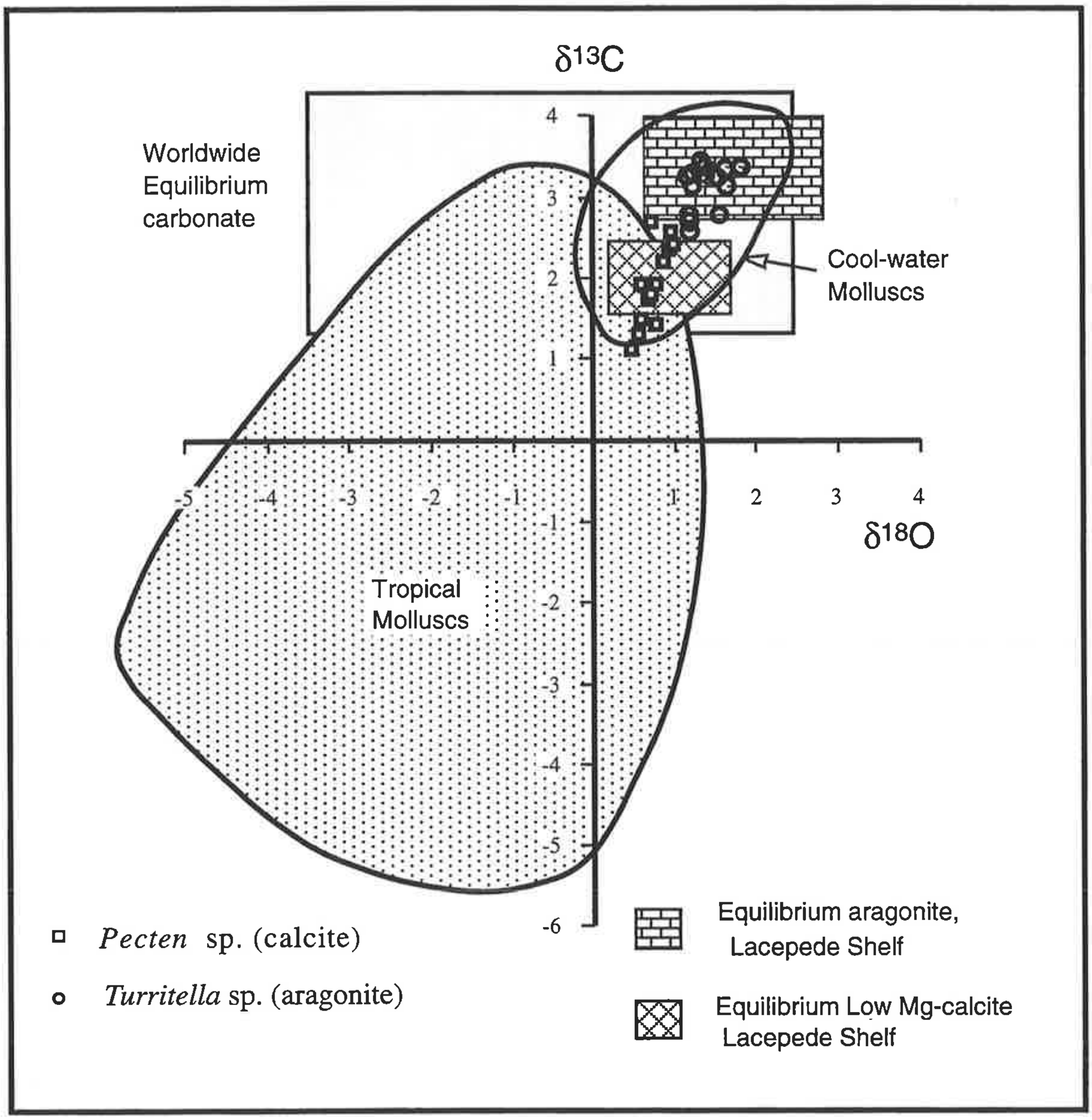


Fig. 3.15. Comparison between isotopic composition of various molluscs from temperate carbonate environment with their tropical counterparts. Tropical data from Land (1989 and references therein) and worldwide equilibrium values from Morrison and Brand (1986), McConnaughey (1989a).

values. In *Turritella* sp., both $\delta^{13}C$ and $\delta^{18}O$ present a unimodal distribution that is in complete equilibrium with ambient waters.

These linear positive correlation between $\delta^{13}C$ and $\delta^{18}O$ of some organisms from the Lacepede Shelf, such as coralline algae and ahermatypic corals (Rahimpour-Bonab et al. 1997a) and *Pecten* sp. (Rahimpour-Bonab et al. 1997b; Figs 3.14 and 3.16) indicate that the isotopic values of ambient waters have narrow ranges. However, other processes, such as fresh water mixing with seawater (Mook 1971), or organism migration (except for sessile and encrusting organisms such as ahermatypic corals and coralline algae) between environments that have different isotopic composition (Mulcahy et al. 1979), could produce linear positive correlation. Mixing of freshwater input on the Lacepede Shelf has no significant influence (James and Bone, 1992). Moreover, if fresh water mixing led to such correlation, it would be more conspicuous in the samples that are closer to the mouth of the River Murray; which is not the case. McConnaughey, (1989a, b) pointed out that in non-photosynthetic corals, linear correlations between skeletal $\delta^{13}C$ and $\delta^{18}O$ is a result of a partial equilibration process. The range of isotopic correlation is apparently dependent on the extent of the partial equilibrium. Whereas ahermatypic corals and coralline algae exhibit a large range for their $\delta^{13}C$ and $\delta^{18}O$ linear correlations, bivalves have a limited $\delta^{13}C$ and $\delta^{18}O$ correlation range (Figs 3.14 and 3.16), demonstrating the greater influence of kinetic effects on the isotopic compositions of corals and coralline algae.

3.8. Brachiopods:

Brachiopods are infaunal and epifaunal organisms, and although they are relatively unimportant in modern tropical carbonate sediments, they are locally

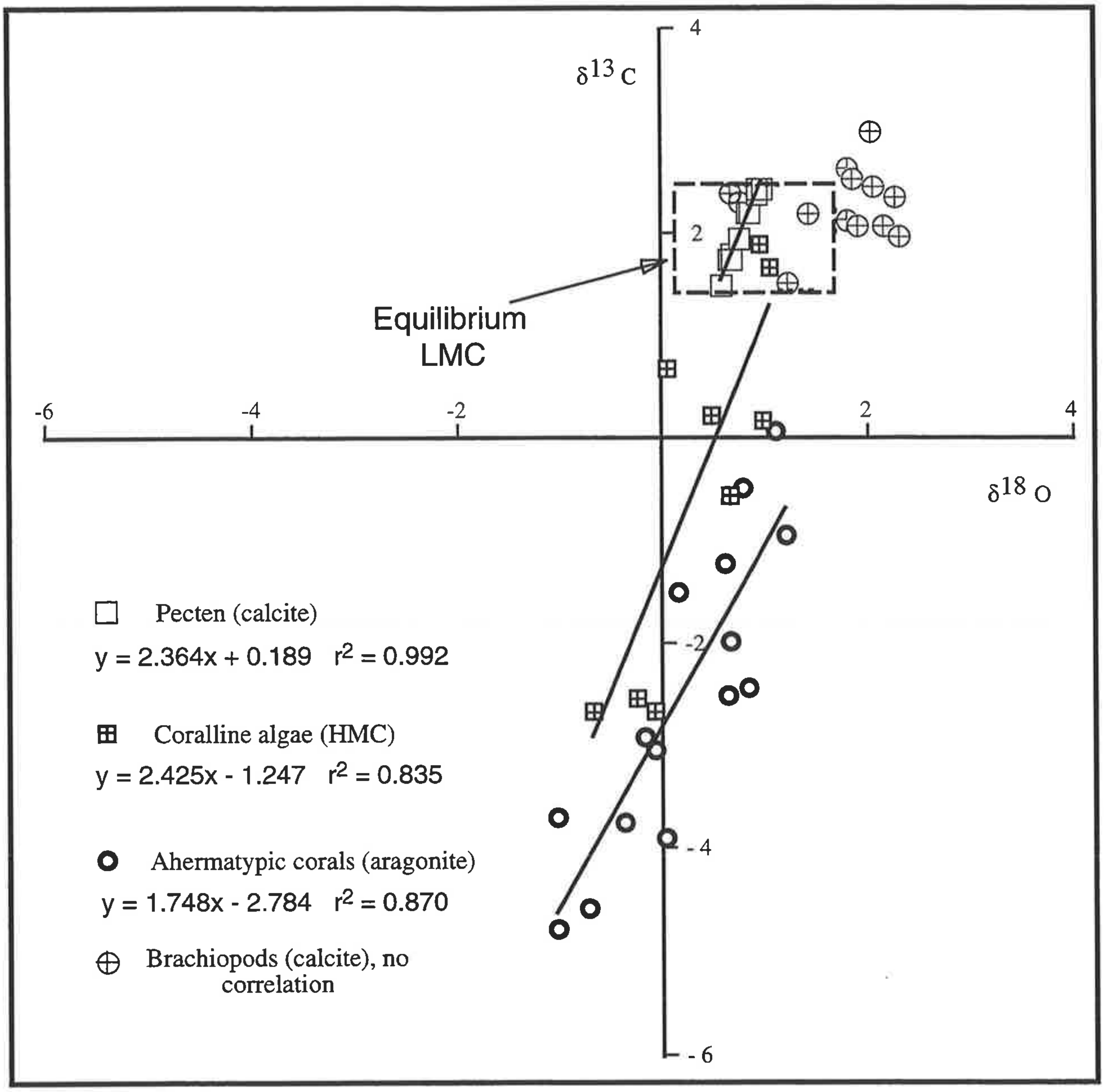


Fig. 3.16. Comparison of the correlation in isotopic composition of different organisms from temperate environments of the Lacepede Shelf, South Australia.

common in temperate carbonate environments, such as the Lacepede and Bonney Shelves. In these areas they are living in depths of 40 m to 300 m.

Inarticulate brachiopods are composed of calcium phosphate and articulate brachiopods contain a chitinous peristracum which covers a calcitic shell. All samples studied here belong to the family Terebratellidae (articulate brachiopods). Brachiopods are prominent in the fossil record and the family Terebratellidae are present from the Silurian to the present. Well-preserved fossils of this family are abundant in the Cenozoic carbonate rocks of the St.Vincent and Murray Basins, which, along with fossil molluscs, have been used in the next chapters for paleoenvironmental reconstructions. Brachiopods have long been regarded as equilibrium calcium carbonate producers and so their $\delta^{18}O$ values are used as proxies for $\delta^{18}O$ of seawater (e.g., Lowenstam 1961; Veizer et al. 1986; Popp et al. 1986a, c; Brand 1989a, b; Grossman et al. 1991). This is also because their shell is composed of LMC, which is less susceptible to diagenetic alterations.

Most studies until now have focused on fossil brachiopods and less attention has been paid to modern samples. Modern carbonate environments, however, provide an excellent opportunity for the comprehension of biomineralisation and geochemistry of brachiopods. Here, the aim is to evaluate the ability of modern brachiopods (Terebratellidae) to record seawater isotopic composition, comparing their pristine isotopic composition with recorded isotopic composition of equilibrium marine calcite. The isotopic values of Terebratellidae have been compared with their co-existing molluscs, to find which is the better isotopic recorder(Table. 4)

The general comparisons between isotopic composition of *Pecten* sp. (LMC) and their co-occurring Terebratellidae (LMC) from the Lacepede Shelf indicate that the $\delta^{18}O$ of the former is closer to the equilibrium values (Fig. 3.16) and that the Terebratellidae exhibit about 1‰ enrichment in their $\delta^{18}O$ average values.

Brachiopods do not show correlations between $\delta^{13}C$ and $\delta^{18}O$ and their $\delta^{18}O$ values are mostly heavier than equilibrium values, which is consistent with the observations of Heibert et al., (1988) and Carpenter and Lohmann (1995). They attributed the observed isotopic deviations from equilibrium values in brachiopods to metabolic effects (Fig. 3.16). The lack of covariations in the $\delta^{18}O$ of these two co-occurring organisms from the same depths could be explained by the influence of vital effects on the $\delta^{18}O$ fractionation in brachiopods. Heibert et al. (1988) and Carpenter and Lohmann (1995) also found various disequilibrium values in different parts of modern brachiopods from diverse areas. On the other hand, comparisons of the $\delta^{18}O$ of the Lacepede Shelf Terebratellidae brachiopods ($\delta^{18}O$ between 0.75 to 2.31‰) with other modern samples from mostly warm water areas ($\delta^{18}O$ values between -4.6 to 1.5‰, Lowenstam, 1961; Lepzelter et al. 1981; Carpenter and Lohmann 1995), indicate higher $\delta^{18}O$ values in the Lacepede Shelf samples, which are close to the $\delta^{18}O$ values from Ross Island, Antarctica (Carpenter and Lohmann 1995).

Previous studies on the $\delta^{13}C$ of different biogenic carbonates have revealed a correlation between the $\delta^{13}C$ of some foraminifera and $\delta^{13}C_{DIC}$ (e.g., Williams et al. 1977; Graham et al. 1981; Grossman 1984). Mook and Vogel (1968), Fritz and Poplawski (1974), and Grossman and Ku (1986) found a similar relationship for molluscs from different environments. The $\delta^{13}C$ of co-occurring *Pecten* sp. and Terebratellidae brachiopods shows strong covariations close to the 1:1 correspondence line (Fig. 3.17). The main reason for such covariations in these organisms is that, despite differences in the $\delta^{18}O$ values, the $\delta^{13}C$ values of both organisms are almost in equilibrium with their ambient waters, and so, these organisms are able to record the approximate $\delta^{13}C_{DIC}$ variations of their environments. This result contradicts Heibert et al. (1988), who suggested both $\delta^{18}O$ and $\delta^{13}C$ in brachiopods show variations of ±1‰, and should not be used as precise indicators of seawater isotopic signature. This observation is also

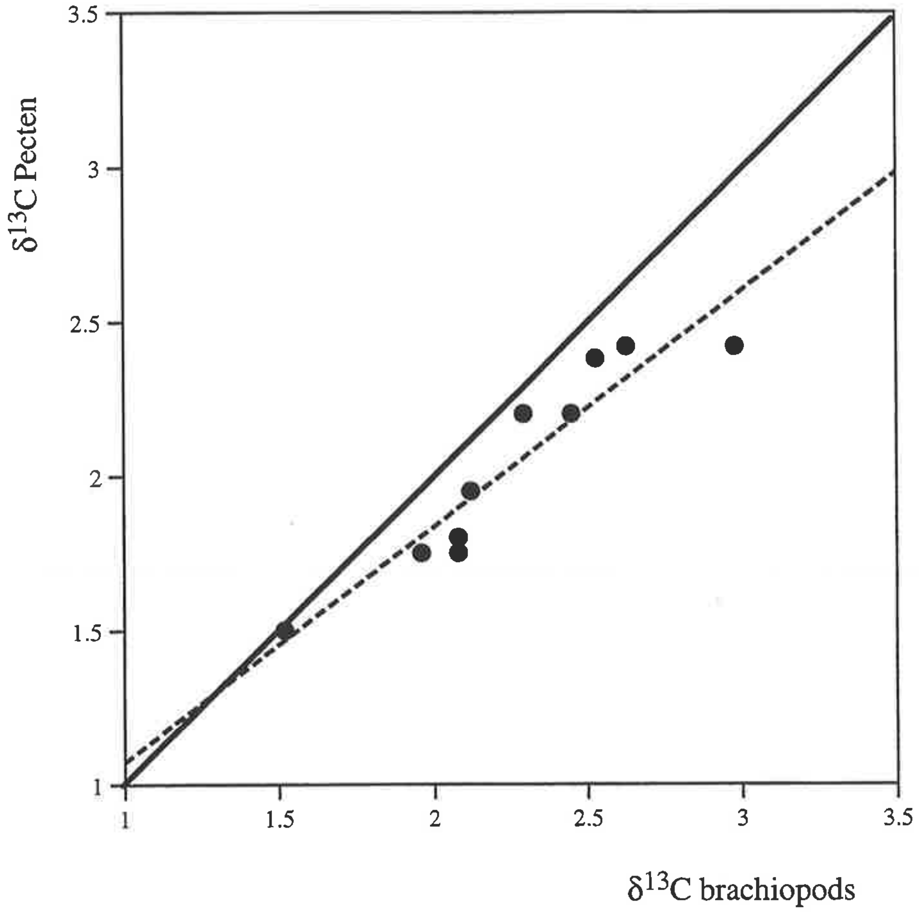


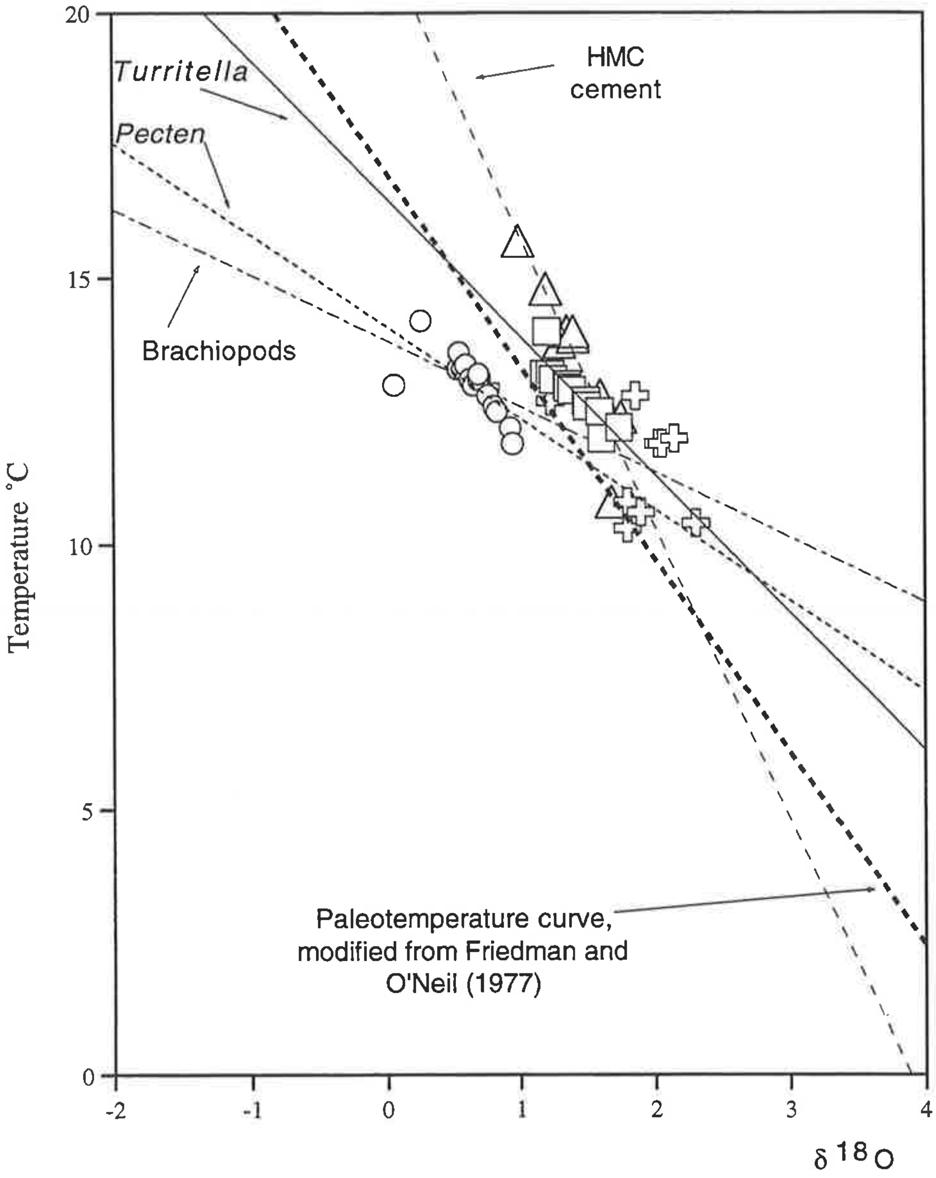
Fig. 3.17. Relationship between the $\delta^{13}C$ of co-occurring *Pecten* sp. and brachiopods from the same depths (the same sampling sites), the Lacepede Shelf. The dashed line is the regression curve and the solid line represent 1:1 correspondence (equivalence line).

contrary to Carpenter and Lohmann (1995) who stated that both $\delta^{18}O$ and $\delta^{13}C$ of modern brachiopods exhibit biological fractionation in their primary and secondary layer calcite. Therefore, although $\delta^{18}O$ values of the studied brachiopods show about +1‰ enrichment, possibly because of vital effects, the $\delta^{13}C$ values of these organisms are close to calculated equilibrium values, and indicate their potential use for paleoenvironmental studies.

The $\delta^{18}O$ values of the mollusc, brachiopods and HMC marine cements from the Lacepede Shelf exhibit clear variations with the temperature of the ambient waters (Fig. 3.18). The temperature-$\delta^{18}O$ curve of aragonitic sample is distinct from that of the calcitic ones and is closer to the HMC and paleotemperature curves of Friedman and O'Neil (1977). Based on these curves, it could be concluded that the $\delta^{18}O$ and water temperature are closely correlated over the temperature spectrum in which these organisms live. Inorganic components (cements) also display these variations. Displacement of the HMC equilibrium curve relative to the paleotemperature curve of Friedman and O'Neil (1977), could be explained by the lower temperature and hence higher $\delta^{18}O$ values in the cool-water samples. Thus, *Pecten* sp. and *Turritella* sp. would be more reliable for paleotemperature studies than the traditionally used brachiopods (Rahimpour-Bonab et al. 1997b). These observations add to the potential credibility of molluscs of temperate environments for paleoenvironmental and paleotemperature studies, which are shown in the next Chapters.

3.9. Conclusion:

Surveys on the isotopic compositions of some cool-water taxa indicate that oxygen isotopes have equilibrium or near equilibrium values and if disequilibrium prevails, the difference from equilibrium remains constant and can be corrected.



□ *Turritella*, aragonite $y = -2.602x + 16.528$ $r^2 = 0.783$

○ *Pecten*, calcite $y = -1.719x + 14.105$ $r^2 = 0.507$

✚ Brachiopods, calcite $y = -1.232x + 13.839$ $r^2 = 0.308$

△ HMC marine cements $y = -5.483x + 21.303$ $r^2 = 0.839$

Fig. 3.18. Relationship between the $\delta^{18}O$ values (PDB) of Molluscs, brachiopods, HMC marine cements and bottom temperature on the Lacepede Shelf. The paleotemperature curve of Friedman and O'Neil (1977) is shown for comparison.

The $\delta^{13}C$ depletion, if not associated with $\delta^{18}O$ offset, is due to metabolic effects, but simultaneous depletion or enrichment in carbon and oxygen isotopes is due to kinetic effects. These covariations of carbon and oxygen isotopes in ahermatypic corals and coralline algae manifests as a strong positive correlation between these two isotopes.

Although all carbonates deposited by ahermatypic corals and coralline algae in temperate environments exhibit some deviations from equilibrium values, because these variations are systematic, they can be corrected for paleotemperature studies. The higher $\delta^{13}C$ values of coralline algae in comparison with the co-existing ahermatypic corals is due to photosynthetic enrichment.

The fenestrate bryozoan *Adeona* sp. secretes its aragonitic skeleton in almost complete equilibrium with its environment, and there is no significant influence of kinetic or metabolic effects on its carbon and oxygen isotopes. Accordingly, $\delta^{18}O$ varies systematically with temperature, so this bryozoan can be used in paleotemperature studies.

Molluscs from this area precipitate their shell carbonate in isotopic equilibrium with their environment. The oxygen and carbon isotope values of these molluscs are close to the measured (marine cements) and calculated equilibrium values in this area. The values vary with depth (temperature) and with the isotopic composition of seawater. Average temperatures which are derived from these molluscs are similar to recorded temperatures. Two quite different organisms give similar calculated temperatures.

The calcitic bivalve *Pecten* sp. of this area is not depleted in $\delta^{13}C$, but is mainly enriched. Unlike $\delta^{18}O$, the $\delta^{13}C$ of the *Pecten* sp. and Terebratellidae brachiopods from the study area exhibit strong covariations. Moreover, the $\delta^{18}O$

values of molluscs and HMC cements represent clear variations with the temperature of the ambient waters.

This study has shown that on the Lacepede Shelf, because of lower temperatures and consequently slower precipitation rates (organic and inorganic carbonates), kinetic effects have a minimum influence on the isotopic compositions of different carbonates (molluscs and brachiopods), and that many of the biogenic carbonates, such as molluscs and bryozoans, and also inorganic marine cements, exhibit equilibrium isotopic values. Although brachiopods show equilibrium $\delta^{13}C$ composition, their $\delta^{18}O$ content is somewhat out of equilibrium. Therefore, generally calcareous organisms living in cool-water are able to record more accurately variations in seawater temperatures and chemistry than do their tropical counterparts. Thus, these temperate-inhabiting organisms are useful in paleoenvironmental, paleoclimatological and diagenetic studies.

In summary, the slow precipitation of inorganic calcite and aragonite at lower temperatures produces an equilibrium isotope fractionation for carbon as well as oxygen, and diminishes the influence of kinetic effects. Consistently, biogenic carbonates produced by some of these organisms, that do not exert significant metabolic effects over their isotopic values, reach equilibrium values due to lower temperatures and so slower precipitation rates, which in turn, diminish the influence of kinetic effects.

CHAPTER FOUR

PETROGRAPHIC EXAMINATIONS AND STABLE ISOTOPE BACKTRACKING TECHNIQUE

4.1. Introduction:

The original stable isotopic composition of calcareous fossils are important to establish a baseline for evaluating secular variations in seawater isotopic composition; climatic changes and glacial events; paleotemperature studies and evaluating diagenetic alterations. On the other hand, the skeletal geochemistry of macrofossils is determined by (1) the physico-chemical features of their habitat, (2) the physiological controls on the skeletal formation processes and (3) post-depositional diagenetic alterations (e.g., Dodd and Stanton 1981). Understandably, any environmental geochemistry study using macrofossils should be preceded by a consideration of the aforesaid controlling factors and their degree of contributions to the isotopic signature of the fossil samples. The third factor is investigated here to retrieve the original isotopic composition of marine fossils. The resulting data will be used in the next chapters as a support for measured isotopic composition of pristine fossils material for paleoenvironmental reconstructions and paleoclimatological studies.

Whereas the geochemical data of diagenetically unaltered molluscan macrofossils can be used as a powerful tool for interpretations of paleoenvironmental geochemistry (e.g., Brand 1986; Whittakel et al. 1987; Brand and Morrison 1987; Pirrie and Marshall 1990 a, b; Rahimpour-Bonab et al. 1997b), in many cases, the fossil materials are partly or completely altered, or in some circumstances, they are contaminated by very fine grained cements with different origins that can not be avoided during sampling for geochemical analysis. Therefore, in such contingencies, the essential first step, when employing fossils for paleoenvironmental and diagenetic studies of ancient carbonate sequences is the estimation of the original isotopic signature and chemical composition of the marine carbonates. These estimations provide a baseline relative to which the effects of diagenesis can be evaluated (Meyers and Lohmann 1985). They also provide the original seawater composition and temperature for paleoenvironmental reconstructions including ice volume and sea-level fluctuations. Consequently, the first prerequisite is to substantiate that these fossils secreted their carbonate shells in isotopic equilibrium with their ambient waters.

Previous studies (e.g., Morrison and Brand 1986; Brand and Morrison 1987; Popp et al. 1986; Wefer and Berger 1991) showed that invertebrates such as certain molluscs and brachiopods precipitate their calcareous shells in approximate ^{18}O equilibrium with their ambient environments. Detailed geochemical studies by the author and colleagues on the Holocene temperate carbonate environment of the shelves of South Australia (Rahimpour-Bonab et al. 1995, 1997a and b) have revealed that *Pecten* sp. and *Turritella* sp. have precipitated their carbonate shells in isotopic equilibrium with their ambient seawater, as their carbon and oxygen isotopic values are in the range of calculated and measured equilibrium values. Additionally, the carbon and oxygen isotopic composition of Terebratulida brachiopods from these Holocene environments are also close to the equilibrium values (Rahimpour-Bonab et al. 1997b).

Accordingly, the mineralogy and chemical composition of different fossils can be retrieved by comparing them with their Holocene counterparts. In this chapter the attempt is to show how isotopic composition and fractionation factors of some

Holocene invertebrates can be employed to retrieve the original isotopic composition of their altered fossil counterparts in a process termed "backtracking".

4.2. Sample Selection, Diagenetic Evaluations And Preservation:

The stable isotopic composition of macrofossils can only be utilised for paleoenvironmental investigations when the possibility of fractionation during biomineralisation, and also secondary alteration during diagenesis can be ruled out (e.g., Marshall 1992). The influences of the diagenetic alterations, which include intraskeletal cementation and recrystallisation during diagenetic reset, can be evaluated by concurrent geochemical and petrographic studies.

More than 250 fossil samples were collected from the Tertiary formations of the St.Vincent and Murray Basins, South Australia. Those macrofossils of which their counterparts are present in Holocene cool-water carbonate environments of the Lacepede Shelf, South Australia, were especially selected for geochemical study including an aragonitic Turritellidae gastropod , low-Mg calcite Pecten bivalve and low-Mg calcite Terebratulida brachiopods. The reasoning behind this selection is that, as mentioned earlier, the detailed biomineralisation study of these taxa has been carried out by the author and among the different organisms living in the cool-water carbonate environment these taxa in particular are in isotopic equilibrium with their ambient seawaters (Rahimpour-Bonab et al. 1995, 1997a, b). Therefore, here the possibility of metabolic influences on the isotopic composition of these fossils is confidently eliminated. To differentiate the preserved fossil samples from altered ones several criteria were employed as follows:

(1) When fossil shells are still aragonitic, generally it is accepted that they are not altered and so they preserved their original isotopic signature (e.g., Buchardt and Weiner 1981). Although, some examples of alteration of aragonite without conversion to calcite has been found (e.g., Bathurst 1975; Scherer 1977). The aragonitic Turritellidae gastropod from different stratigraphic levels, such as the Gull Rock Member and the Cadell Marl, are still aragonitic and they show their original isotopic signature which is heavier than that of their co-existing Pecten bivalves (Figs 4.1 to 4.3). However, in other units such as the Tortachilla Limestone they are replaced diagenetically by low-Mg Calcite (dLMC) cement and show lighter isotopic composition than that of their co-existing well-preserved Pecten bivalves (See Fig. 5.1). Accordingly, aragonitic fossils are preferred for geochemical-diagenetic studies of paleoenvironment because they record postdepositional alteration more readily than the calcitic ones.

(2) Diagenesis tends to homogenise the carbonate rock, eliminating all the original chemical signature. Moreover, diagenetic fluids are usually meteoric in origin and so are depleted in heavy isotopes and also are undersaturated with respect to aragonite and HMC calcite. The presence of seasonal variations in the isotopic composition of fossils, revealed by sampling along the growth lines of fossil shells, indicates preservation of the original mineralogy and chemical composition. Such isotopic variation along growth lines has been found in studied fossil samples that are here claimed to be unaltered (Chapter Nine). In the Turritellidae fossils of the Tortachilla Limestone there is no isotopic variation along the growth lines, thus indicating diagenetic resetting. As mentioned earlier, diagenesis would eventually erase isotopic differences between fossils and their embedding matrix, but as the results of this study show, the isotopic composition of the matrix of the Cadell Marl, for example, differs from its various fossils such as bivalves, gastropods and brachiopods (Figs 4.1 to 4.3). Moreover, "pristine" fossil samples of this study exhibit narrow ranges of isotopic composition that

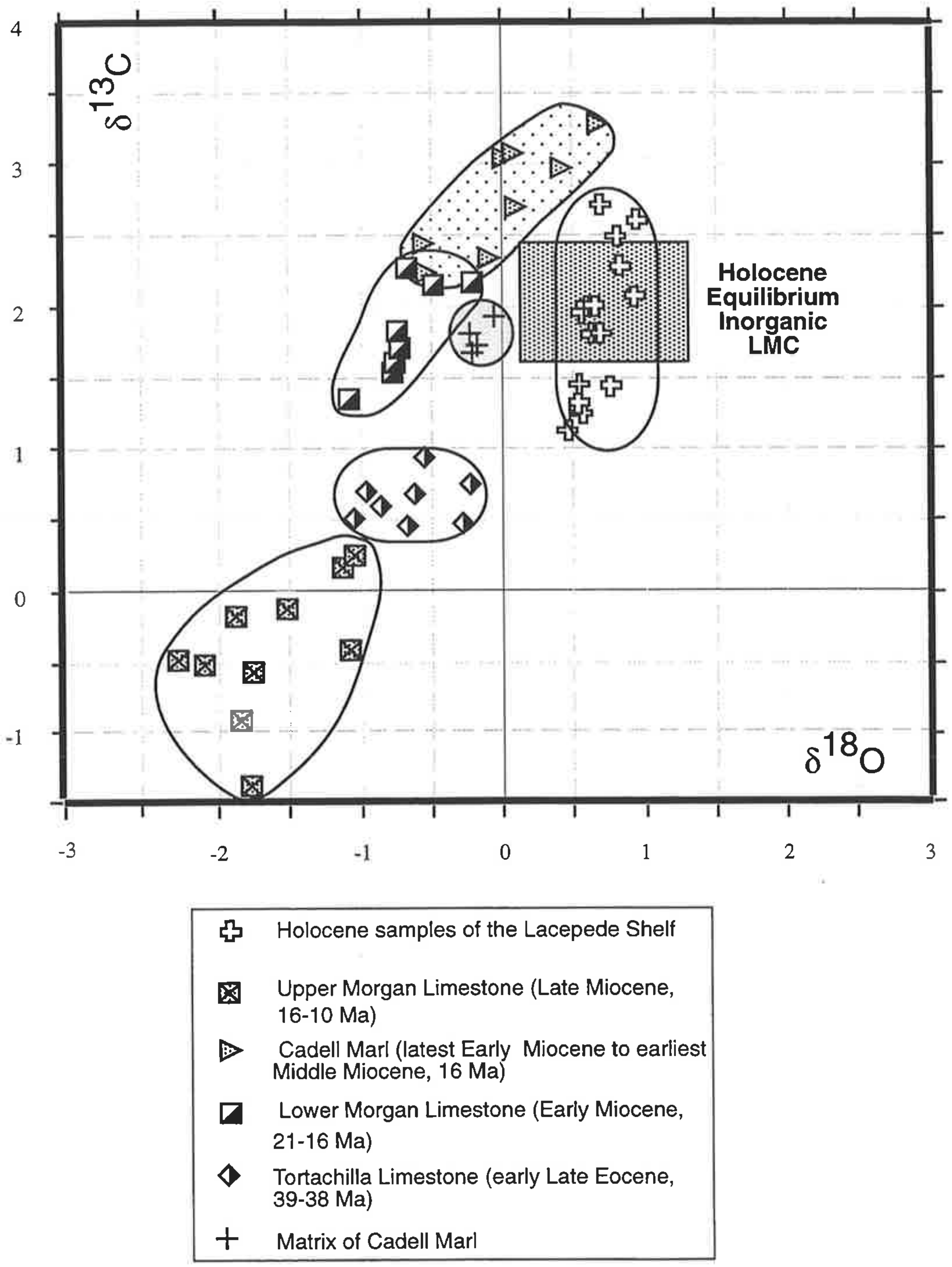


Fig. 4.1. Scattergraph of the isotopic composition of Cenozoic Pecten bivalves from the study areas. The isotopic equilibrium values for Holocene inorganic LMC from the Lacepede Shelf are also shown.

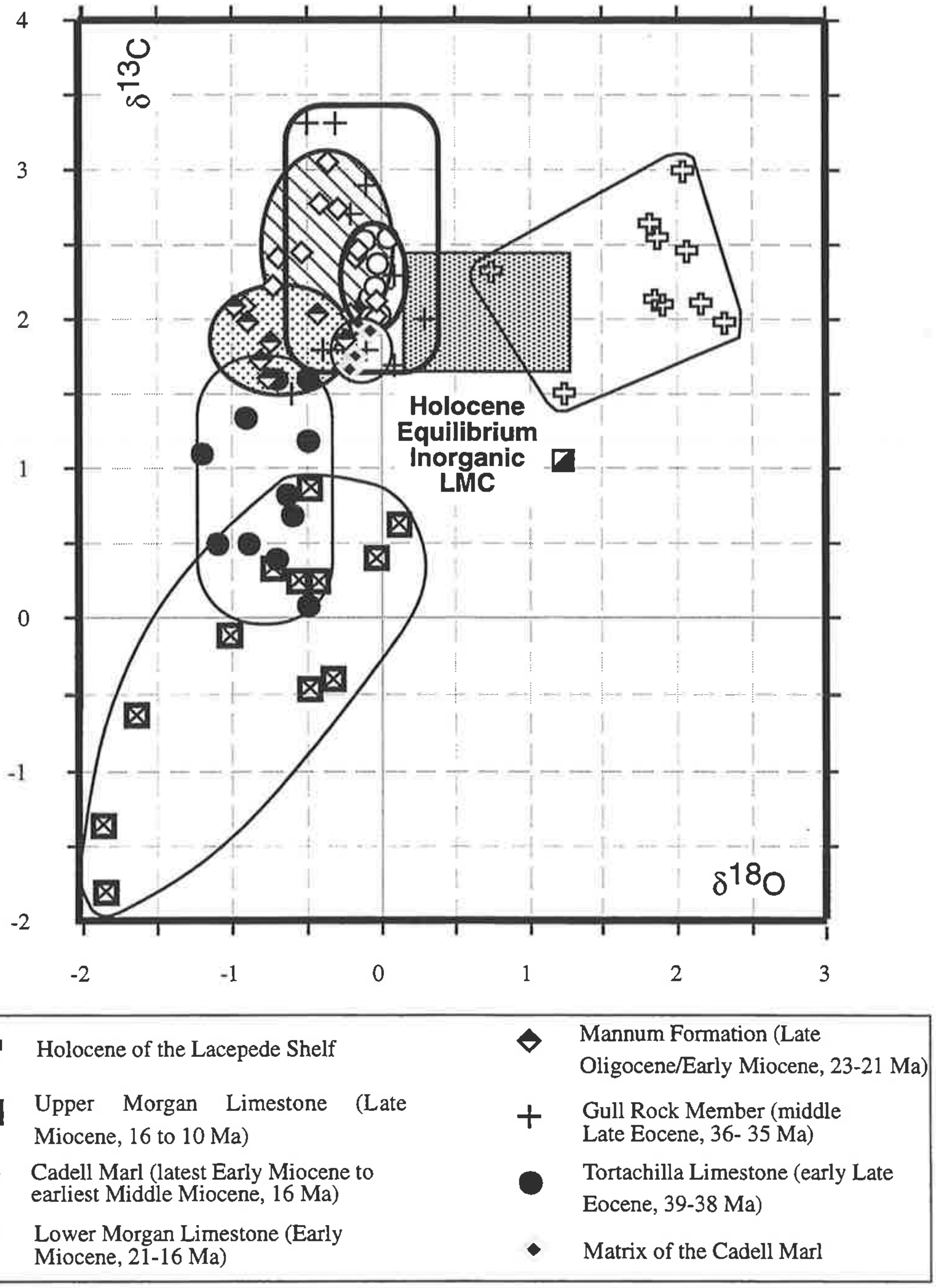


Fig. 4.2. Scattergraph of the isotopic composition of Cenozoic Terebratellidae brachiopoda from the study area.

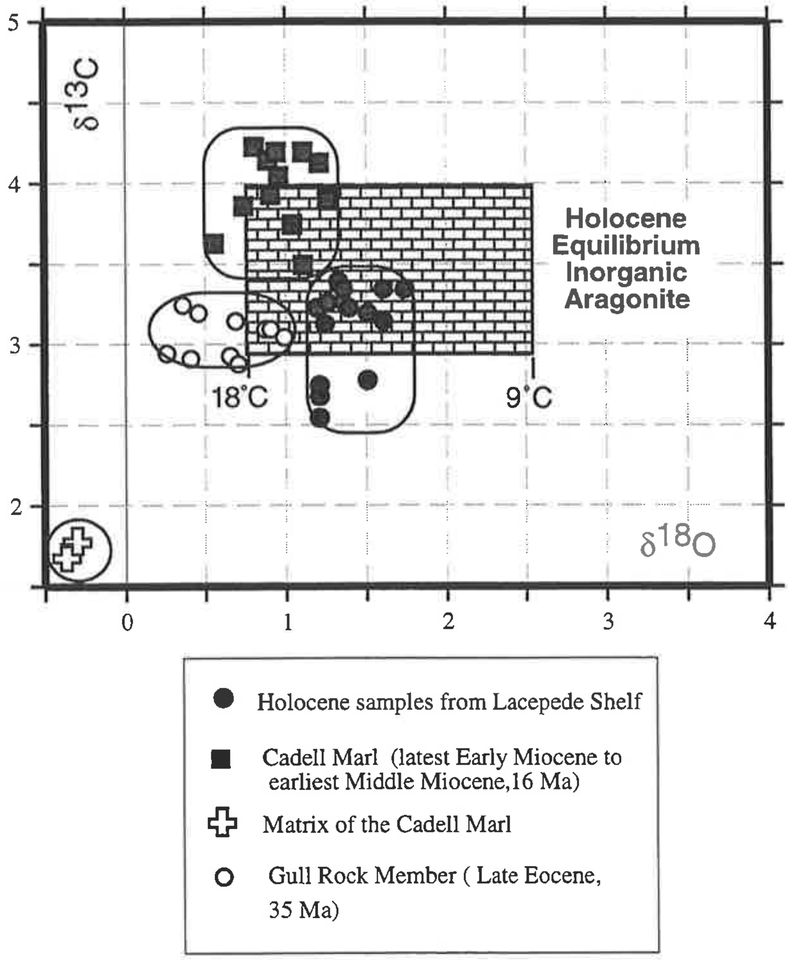


Fig. 4.3. Scattergraph of the isotopic composition of Cenozoic Turritellidae from the study area. The Holocene equilibrium isotopic values of inorganic aragonite from the Lacepede Shelf are also shown.

according to many workers (e.g., Hudson 1977; Marshall 1992) indicate the absence of diagenetic reset (Figs 4.1 to 4.3).

(3) In a suite of fossil samples from the same formation or the same age, the heaviest $\delta^{18}O$ values have most likely retained their original values, because, when oxygen isotopes are affected by diagenesis (e.g., meteoric water alteration) the $\delta^{18}O$ values are lowered (e.g., Hudson 1977; O'Neil 1987). However, Holocene non-altered invertebrate samples may also display scattered $\delta^{18}O$ values because of seasonal temperature variations in their ambient environment (Figs 4.1 to 4.3). Therefore, similar seasonal variations in the $\delta^{18}O$ composition of fossil shells should not be confused with the diagenetic imprint and consequently all observed scattered $\delta^{18}O$ values in the fossil samples should not be attributed to diagenetic alterations.

(4) Low-Mg calcite (LMC) is more stable than high-Mg calcite (HMC) during diagenesis and alteration. Accordingly, LMC fossils such as the Pecten bivalve and Terebratulida brachiopods have often retained their original isotopic values and could be used for isotopic analysis. On the other hand, preservation of HMC organisms indicates that no alteration has taken place and the fossil sample are pristine.

(5) The isotopic fractionation factor between the aragonitic gastropod *Turritella* sp. and the calcitic bivalve *Pecten* sp. in the Holocene samples is about $\Delta\delta^{18}O_{\text{Turritella-Pecten}}$ = 0.8‰ and $\Delta\delta^{13}C_{\text{Turritella-Pecten}}$ = 1.5.‰ (Rahimpour-Bonab et al. 1997b). Accordingly, if the fossil samples have retained their original isotopic composition, they should represent these isotopic fractionations between aragonitic and calcitic mineralogy. This aspect is examined later in this chapter.

(6) Diagenesis is commonly accompanied by a loss of marine Mg and Sr and by an increase in both Mn and Fe (reducing diagenetic environment) (e.g., Brand and Veizer 1981; Marshall 1992). The introduction of Mn (as an activator ion) to carbonate during diagenesis, intensifies its luminescence under cathodoluminescence (CL). Therefore, CL studies reveal any partial or complete replacements of fossil shells by meteoric cements in a reducing environment. In the studied samples those fossils considered as well-preserved are non-luminescent under CL. Additionally, the preservation degree of the non-altered fossil samples was further examined by staining in thin section. This did not show any ferroan (diagenetic) carbonates in shell materials.

The petrographic studies of the microtexture of different fossils in the study area have also been accomplished to distinguish the degree of preservation and possible diagenetic resetting. Accordingly, Turritellidae samples from the Tortachilla Limestone, which originally were aragonite, have been replaced during diagenesis by equant drusy dLMC meteoric cements that exhibit bright luminescence under CL (Fig. 4.4). The Pecten and Terebratulida brachiopods fossils of this unit, however, have retained their original LMC mineralogy and microtexture (Figs 4.5, 4.6). These samples do not luminescence under CL.

Similar petrographic studies were undertaken on all of the fossil samples studied, showing the Turritellidae from the Gull Rock Member and the Cadell Marl are remarkably well-preserved and that their shell walls have retained their original multilayer microtexture (Fig. 4.7). Pecten fossil samples of the Mannum Formation also show well-preserved microtexture. However, they are partially contaminated and infilled by very fine grained dLMC cement in many places such as pores and fractures (Fig. 4.8). Other Pecten fossils from the Lower Morgan Limestone, Cadell Marl and Upper Morgan Limestone are remarkably well-preserved and show their original foliated and fibrous calcite microtexture (Fig. 4.9). The

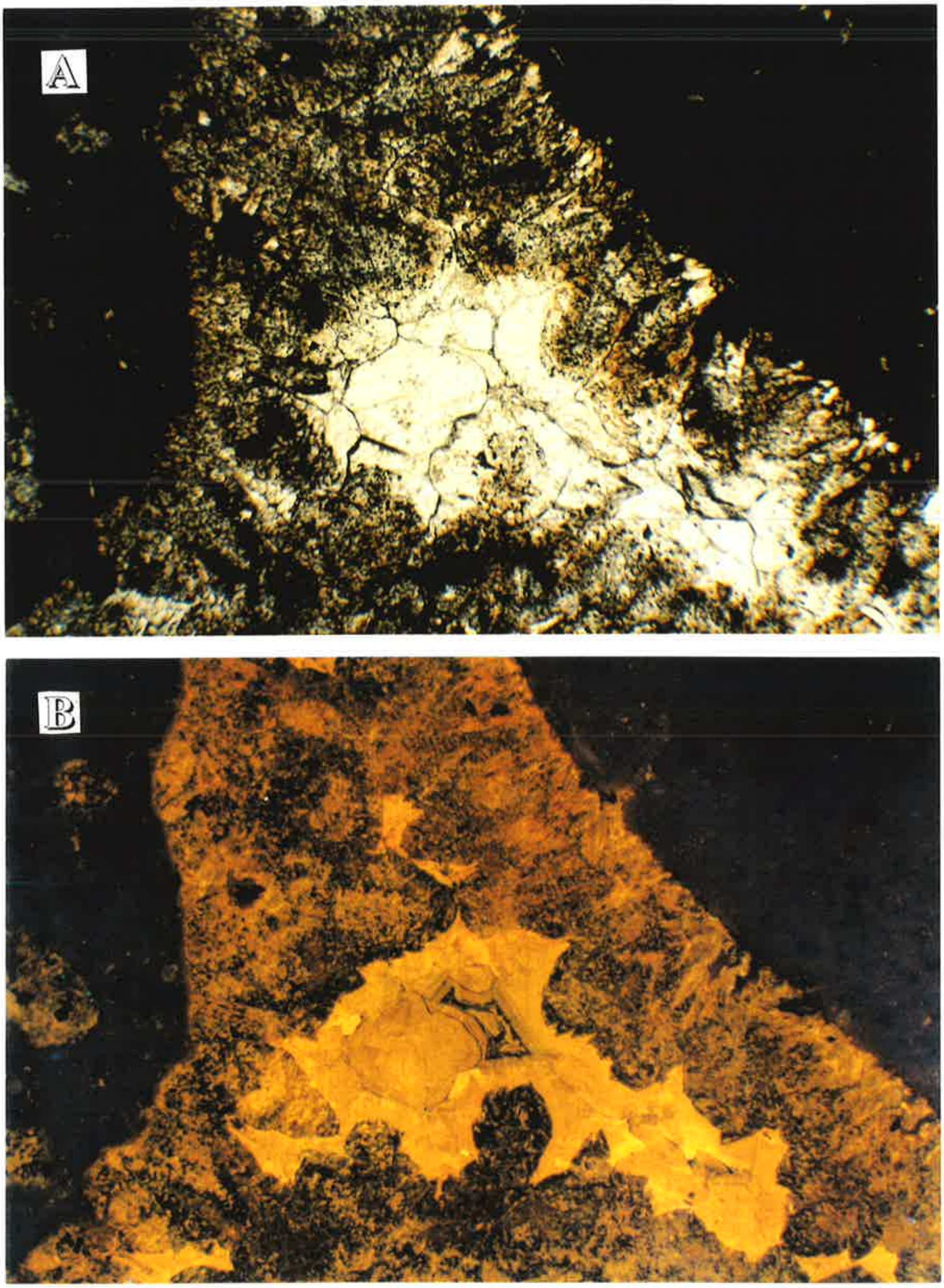


Fig. 4.4. A- Meteoric drusy dLMC cement which replaced the original aragonitic composition of Turritellidae gastropod (PL). B- CL photomicrograph of this cement that shows bright luminescence. The darker areas are due to subsequent exposure of this unit to the vadose zone and consequent oxidation of iron ions and staining of meteoric cements. In hand specimens, because of oxidation these altered fossils are reddish-brown (Field of view 3mm, CL conditions: 195µA, 20kV, 6mins 15sec. exposure time).

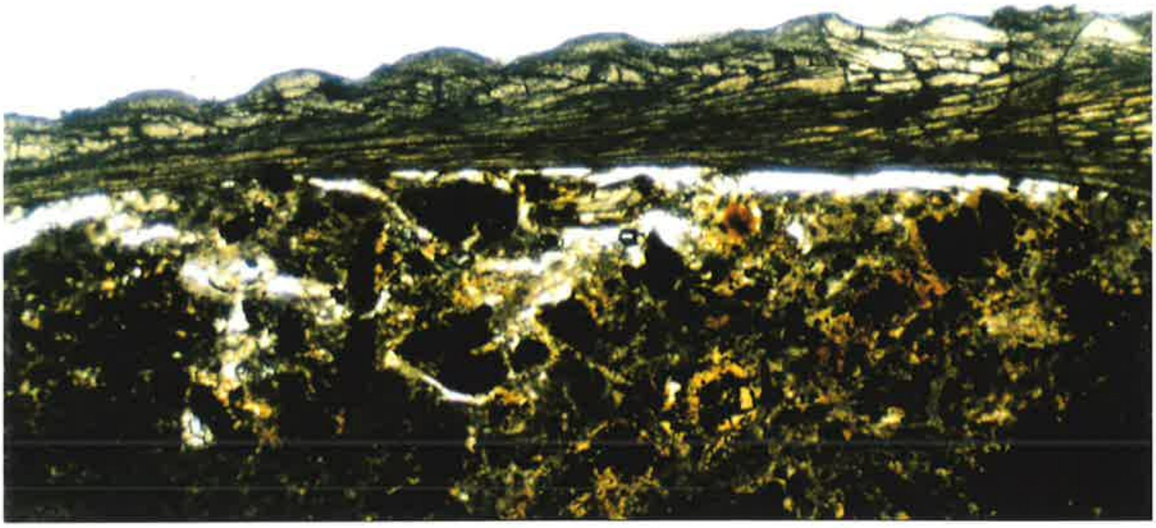


Fig. 4.5. Transverse section through fossil Pecten of the Tortachilla Limestone which shows its original foliated microtexture (LN, Field of view 4mm).

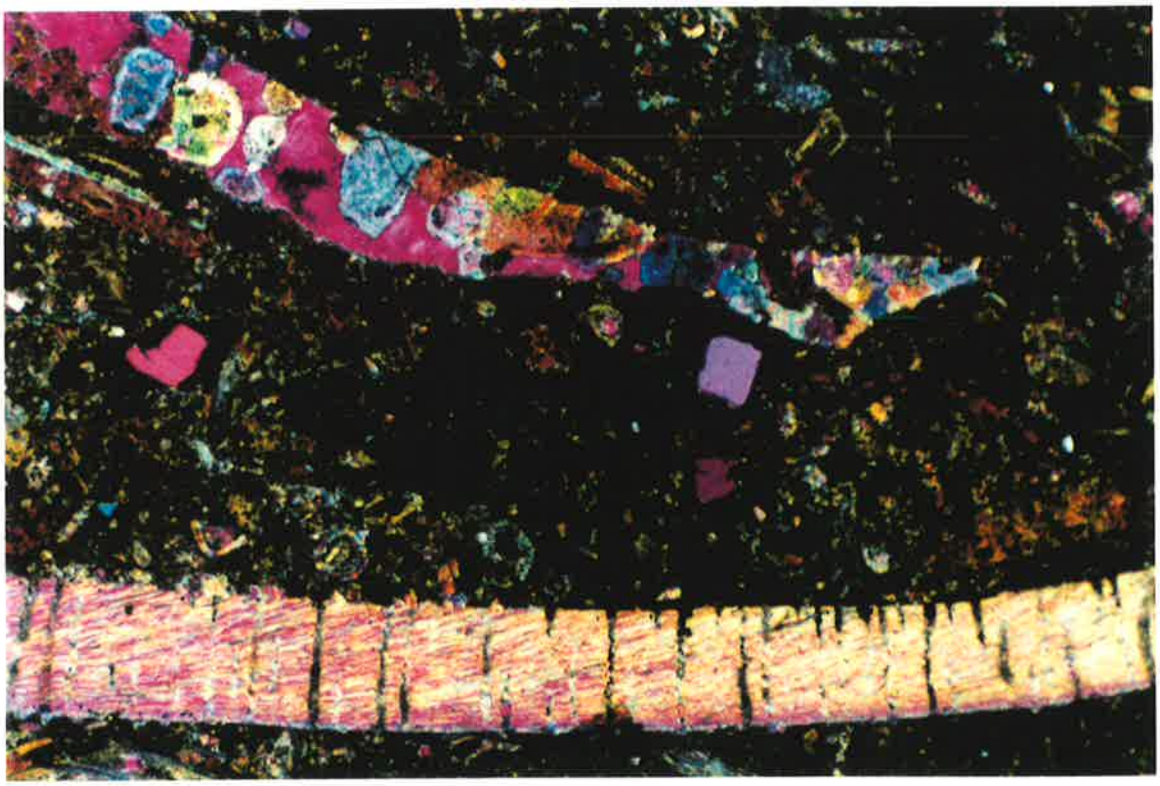


Fig. 4.6. The longitudinal section of a brachiopoda fossil from the Tortachilla Limestone shows its original endopunctate microtexture (up). In the lower part of the photograph, the remaining cast of a dissolved aragonitic gastropod which is partially filled by meteoric cements is also shown (LP, field of view 4 mm).

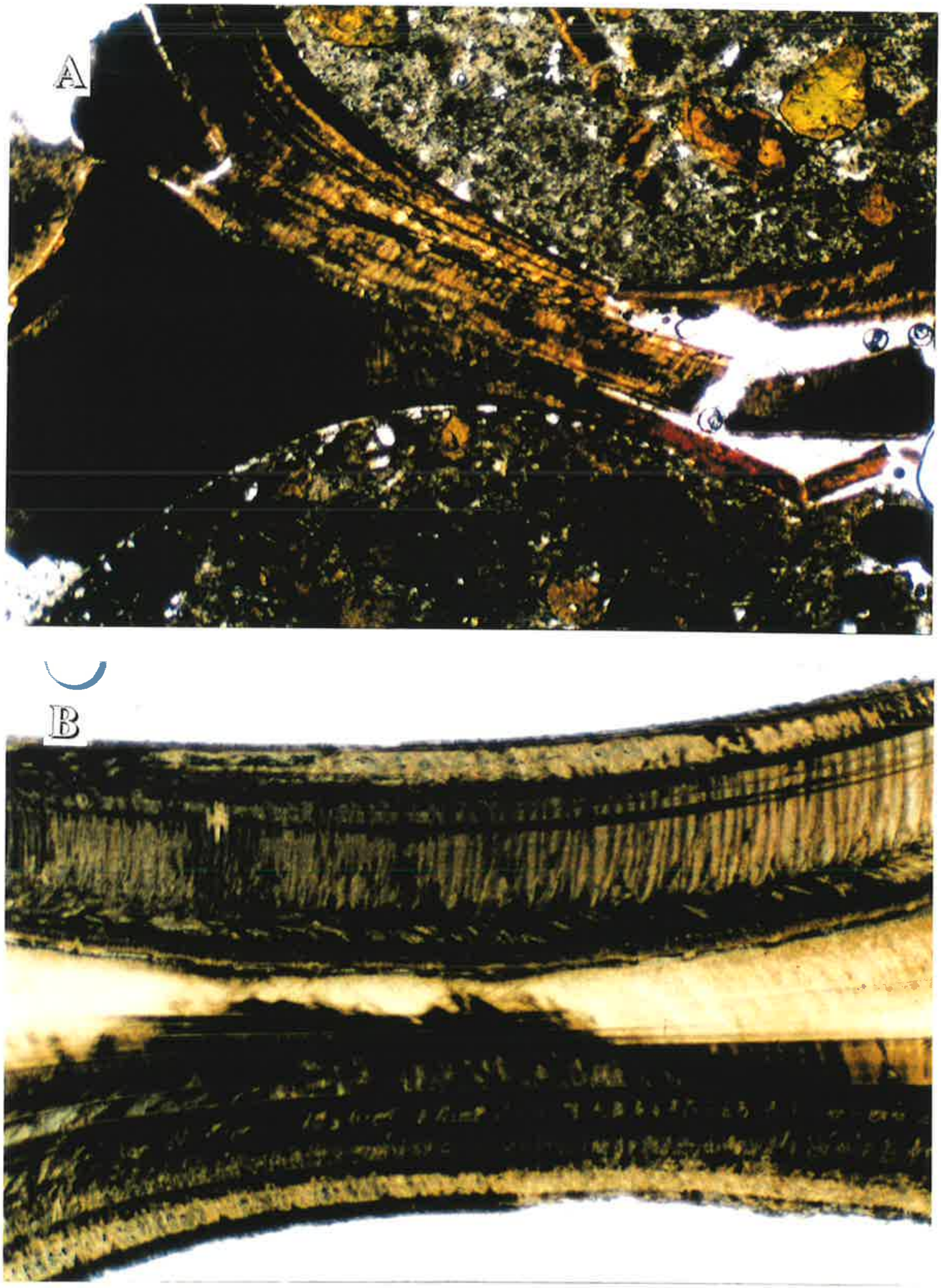


Fig. 4.7. The longitudinal sections of fossil *Turritella* sp. from the Gull Rock Member (A) and Cadell Marl (B) which showing the original multi-layered microtextures (LN, Field of view 3mm, thin sections 100μm thick).

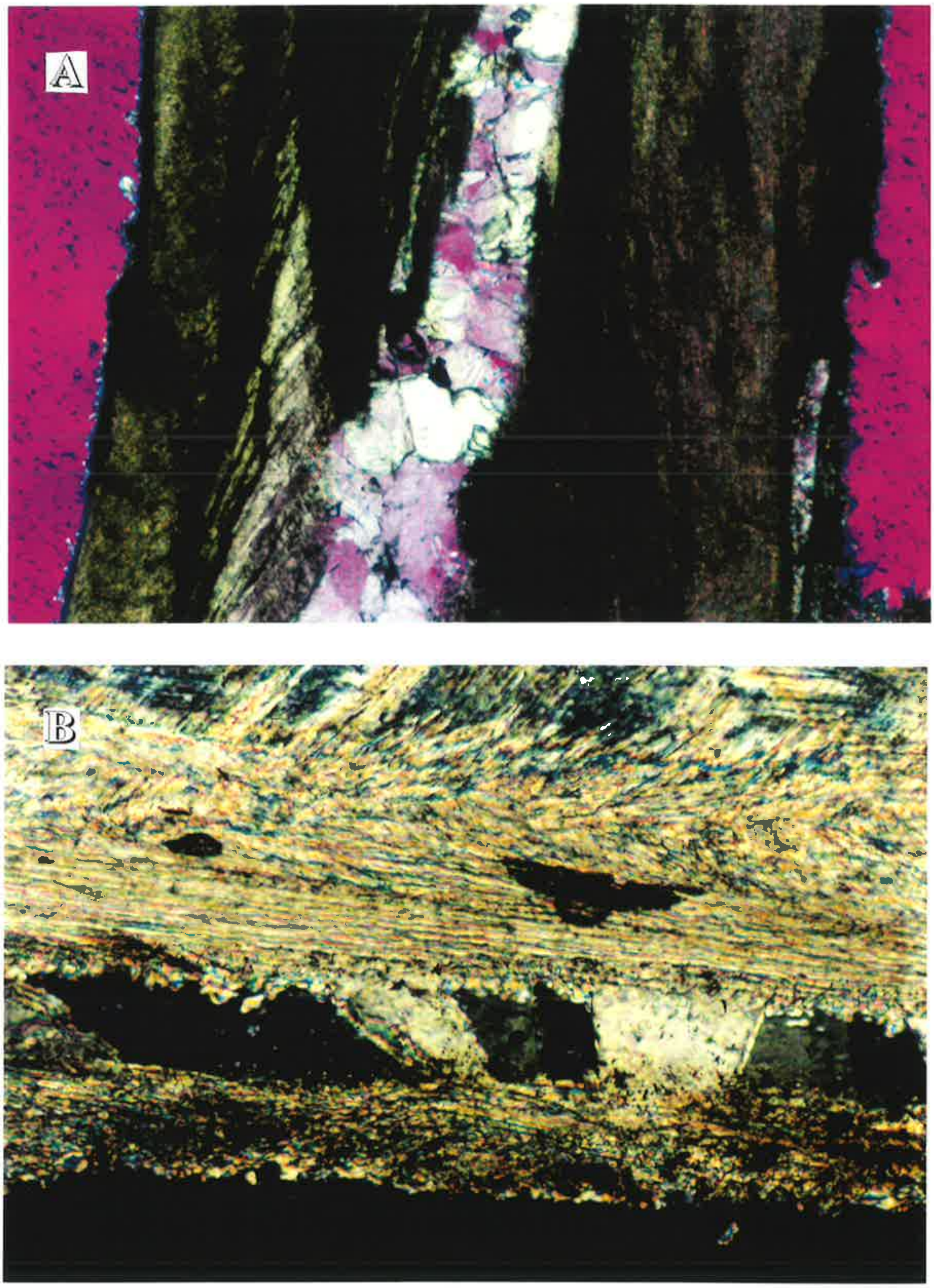


Fig. 4.8. Transverse section through fossil *Pecten* sp. from the Mannum Limestone showing its original horizontal folia and vertical oriented folia. However, the fractures in the shell wall are filled with dLMC cement which originated in the vicinity of the soil/calcrete-zone (A). Another example of this contaminating and infilling cement in a well-preserved fossil *Pecten* sp. of this unit (B) (LP, field of view 2mm).

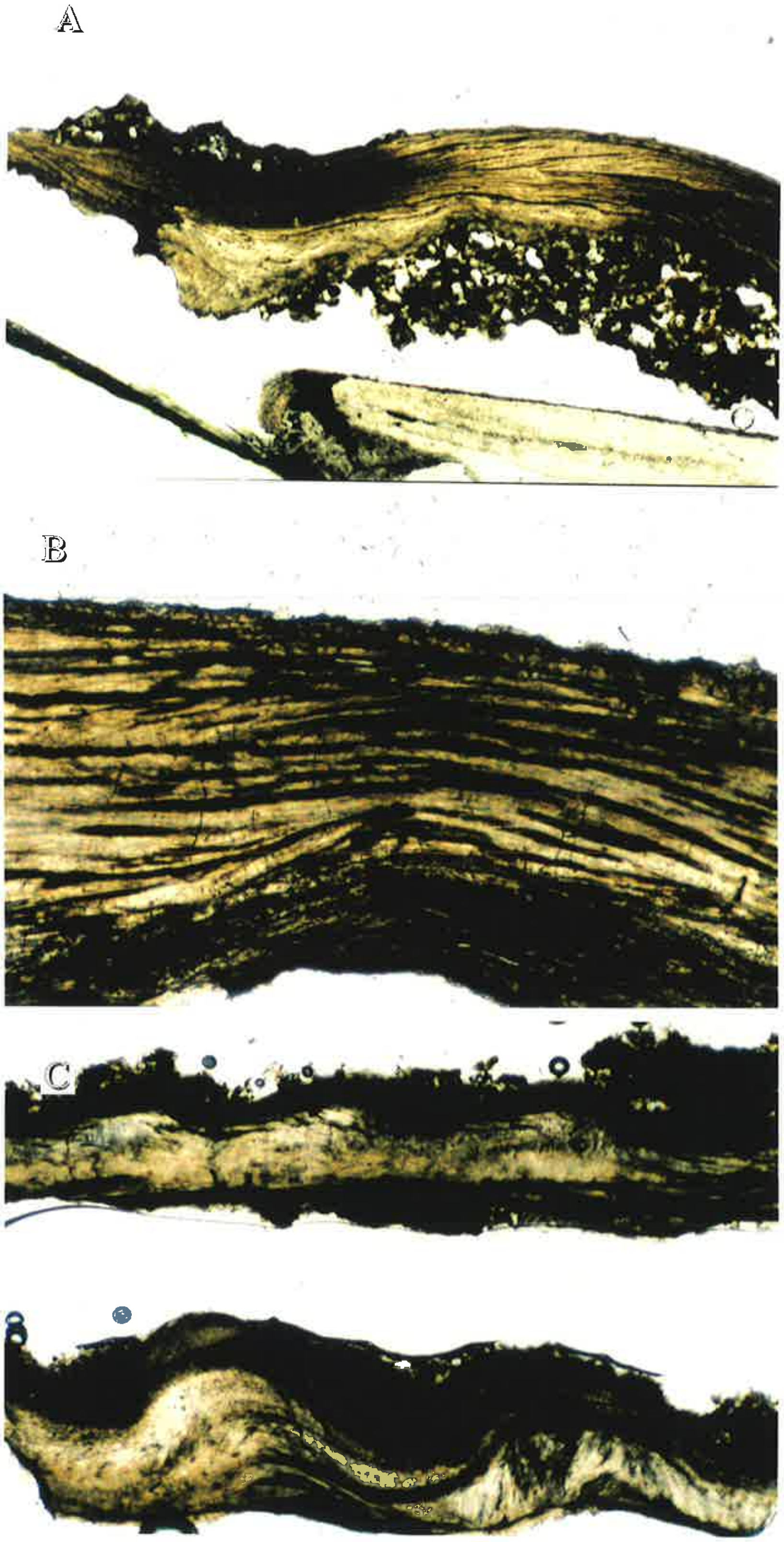


Fig. 4.9. Well-preserved fossils of Pecten from the Lower Morgan Limestone (A), Cadell Marl (B) and Upper Morgan Limestone (C), all showing their original foliated microtexture (LN, field of view 4, 2 and 4mm, respectively).

Terebratulida brachiopod fossils from all the different units of the study area are all well-preserved and show their original endopunctate microtexture. (Fig. 4.10).

(7) Generally, processes that can affect the post-depositional oxygen isotopic composition of fossils on the seafloor (early diagenesis) are: (1) recrystallisation at a lower in situ temperature, (2) recrystallisation in equilibrium with porewaters that contain low ^{18}O composition due to basalt and clay mineral alteration and (3) recrystallisation in a closed system (e.g., Anderson et al. 1976; Killingley 1983). There is no evidence of higher temperatures and such recrystallisation in the studied sections. The secondary processes that can increase the ^{18}O content of marine carbonates after their deposition are, first, preferential dissolution of ^{18}O-depleted materials, for example, in skeletons that have different mineralogy (e.g., *Cellaria* bryozoans - Bone and James, 1997) or in a rock composed of different mineralogies and compositions. Thus, this preferential dissolution would result in an increase in the proportion of heavy ^{18}O-content material. Second, recrystallisation at low temperatures on the seafloor (Kastner et al. 1986), can increase the ^{18}O content of marine carbonates. In the studied fossil samples there is no evidence of preferential dissolution of unstable light-$\delta^{18}O$ components or recrystallisation.

4.3. The Backtracking Process:

In some of the studied Tertiary units, some of the aragonitic and sometimes even the calcitic fossils are dissolved or recrystallised during diagenetic stabilisation and resetting of carbonate sediments in freshwater phreatic and vadose zones. The traces of them now exist as moulds and casts. Less obvious, but critical, is that in some circumstances the original fossil shell microtexture has been preserved but it is contaminated by dLMC cement precipitated in the shell pores

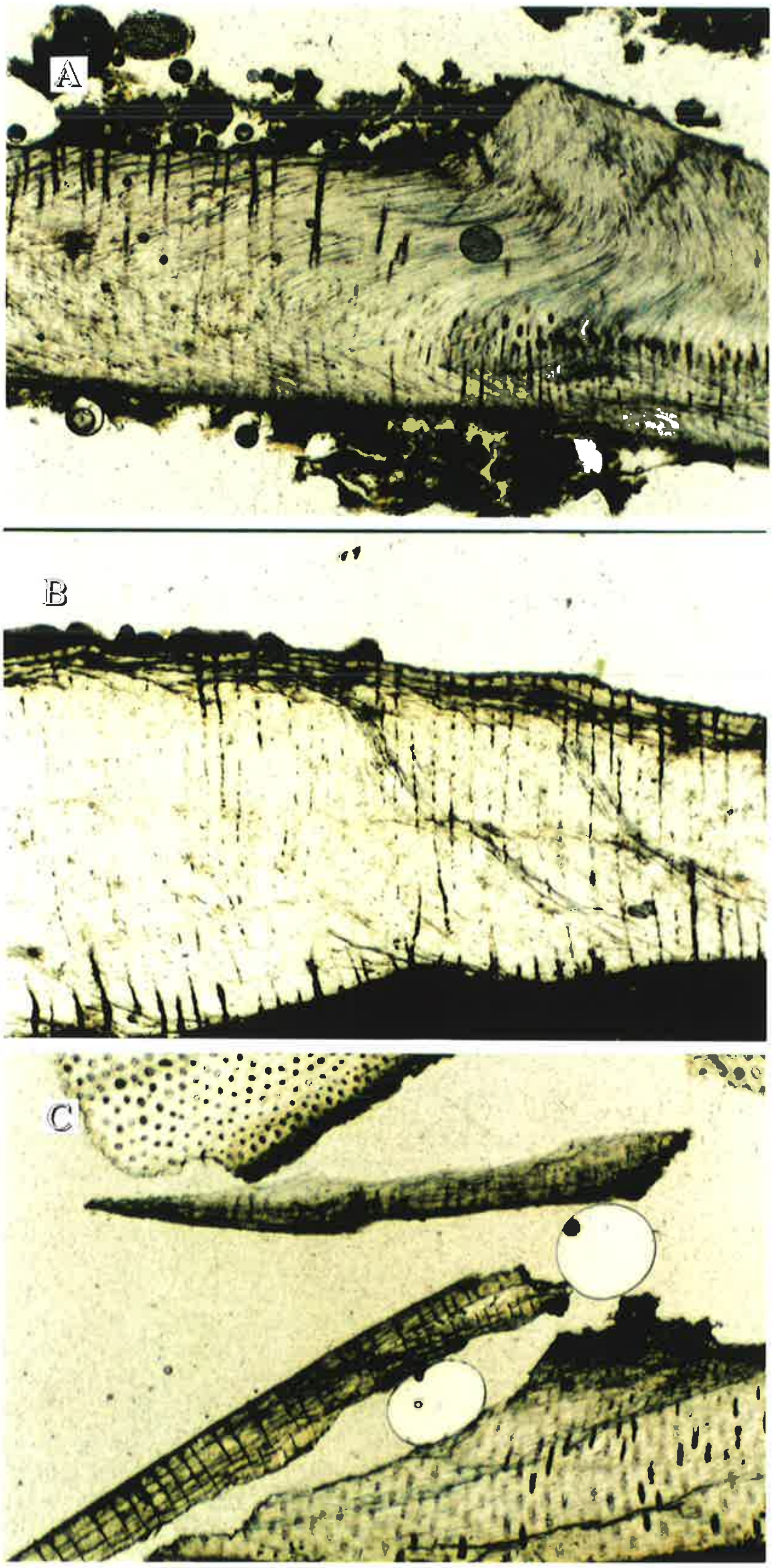


Fig. 4.10. Well-preserved fossils of brachiopoda from the Lower Morgan Limestone (A), Cadell Marl (B) and Upper Morgan Limestone (C), all showing their original endopunctate microtexture (LN, field of view 2, 2 and 4mm, respectively).

(Fig. 4.8). This dLMC cement is sometimes so fine-grained that it could not be separated during sample preparation. Here, the aim is to calculate the original and potential isotopic composition of different dissolved, recrystallised or contaminated Tertiary fossils of the study area by employing previous data on the isotopic compositions and fractionation factors of their Holocene counterparts from the continental shelf of South Australia. In this way, the isotopic fractionation factors observed in different mineralogies and organisms (molluscs and brachiopods) of the Holocene samples are applied to their fossil counterparts, with the knowledge that:

(1) all of the studied Holocene molluscs and brachiopods samples are mineralogically not altered,

(2) most of them do not exhibit significant metabolic and kinetic effects over their isotopic composition,

(3) they are mostly in isotopic equilibrium with their ambient waters and their isotopic composition is in the range of calculated and recorded isotopic equilibrium values (Rahimpour-Bonab et al. 1997b),

(4) using this assumption that, as Dodd and Stanton (1981) suggested, there was no significant changes in the physiology of different taxa (for example brachiopods and molluscs) since Cretaceous time. This assumption is reconfirmed later in this Chapter, by comparisons of the well-preserved fossils of the Cadell Marl and Holocene samples.

It should be mentioned that, in many studies disequilibrium foraminifera species have been used for paleoenvironmental studies after corrections for the metabolic effects on their isotopic composition (e.g., benthic foram *Cibicidoides wuellerstorfi* - Vincent et al. 1980; Keigwin and Corliss 1986).

4.3.1. Tortachilla Limestone:

As mentioned earlier, the aragonitic Turritellidae of this unit are dissolved in the phreatic zone due to diagenetic stabilisation and then replaced by dLMC drusy meteoric cement (Fig. 4.4). Similar to the other meteoric cements, this replacive cement shows growth toward the centre of the pore and brightly luminescences under CL (Fig. 4.4). The most negative values of $\delta^{13}C$ and $\delta^{18}O$ are -7.80 and -4.85‰ respectively, which are also characteristic of its meteoric origin (See Fig. 5.1).

This diagenetic resetting could have occurred in either the meteoric or the mixing zone (e.g., Lohmann 1988), or by porewaters during burial diagenesis (e.g., Choquette and James 1987) (See Chapter Five). To retrieve the original isotopic composition of these fossils the isotopic composition of their co-occurring well-preserved fossils of Pecten has been used. By applying corrections obtained from isotopic studies of their Holocene counterparts ($\Delta\delta^{18}O_{\text{Turritella-Pecten}}$ = 0.8‰ and $\Delta\delta^{13}C_{\text{Turritella-Pecten}}$ = 1.5‰), the average values of $\delta^{13}C_{\text{Turritella}}$ = 2.15 ‰ and $\delta^{18}O_{\text{Turritella}}$ = 0.15‰ resulted (Fig. 4.11).

4.3.2. Gull Rock Member:

In this unit Turritellidae fossils have preserved their aragonitic mineralogy and thus their original isotopic signature (Figs 4.3, 4.7). However, no fossil Pecten were found in this unit and therefore the potential isotopic composition of the missing Pecten is calculated by using the Turritellidae fossils, which gave average isotopic values of $\delta^{13}C_{\text{Pecten}}$ = 1.45‰ and $\delta^{18}O_{\text{Pecten}}$ = -0.2‰ (Fig. 4.12).

4.3.3. Mannum Formation:

The fossil Pecten from this unit show very light $\delta^{13}C$ but relatively normal (marine) $\delta^{18}O$ values, that initially were ascribed to diagenetic alterations.

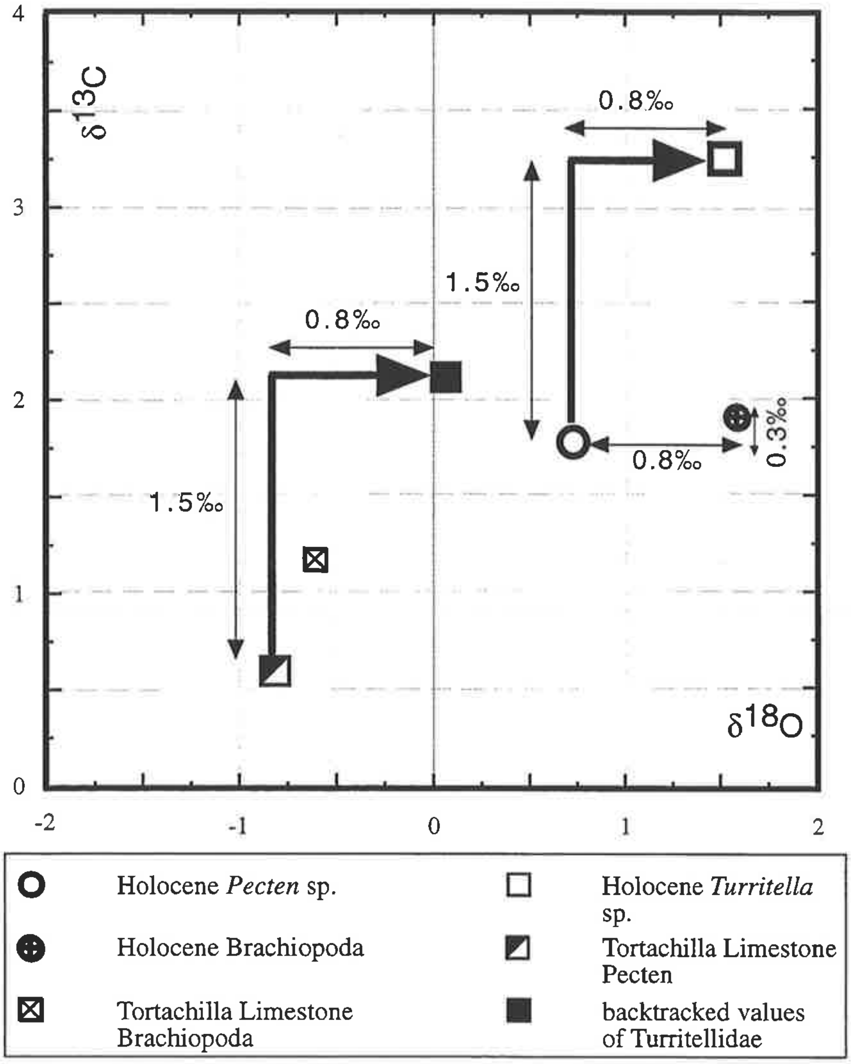


Fig. 4.11. Isotopic backtracking process for fossil samples from the Tortachilla Limestone. The original isotopic composition of the altered Turritellidae, derived from its co-existing well-preserved Pecten by using isotopic fractionation values of their Holocene counterparts, is shown. The isotopic composition of brachiopoda of the Holocene and Tortachilla Limestone, are also shown. All data are average isotopic compositions from several samples (Appendix II).

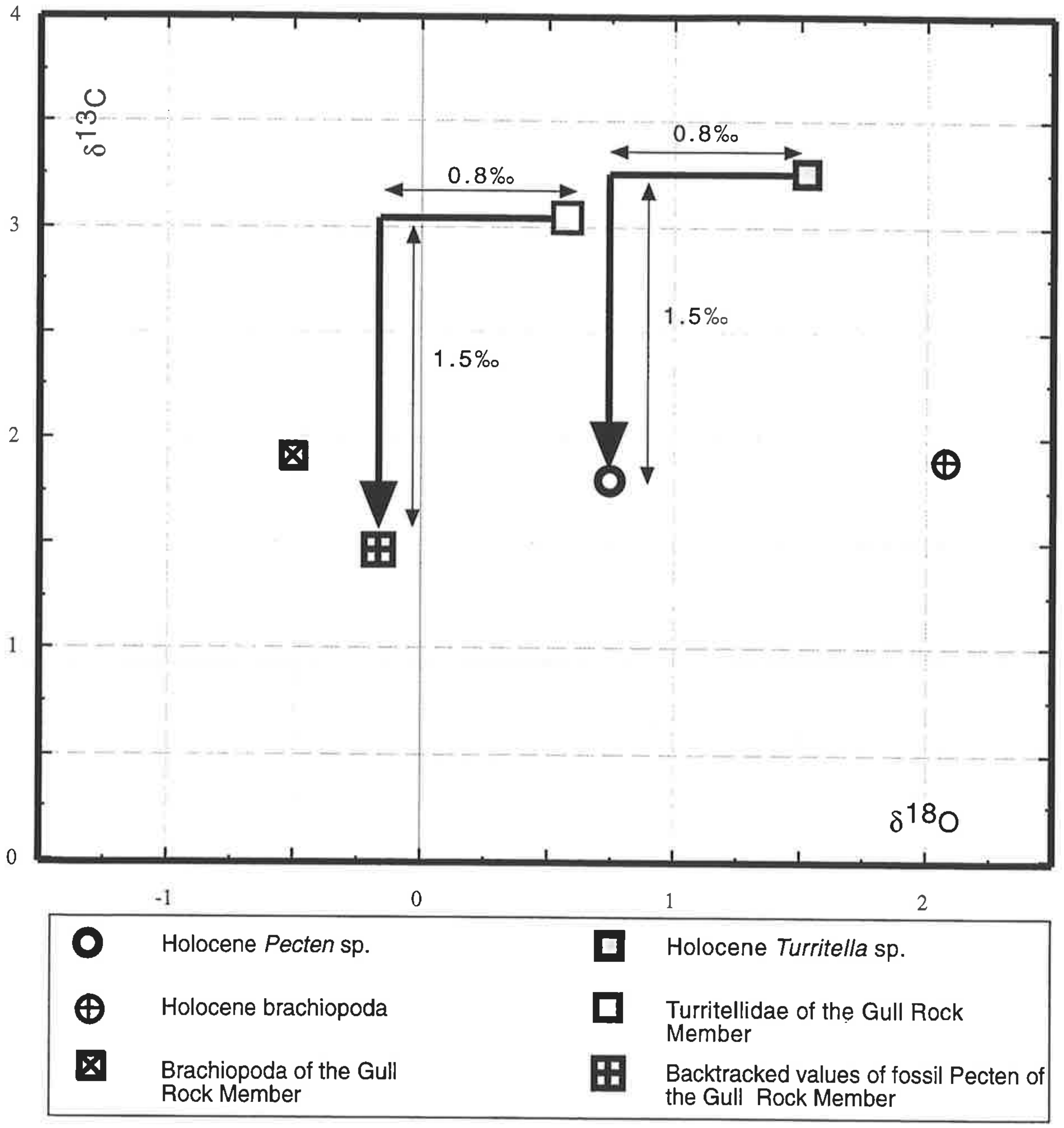


Fig. 4.12. Isotopic backtracking process for fossil samples of the Gull Rock Member. The original isotopic composition of fossil Pecten is predicted from its co-existing well-preserved Turritellidae.

However, this $\delta^{13}C$ depletion is only presented by Pecten fossils of this unit and Terebratellidae brachiopods of this unit show heavy $\delta^{13}C$ values (Figs 4.1, 4.2). This fossil bivalve was collected from the top of the Palaeozoic granite and immediately below the soil/calcrete zone, whereas the brachiopods were collected some distance from the soil/calcrete horizon. At first, it seemed that these LMC fossil Pecten had been diagenetically altered and had lost their original marine isotopic composition. But detailed petrographic studies have revealed that these fossils are well-preserved and have retained their original mineralogy and microtexture (Fig. 4.8). Therefore, the reason for such an apparently anomalous isotopic value (in these fossils) is the contamination of samples with diagenetic products of the vadose zone, which is discussed in the following section.

4.3.3.1. Diagenetic Contamination Of Mannum Formation Pecten Fossil:

Limestones that have undergone near-surface diagenesis show large changes in $\delta^{13}C$ values (up to -8‰) compared to their precursor sediments (e.g., James and Bone 1989). This is due to the low ^{13}C composition of meteoric water, especially when charged with ^{13}C -depleted soil-CO_2 that has a $\delta^{13}C$ of -20 to -30‰ (e.g., Rightmire and Hanshaw 1973; Lohmann 1988). Accordingly, where diagenetic cements formed in the vicinity of soil and especially calcrete zones, they characteristically show negative $\delta^{13}C$ values that reflect the input of large amounts of carbon derived from plant respiration and the decay of plant-derived organic material (e.g., Saller and Moore 1991). Allen and Matthews (1982) suggested that limestones that have undergone diagenetic alteration close to a soil zone are depleted in ^{13}C by about 2-4‰ with respect to similar limestones that have been diagenetically altered in deeper parts of the vadose zone or in freshwater phreatic environments (below the water table).

The Mannum Formation fossil Pecten that were collected from under a soil/calcrete horizon show $\delta^{13}C$ values which are abnormally light (between -1 to

-4‰) compared with the expected marine values (Fig. 4.13). On the other hand, petrographic and CL studies of these fossils revealed that they are not altered texturally, as they retained their original calcitic foliated (LMC) microtexture (Fig. 4.8). Detailed microscopic studies have revealed that they are contaminated by minor fine-grained dLMC cement formed in the vadose zone that could not be separated during sample preparation for isotopic analysis. This fine grained cement, which is infilling micropores, fractures and other voids in the shell microtexture, originated in the vicinity of the soil/calcrete zone and consequently its ^{13}C composition is partially derived from soil/calcrete-CO_2. This light-$\delta^{13}C$ CO_2 when dissolved in meteoric waters, produces light H_2CO_3 that reacts with carbonate as follows:

$$CaCO_3 + H_2CO_3 \rightleftharpoons Ca^{2+} + 2HCO_3$$

One carbon atom is contributed by the parent carbonate and one by the organically derived (soil-CO_2) bicarbonate. This bicarbonate solution, which is moderately depleted in ^{13}C, reacts with the marine origin carbonate and produces new carbonate with $\delta^{13}C$ values as low as -12‰. The continuation of this process and the production of more H_2CO_3 from soil-CO_2 may lead to $\delta^{13}C$ values even less than -12‰. However, interaction of H_2CO_3 with the atmospheric CO_2 ($\delta^{13}C$ = -8‰) leads to a higher carbonate $\delta^{13}C$ (because of the higher $\delta^{13}C$ of atmospheric CO_2). Keith and Weber (1964) showed that tufas and freshwater limestones, formed as a result of this process, exhibit a wide range of $\delta^{13}C$ values as light as -12‰.

In this study, soil/calcrete-CO_2-derived dLMC vadose cement has caused about 5.5 to 6.0‰ depletion in the total $\delta^{13}C$ composition of Pecten fossils from the Mannum Formation (Fig. 4.13). However, this $\delta^{13}C$ signature is still far heavier than the pure soil/calcrete-CO_2-derived cements observed by many workers

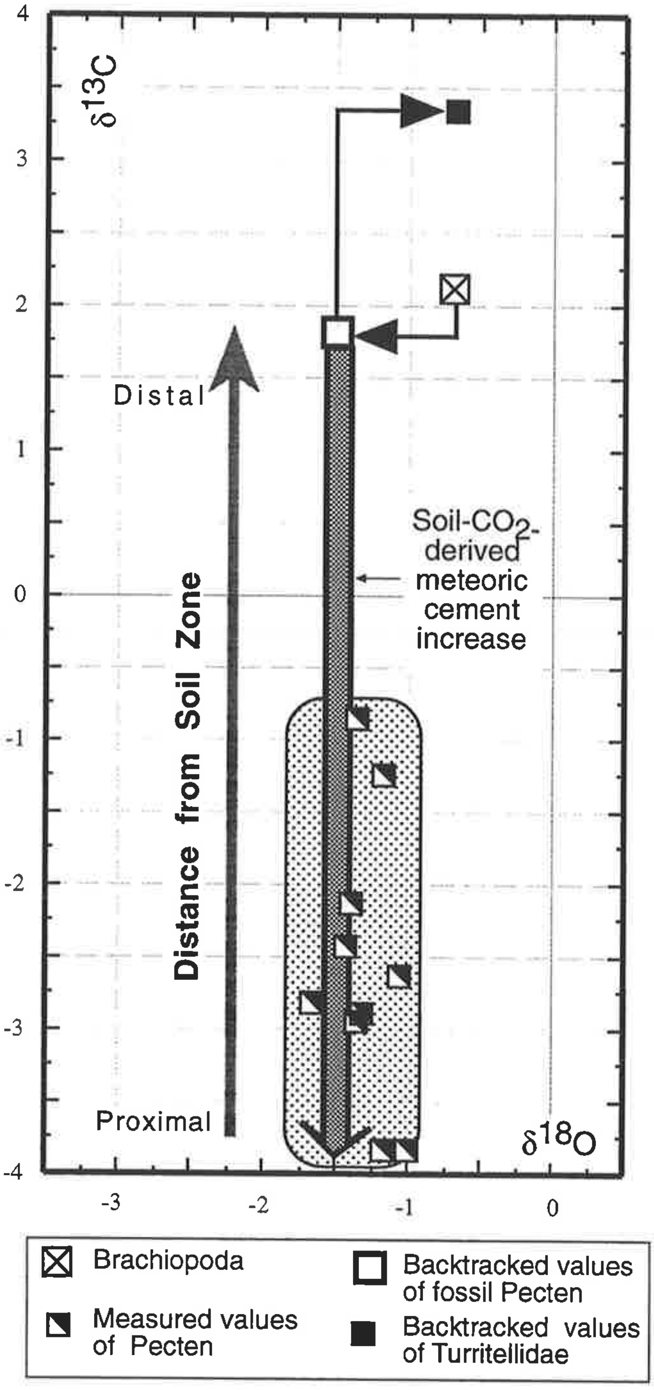


Fig. 4.13. The isotopic backtracking of the Mannum Limestone fossil Pecten from well-preserved brachiopoda of this unit. The measured isotopic composition of Pecten is distorted due to contamination with fine grained soil/calcrete-CO_2-derived vadose cement that producing an abnormally light $\delta^{13}C$ signature in this well-preserved fossil Pecten. The isotopic composition of dissolved Turritellidae of this unit is also extrapolated.

(about -20 to -30‰ - e.g., Rightmire and Hanshaw 1973; Lohmann 1988). There are three reasons for the relatively heavy $\delta^{13}C$ values of Pecten samples compared to pure soil-derived cements. First, as mentioned earlier, the Pecten fossil itself has preserved its original (heavy) marine $\delta^{13}C$ values. Second, as petrographic studies showed, the volume of this vadose cement is insufficient to cause greater negative shifts to the overall (mixed) $\delta^{13}C$ values. Third, the H_2CO_3 is usually produced by the contribution of one carbon atom from soil-CO_2 (very light $\delta^{13}C$) and another one from the original marine carbonates (relatively heavy). In the studied area, the carbon contributed by the marine carbonates is mainly produced by dissolution of the ^{13}C-enriched aragonitic fossils such as gastropods during diagenetic stabilisation of the Mannum Formation. Moulds of these fossils are widespread in this formation.

The reaction of meteoric water as a diagenetic fluid with the marine carbonates can produce dLMC cement in vadose or phreatic environments. Accordingly, as soil-gas CO_2-charged porewaters (meteoric) react with the different rock components, they dissolve the most unstable aragonitic components and precipitate new carbonates as dLMC cements that have lighter $\delta^{13}C$ values than the original marine carbonates (see above). However, the concomitant change in oxygen isotope composition of this newly generated dLMC cement is negligible (Lohmann 1988). Hence, the total isotopic composition of fossil Pecten samples of the Mannum Formation that were contaminated by diagenetic cement, exhibit a highly variable carbon but relatively invariant oxygen composition (Fig. 4.13).

Due to a smaller reservoir of $\delta^{18}O$ (meteoric water) and conversely, a larger reservoir of $\delta^{13}C$ (rock), cement precipitated in meteoric environments shows relatively invariant $\delta^{18}O$ coupled with strongly variant $\delta^{13}C$ (e.g., Lohmann 1988; Saller and Moore 1991). Usually, the $^{18}O_{limestone}/^{18}O_{water}$ ratio and $\delta^{18}O$ of local rainfall and groundwater remains relatively constant during subaerial diagenesis and meteoric cementation, as seen in Barbados by Allen and Matthews (1982). The measured $\delta^{18}O$ values of the Mannum Formation Pecten are close to the marine values that resulted from the backtracking process (Fig. 4.13). This observation demonstrates the relatively heavy $\delta^{18}O$ composition of this dLMC vadose cement, which could have been generated by evaporative enrichment of meteoric waters in the near-surface environment, or, alternatively, reflects the higher rates of water/rock exchange achieved during cementation (See Fig. 5. 1). Gypsum is observed in many places throughout the Murray Basin (Y. Bone, *pers. comm.* 1997).

The original isotopic composition of these fossil Pecten can be calculated by the backtracking technique using the isotopic composition of the well-preserved Terebratellidae brachiopods present in this unit, and comparison with the compositional isotopic relationship of their Holocene counterparts. In the Holocene samples, the average $\delta^{18}O$ values of Terebratellidae brachiopods are about 0.8‰ higher than the co-existing *Pecten* sp. and the $\Delta\delta^{13}C_{brachiopod\text{-}pecten}$ is 0.3‰ (Rahimpour-Bonab et al. 1997b). Thus, the average $\delta^{13}C$ of unaltered *Pecten* sp. would be about 1.5‰ and $\delta^{18}O$ about -1.5‰. The average backtracked values of $\delta^{18}O_{pecten}$ are close to the measured $\delta^{18}O$ values of the contaminated fossil Pecten of this unit (Fig. 4.13), which substantiates the contention about the abnormally heavy $\delta^{18}O$ values of the aforesaid contaminating dLMC cement.

Hence, the stratigraphic/geomorphic position of the sampling site is responsible for the $\delta^{13}C$ depletion observed in the Pecten, while the brachiopods collected from elsewhere in the Mannum Formation, some distance from the soil/calcrete zone, do not exhibit any isotopic depletion (Fig. 4.2). Therefore, the $\delta^{13}C$ depleted values in these fossil Pecten result from incorporation of soil gas CO_2 at the particular sampling site. The average backtracked isotopic values of Turritellidae in this unit are $\delta^{13}C = 3.4‰$ and $\delta^{18}O = -0.65‰$ (Fig. 4.13).

4.3.4. Lower Morgan Limestone:

Pecten fossils of this unit are well-preserved but aragonitic Turritellidae are dissolved during diagenetic stabilisation and are present as moulds and casts. The original isotopic composition of these gastropoda calculated by the backtracking method gives average values of $\delta^{13}C = 3.40‰$ and of $\delta^{18}O = 0.20‰$ (Fig. 4.14).

4.3.5. Cadell Marl:

All fossil samples of this unit are remarkably well-preserved. The isotopic composition of different fossils has been measured to be used as a reference for comparison between different fossils and to retrieve the potential marine isotopic signature of the Upper Morgan Limestone (Figs 4.1, 4.2, 4.3, 4.15).

4.3.6. Upper Morgan Limestone:

All of the Pecten and Terebratellidae brachiopod fossil samples of this unit exhibit very light $\delta^{13}C$ values and are also associated with light $\delta^{18}O$. However, petrographic studies revealed that they all have retained their original microtexture and show neither diagenetic alteration nor contamination by diagenetic cements (Figs 4.9, 4.10). Therefore, these light isotopic values can be ascribed to their ambient marine environment and consequently are original. The $\delta^{13}C$ depletion in these fossils is partly induced by the global negative shift of $\delta^{13}C_{DIC}$ at Middle Miocene to Late Miocene time and partly by regional effects due to the influx of organic matter to the basin from the surrounding continent (See Chapter Six). The maximum $\delta^{13}C$ offset of the Middle Miocene observed in benthic foraminifera is about 1‰ (e.g., Woodruff and Savin 1985), which is much

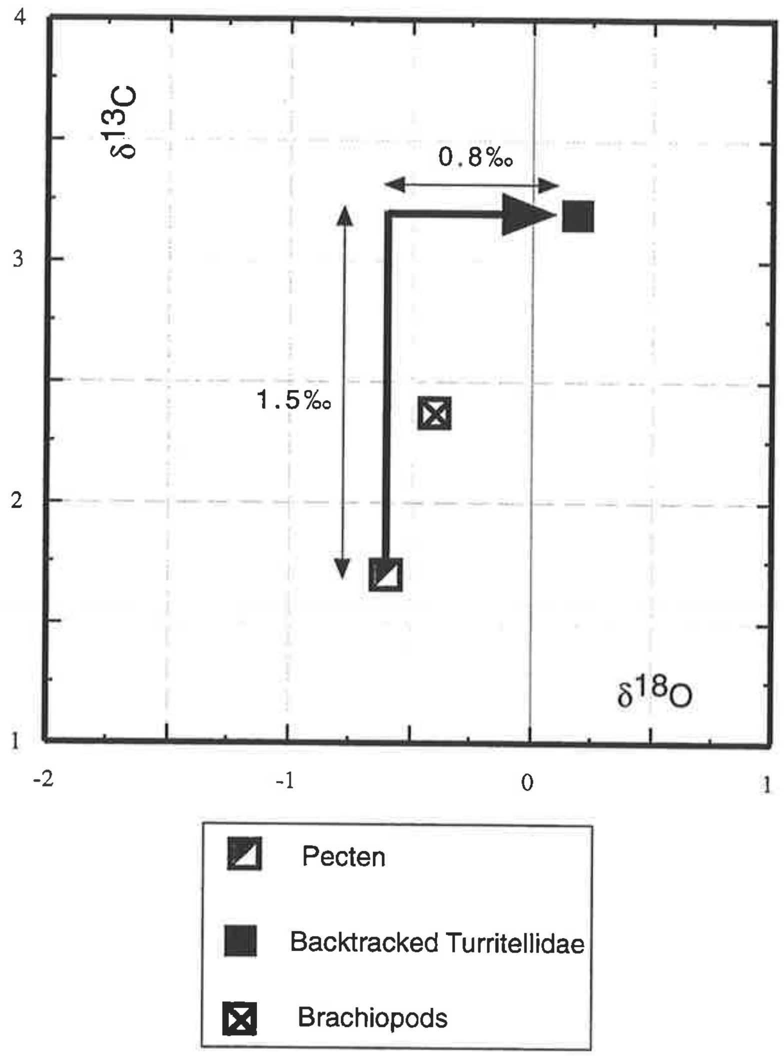


Fig. 4.14. Isotopic backtracking process of dissolved Turritelllidae of the Lower Morgan Limestone from its coexisting well-preserved Pecten.

less than the total average $\delta^{13}C$ negative excursion of Upper Morgan Limestone fossils compared to those from the Cadell Marl (about 3.0‰) (Fig. 4.15). Therefore, most of the $\delta^{13}C$ negative shifts in the Upper Morgan Limestone samples is caused by regional conditions. The ice-build-up intensification of Middle Miocene time did not lead to total retreat of the sea from the Murray Basin but imposed restricted circulation in the basin and limited access to the open ocean (See Chapter Six). On the other hand, because of global climatic deterioration and aridification which was also prevailing in Australia at this time, the biomass had commenced to transfer from the continents toward the marine environments and consequently introduced large amount of $\delta^{13}C$-depleted organic material to the ocean waters that led to depletion of $\delta^{13}C_{DIC}$ in the world ocean waters and including the Murray Basin waters. This eventually led to negative shifts in the $\delta^{13}C$ composition of diverse carbonate-producing organisms, as seen in different fossils of the Upper Morgan Limestone. By considering the $\delta^{13}C$ values of Cadell Marl fossils, and applying about 1‰ correction for global depletion in $\delta^{13}C_{DIC}$ of that time (e.g., Woodruff and Savin 1985), the $\delta^{13}C$ average backtracked values of the Upper Morgan Limestone fossils would be about 1.7‰ for Pecten., 1.25‰ for brachiopods, and 3.0‰ for Turritellidae (Fig. 4.15).

Due to restriction and shoaling of the Murray Basin during the Late Miocene, the influence of continental runoff had increased and led to abnormally light $\delta^{18}O_{seawater}$, as well, which is reflected in the $\delta^{18}O$ composition of different fossils of the Upper Morgan Limestone (Fig. 4.15). This light $\delta^{18}O$ composition is contrary to the expected values for the glacially active Middle Miocene, which caused high $\delta^{18}O$ signatures all over the world. Therefore, the $\delta^{18}O$ values of the Upper Morgan Limestone fossils are possibly reduced (negative excursion) due to freshwater influx into the basin. Hence, considering about a 0.96‰ positive shift of $\delta^{18}O$ for that time and using the average $\delta^{18}O$ of the Cadell Marl fossils,

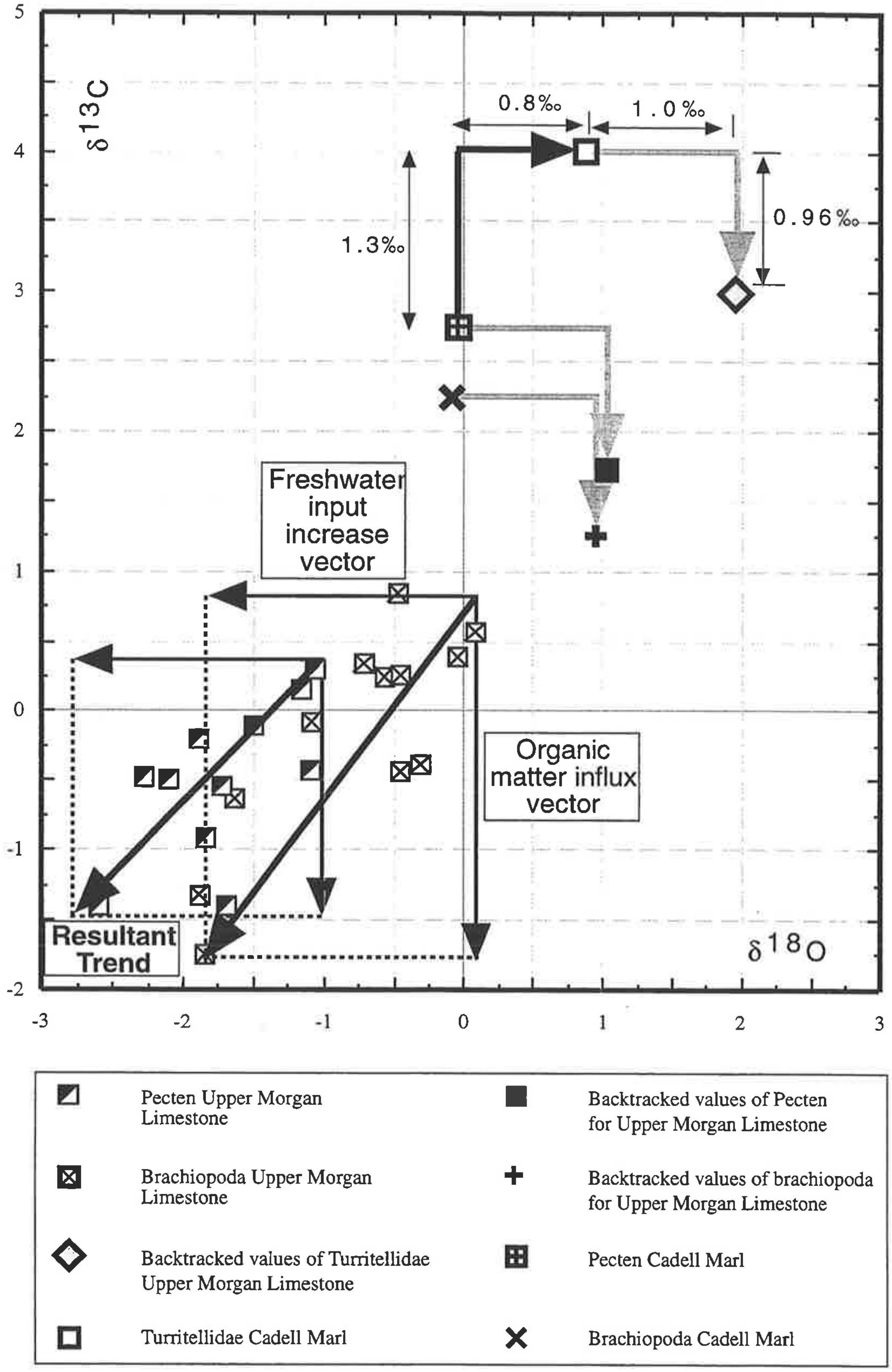


Fig. 4.15. The isotopic backtracking process in different fossils of the Upper Morgan Limestone. The data are average values. As shown in the bottom-left corner of the graph, the original isotopic composition of the Upper Morgan Limestone Pecten and brachiopods show some depletion in their isotopic composition because of the organic matter-charged freshwater influx. The fractionation between well-preserved Turritellidae and Pecten of the Cadell Marl is very close to the fractionation shown by their Holocene counterparts.

the average $\delta^{18}O$ values of 1.1‰ in Pecten, 0.95‰ in brachiopods and 1.9‰ in Turritellidae are obtained (Fig. 4.15). As shown here by this backtracking technique, even potential marine isotopic signatures can be extracted from the mixed marine-freshwater isotopic signatures. The isotopic composition extrapolated for these fossils by the backtracking technique is in the range of values expected for Late Miocene time (See Chapter Six).

4.4. Conclusion:

The fractionation factors between coexisting well-preserved Terebratellidae brachiopods and Pecten ($\Delta\delta^{13}C_{\text{brachiopod-Pecten}}$ and $\Delta\delta^{18}O_{\text{brachiopod-Pecten}}$) of different units are compared, to examine the accuracy of the backtracked isotopic values in different units. The average $\Delta\delta^{13}C_{\text{brachiopod-Pecten}}$ for the Tortachilla Limestone is 0.6‰ (Fig. 4.11), for the Gull Rock Member is 0.45‰ (Fig. 4.12) and for the Lower Morgan Limestone is 0.6‰ (Fig. 4.14), all of which are close to the Holocene values of $\Delta\delta^{13}C_{\text{brachiopod-Pecten}} = 0.3$‰ (Fig. 4.11). The average $\Delta\delta^{18}O_{\text{brachiopod-Pecten}}$ values for the Tortachilla Limestone is 0.2‰, for the Gull Rock Member -0.3‰, for the Lower Morgan Limestone 0.2‰ and for the Cadell Marl 0.1‰. These values show some inconsistencies (in some fossils) in comparison with $\Delta\delta^{18}O_{\text{brachiopod-Pecten}} = 0.8$‰ of the Holocene samples which can be attributed to microhabitat effects.

The isotopic composition of Turritellidae and Pecten from the Cadell Marl is $\Delta\delta^{13}C_{\text{Turritella-Pecten}} = 1.3$‰ and $\Delta\delta^{18}O_{\text{Turritella-Pecten}} = 0.9$‰. These fractionation values are very close to their Holocene counterparts ($\Delta\delta^{13}C_{\text{Turritella-Pecten}} = 1.5$‰ and $\Delta\delta^{18}O_{\text{Turritella-Pecten}} = 0.8$‰), which reconfirms the confidence in the backtracking process.

This study shows the importance of geochemical investigations of the Holocene carbonate environments for geochemical evaluation of their ancient counterparts. The isotopic composition of altered fossil samples can be retrieved in many cases by having a sound data base for their Holocene counterparts. Accordingly, the backtracking process can be employed to retrieve the original isotopic signature of the recrystallised, dissolved or contaminated fossil material. Of course, the interpretation is not based merely on the backtracking data, but they rather used as supportive and complementary data for measured isotopic data, resulting from analysis of unaltered (pristine) fossil materials. Therefore, measured isotopic values along with isotopic data retrieved by the backtracking process, can be confidently used for paleoenvironmental reconstructions and paleoclimatological investigations (See Chapter Six).

CHAPTER FIVE

GEOCHEMICAL IMPLICATIONS FOR DIAGENETIC PROCESSES AND ESTIMATIONS OF ISOTOPIC COMPOSITION OF DIAGENETIC FLUIDS

5.1. Introduction:

The chemical and isotopic composition of meteoric waters vary during passage through sedimentary carbonate sequences due to rock-water interactions, uptake of organically derived CO_2 and mineralogical discrepancies of different carbonate sequences. Accordingly, the $\delta^{18}O$ value of meteoric groundwater is mainly invariable (constant) at a geographic location, whilst the $\delta^{13}C$ of this water is variable due to variations in the amount of dissolved soil-gas CO_2 and in the extent of rock-water interaction. This concomitant invariability in $\delta^{18}O$ and variability in $\delta^{13}C$ signatures of meteoric waters is reflected in its diagenetic products, producing a distinct geochemical trend, termed the meteoric calcite line (Lohmann 1988). Lohmann (1988) suggested that this line can serve as a baseline for distinguishing different diagenetic environments, using the isotopic signature of their products.

Meteoric calcite cements are usually 2.0‰ lighter in $\delta^{18}O$ than the contemporaneous marine calcite (e.g., Frank et al. 1995). Craig (1961) and Dansgaard (1964) have shown that the $\delta^{18}O$ values of meteoric waters generally become lighter with increasing latitude. The $\delta^{18}O$ value of shallow meteoric cements (near surface) is controlled by the isotopic composition of rain-water in the region, and climatic variations (See Chapter Eight). Modern rain-waters vary in $\delta^{18}O$ value, from as much as 0.0‰ (low latitude in arid regions) to -5.0‰ (in humid monsoon climates - e.g., Aharon 1983, Anderson and Arthur 1983). Therefore, the $\delta^{18}O$ values of meteoric cement can vary drastically and are only partially dependent on the rock reservoir $\delta^{18}O$ value (e.g., Saller and Moore 1991). In this chapter, some of the diagenetic implications of meteoric cements from different carbonate units in the study areas are investigated and the isotopic signature of diagenetic fluids is estimated.

5.2. Tortachilla Limestone:

The stable isotopic ratio from the Tortachilla Limestone (See Fig. 1.4) coarse diagenetic Low-Mg-Calcite cement (dLMC) is plotted in Fig. 5.1. Also shown are average values of the isotopic composition of Tortachilla Limestone Pecten and brachiopoda calcites, which are precipitated approximately in isotopic equilibrium with their ambient seawater. Consequently, these can be considered as proxies for seawater isotopic composition of the early Late Eocene. The majority of dLMC cement in this unit shows relatively invariant $\delta^{18}O$ and highly variant $\delta^{13}C$. The overall isotopic composition range between -3.85 and -4.8‰ for $\delta^{18}O$ and -3.85 and -7.8‰ for $\delta^{13}C$. As shown, all dLMC cement isotopic values are depleted with respect to the Tortachilla Limestone marine calcite (Pecten and Terebratellidae brachiopoda).

In Fig. 5.2, the $\delta^{18}O$ range of this dLMC cement is overlain on an equilibrium fractionation diagram which relates calcite $\delta^{18}O$ PDB values to temperature for a range of pore fluid (diagenetic pore fluid) compositions (relative to SMOW). If the temperature of dLMC cement precipitation is constrained between 20 to 30°C (probable temperature range, See Chapter Six), $\delta^{18}O$ values of the diagenetic fluids range from -2.7 to -5‰ (SMOW). The only curve that passes through the

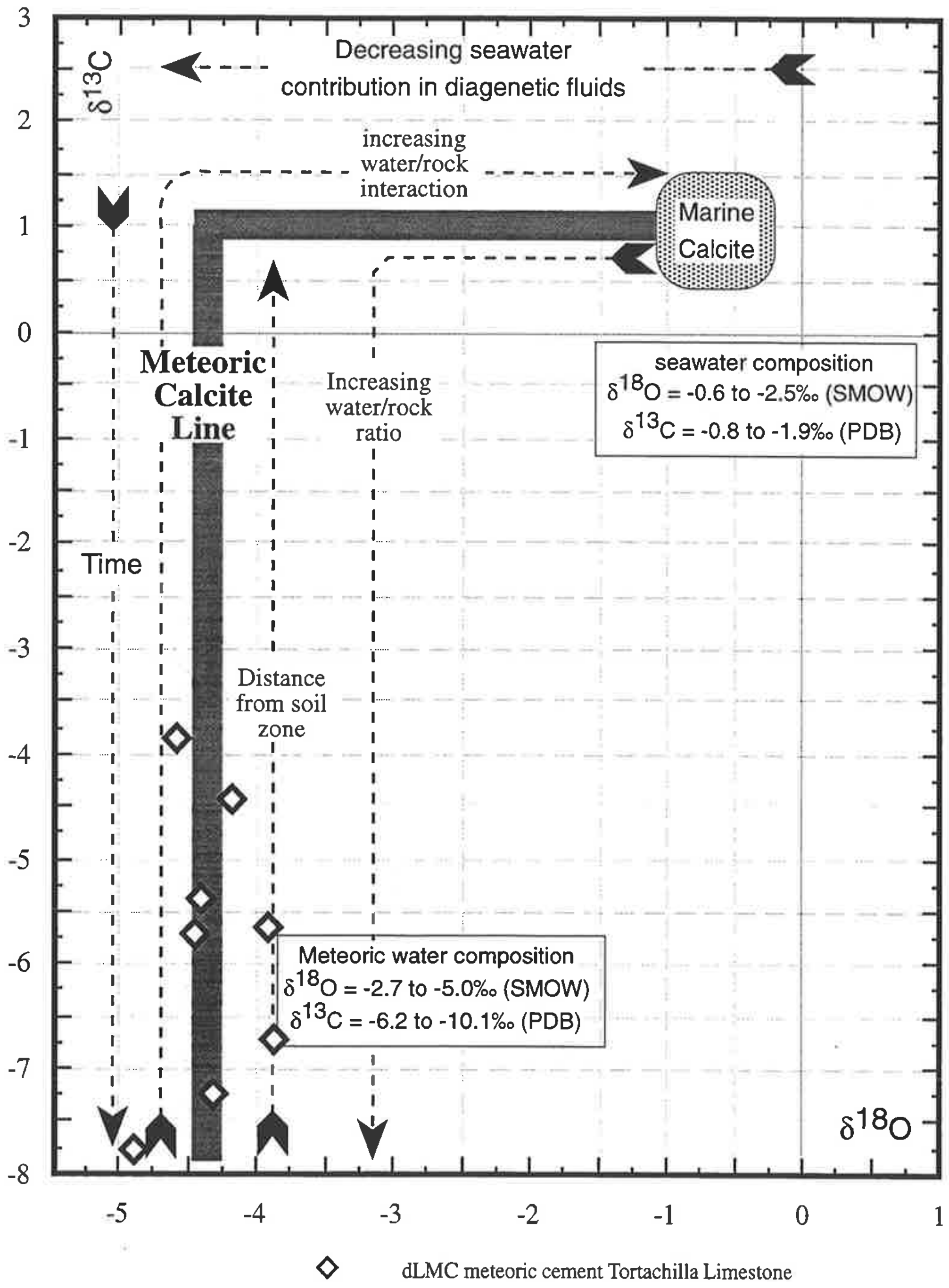


Fig. 5.1. The inverted-J pattern in the isotopic composition of the dLMC meteoric cement of the Tortachilla Limestone which replaced the aragonitic Turritellidae gastropoda. The isotopic composition of the Pecten and Terebratellidae brachiopoda are used as a proxy for marine calcite isotopic composition (Rahimpour-Bonab et al. 1997b). The estimated average isotopic composition of meteoric water is based on the fractionation equation of Friedman and O'Neil (1977) (Fig. 5.2) at 25°C. The carbon isotopic composition is based on the most negative values of dLMC cement and applying a fractionation factor of 2.3‰ for calcite-bicarbonate (Turner 1982). The oxygen isotope of seawater is also constrained by using average $\delta^{18}O$ marine calcite in that equation at 16°C (Fig. 5.2) and the carbon isotope resulted from the average $\delta^{13}C$ marine calcite after 2.3‰ correction.

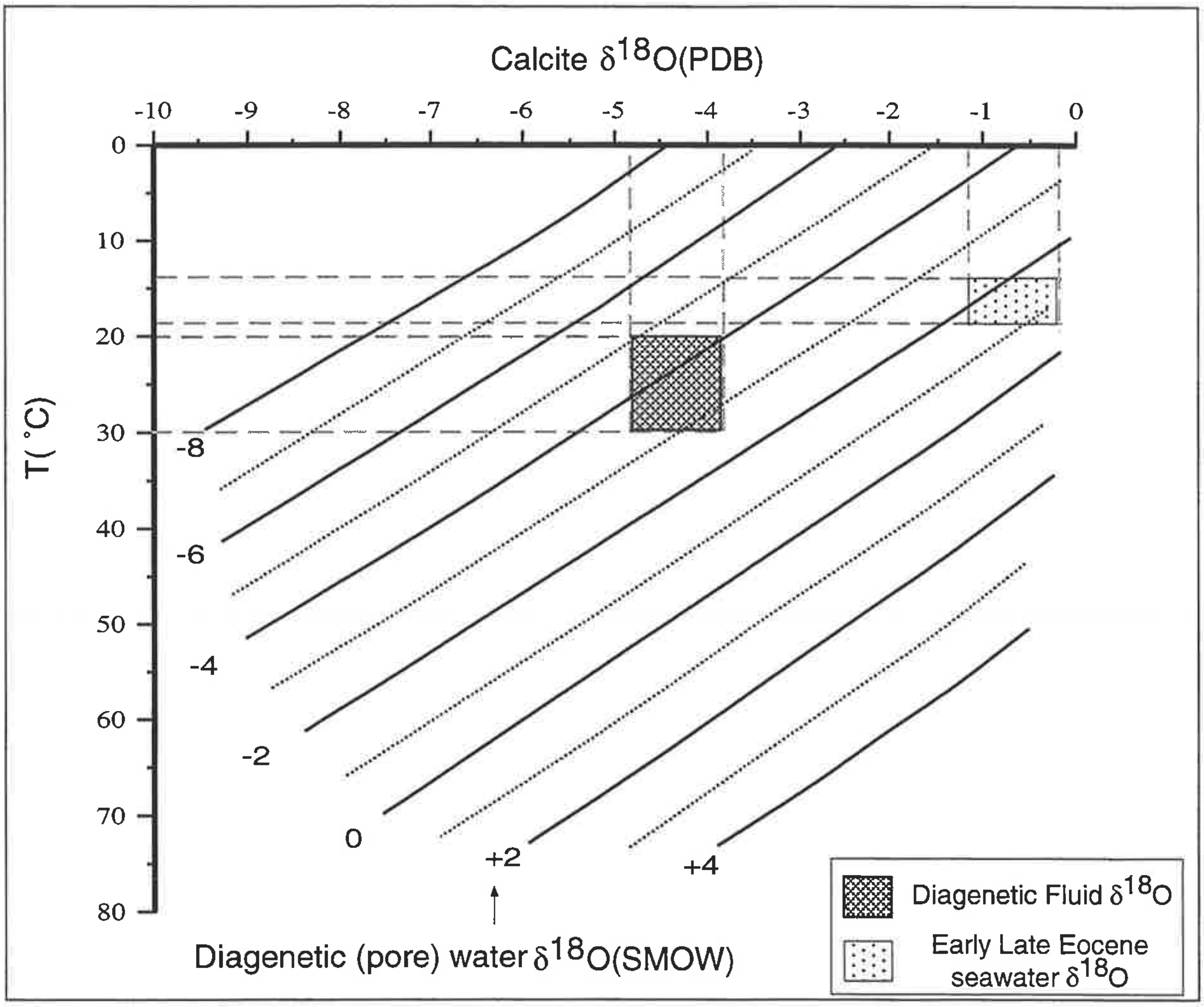


Fig. 5.2. The calculated $\delta^{18}O$ composition of calcite precipitated at equilibrium from waters of various compositions over a range of temperatures, using the calcite-water oxygen isotope fractionation equation of Friedman and O'Neil (1977). The range of possible water compositions from which the Tortachilla Limestone cement could have been precipitated is defined by the curves which pass through the stippled box between the 20 to 30°C temperatures, in this case, about -2.6 to -5‰ SMOW. The $\delta^{18}O$ composition of this diagenetic fluid at 14 to 30°C, is also demonstrated. Only a single curve (δw= -4‰) can account for the entire range of cement composition within the permitted temprature values.
The seawater isotopic composition of the early Late Eocene at temperatures of 14 to 18°C, which was the range of the bottom water temperature for that high latitude basin is also shown.

entire range of cement compositions is the -4.0‰ (SMOW), which probably displays the average $\delta^{18}O$ value of the diagenetic pore fluids.

The oxygen isotope values of seawater are also constrained by using $\delta^{18}O$ values of marine calcite and a temperature range of 14 to 18°C (See Fig. 6.2), results $\delta^{18}O_{SW}$ values are about -0.6 to -2.5‰. In addition, the carbon isotopic composition of seawater in the early Late Eocene can be constrained from the isotopic composition of equilibrium marine calcites. Using the $\delta^{13}C$ values of these biogenic equilibrium marine calcites and considering a fractionation factor of 2.3‰ between calcite and dissolved bicarbonate (Turner 1982), average values of -0.8 to -1.9‰ for $\delta^{13}C_{seawater}$ of early Late Eocene are obtained.

Considering an early diagenetic marine origin for this cement is incompatible with the paleotemperature estimates, as even the heaviest $\delta^{18}O$ values of cement (-3.9‰ PDB) could only have precipitated from diagenetic pore fluids with $\delta^{18}O$ values of -2.7‰ SMOW at a maximum temperature of 30°C (Fig. 5.1), which is lighter even than the lightest $\delta^{18}O_{seawater}$ (-2.5‰). Moreover, this cement has coarse equant blocky texture and LMC mineralogy, both of which are characteristic of meteorically precipitated cements. This cement also shows bright luminescence under CL, which denotes precipitation in a reducing environment, an indicator of meteoric diagenetic settings (See Fig 4.4).

Therefore, the $\delta^{18}O$ and $\delta^{13}C$ values of the diagenetic cement in Tortachilla Limestone indicate that they formed mostly in the meteoric phreatic zone from meteoric groundwater with a characteristic $\delta^{18}O$ isotopic composition (-2.7 to -5‰ SMOW). The meteoric origin for these pore fluids is also supported by consideration of $\delta^{13}C$ signature of this dLMC cement. The negative $\delta^{13}C$ signature in this cement is indicative of the introduction of isotopically depleted bicarbonate to the pore fluids (Fig. 5.1). This negative carbon introduced to the diagenetic pore fluids could have originated from thermal degradation of organic matter, and then its incorporation into the subsurface carbonate cement. However, the process of thermal degradation of organic matter (decarboxylation) requires relatively higher (geothermal) temperature (about 150°C, Hesse 1990) which is not consistent with the shallow burial depth of the studied sedimentary sequence. The compaction of basinal shale is another possible source for $\delta^{13}C$ depleted bicarbonate but there is no evidence of this. The most probable source of negative carbon in such shallow burial dLMC cement is organically-derived CO_2 during meteoric water infiltration through the soil zone (e.g., Anderson and Arthur 1983; Lohmann 1988). Therefore, both carbon and oxygen isotopic data indicate that this dLMC cement is precipitated mainly from diagenetic pore fluids of meteoric origin. Further important evidence for a meteoric origin of the diagenetic pore fluids and the prevailing meteoric system in the sedimentary sequence, is the wholesale dissolution of skeletal aragonite in this unit, which in many cases is replaced by dLMC cement (See Fig. 4.4).

The isotopic composition of meteoric water depends on the latitude and geographical setting (coastal setting versus continental settings). The isotopic fractionation during frequent evaporation-precipitation (Rayleigh effect) gives rise to progressive depletion in $\delta^{18}O$ values of rainfall towards the interior of continents and at higher latitudes, compared with the coexisting marine reservoir. In marginal basins (such as the studied area) this difference is only a few per mil (Anderson and Arthur 1983; Lohmann 1988). Fig. 5.2 demonstrate that the most negative $\delta^{18}O$ values of the diagenetic pore fluids, that could have produced this dLMC cement of the Tortachilla Limestone, is a water of -5.0‰ SMOW. This value is close to the values reported for modern meteoric water of coastal areas for a similar latitude (51.5° - See Fig. 6.3) which are about -7‰ (cf. Hays and Grossman 1991). However, only the lightest dLMC cement could have been precipitated from the estimated meteoric water composition of -5‰ SMOW, and the heaviest dLMC cement apparently precipitated from more positive meteoric water with a composition of -2.7‰ SMOW (Fig. 5.2). Hendry (1993) suggested three possibilities for such circumstances:

1) The meteoric water was considerably more enriched in $\delta^{18}O$ compared to normal values,

2) The meteoric water composition originally was about -5‰ SMOW but $\delta^{18}O$ values were altered by progressive water-rock interaction prior to or during dLMC cementation,

3) Mixing of meteoric water with marine water or compactional fluids prior to or during cementation.

The first option requires that meteoric water was derived from coastal precipitation, with minimal altitude-related isotopic fractionation (e.g., de Wet 1987). Fig. 5.2 shows that a diagenetic pore fluid of -4‰ (SMOW) could have produced all of the dLMC cement, if cementation continued from near-surface temperatures to maximum burial. Therefore, the relatively heavy $\delta^{18}O_{\text{meteoric water}}$ because of the geographic setting of the study area (coastal marginal basin) can be regarded as the main reason for such relatively heavy (on average) $\delta^{18}O$ values of the dLMC cement.

During meteoric diagenesis, progressive water-rock interaction leads to wholesale dissolution of metastable marine carbonates (e.g., aragonite) by undersaturated recharging meteoric waters, and precipitation of calcite cements where supersaturation is attained. This process can produce characteristic compositional patterns in dLMC cement known as " inverted J" trends (Meyers and Lohmann 1985; Lohmann 1988). This trend arises from the smaller concentration of DIC in diagenetic pore fluid compared with the rock (reactive marine carbonate) carbon reservoir, associated with a significant larger reservoir of $\delta^{18}O$ in the fluid phase compared to a much smaller reservoir of $\delta^{18}O$ in the solid phase (rock). Thus, because mole fractions of carbon differ significantly in the water and rock reservoir (oxygen concentrations, in contrast, are roughly equal), the isotopic composition of meteoric water (and cement) should evolve such that the fluid carbon isotopic compositions equilibrate more rapidly with the marine carbonate than do fluid oxygen isotope compositions (Lohmann 1988; Banner and Hanson 1990). Consequently, as a result of the larger reservoir of $\delta^{18}O$ water and adversely, larger reservoir of $\delta^{13}C$ rock, meteoric cement precipitated in a carbonate aquifer shows relatively invariant $\delta^{18}O$, coupled with strongly variant $\delta^{13}C$ (e.g., Lohmann 1988; Saller and Moore 1991). The isotopic composition of the dLMC cement of the Tortachilla Limestone shows such a trend which indicates the high water/rock interaction due to the wholesale alteration of all aragonitic components in this unit and their partial replacement by dLMC cement.

This theory that the relatively heavy $\delta^{18}O$ of dLMC is due to mixing of meteoric fluids with marine water cannot be the case here because such mixing would result in undersaturation with respect to calcite and therefore dissolution rather than precipitation (e.g., Lohmann 1988). In addition, as mentioned earlier, the $\delta^{13}C$ of dLMC is too light and so a significant contribution of marine water in its precipitation seems unlikely.

The isotopic composition of the Tortachilla Limestone dLMC cement shows a pattern of strongly variable $\delta^{13}C$ (-3.85 to -7.8‰) and relatively invariant $\delta^{18}O$ values (-3.8 to -4.8‰ - Fig. 5.1) that is typical for cement precipitated during meteoric alteration. The $\delta^{18}O$ variation is about 1.0‰ which is not unusual for meteoric groundwater in modern carbonate terrains (e.g., Frank et al. 1995). Therefore, this pattern of approximately invariant $\delta^{18}O$ coupled with variant $\delta^{13}C$ in the cement of this unit indicates its meteoric origin (e.g., Allen and Matthews 1982, Lohmann 1988). In this regard, the most negative values of $\delta^{13}C_{meteoric}$

cement can be considered the best estimate for the value of pure meteoric calcite ($\delta^{13}C$ = -7.8‰), which suggests light $\delta^{13}C$ values for soil-CO_2 (-18.0 to -20.0‰ - Romanek et al. 1992). The low $\delta^{13}C$ values of this cement reflect decreasing water-rock exchange as the primary marine metastable aragonitic component (aragonitic gastropods, for example) was diagenetically stabilised. The extent of rock-water interaction can be quantified as rock to water volume. This ratio represents the relative volume of rock permeated by a single volume of water in response to dissolution-precipitation reactions. Hence, a high rock-water ratio exemplifies a system in which fluid chemistry is dominated by the composition of the dissolving rock phases. Therefore, due to the small total concentrations of dissolved carbon in water, the $\delta^{13}C$ values of water rapidly converges to the values of the dissolved metastable carbonate phases (Lohmann 1988).

The carbon isotope in meteoric cements could have different sources such as: 1) atmospheric CO_2 (about -8.0‰), 2) dissolved metastable minerals such as aragonite (e.g., aragonitic gastropod with $\delta^{13}C$ of about +3.0‰), and 3) CO_2 from soil/calcrete organic matter decay ($\delta^{13}C \leq -20‰$). Carbonate precipitated in surface or shallow diagenetic settings with an open-system exchange with atmospheric CO_2 will have an isotopic composition which reflects the air-CO_2 signature. In general, calcite precipitated in an open-system equilibrium with soil-gas CO_2 is limited to about -15‰ $\delta^{13}C$ (Rightmire and Hanshaw 1973).

The $\delta^{13}C$ isotopic value of meteoric water percolating through the soil zone containing organic-CO_2 (produced by oxidation of soil-organic matter) rapidly shifts towards negative values. The $\delta^{13}C$ isotopic value of the organically produced CO_2 has values of about -16 to -25‰ which is quite different compared to atmospheric CO_2 ($\delta^{13}C$ = -8‰). The contamination of meteoric water by soil-CO_2 produces a distinguishing isotopic signature for meteoric water, compared to other diagenetic fluids. On the other hand, the final isotopic composition of meteoric cement precipitated from this highly depleted (light $\delta^{13}C$) meteoric water is controlled by the isotopic composition of the dissolved phase which is usually metastable marine carbonates. Accordingly, during dissolution of the metastable carbonate phase, isotopic exchange between the fluid (meteoric water) and rock reservoir (metastable carbonate phase), modifies the highly depleted meteoric waters. During carbonate dissolution:

$$H_2CO_3 + CaCO_3 \rightleftharpoons Ca^{+2} + 2HCO_3^-$$

half of the carbon is derived from dissolving calcite and half from H_2CO_3 of the fluid (e.g., Allen and Matthews 1982). Although, $\delta^{13}C$ value of a meteoric water changes towards negative value due to the influence of the soil-CO_2 (about -20‰ - Romanek et al. 1992), however dissolution of isotopically heavy aragonitic fossils of this unit ($\delta^{13}C$ about 2.2‰, Chapter Four) modify the meteoric water isotopic composition to intermediate values. These intermediate values, which are reflected in the $\delta^{13}C$ value of dLMC cement of the Tortachilla Limestone by values of -7.85 to -3.9‰, demonstrate that they are precipitated from meteoric water with $\delta^{13}C$ value of -10.15 to -6.2‰, which is much heavier than the ultimate negative values of the soil-CO_2 carbon isotope. This suggests that the meteoric water was buffered isotopically by the dissolving carbonate precursors (i.e., aragonite) in that unit. However, those cements with the lightest $\delta^{13}C$ values which are clustered at the depleted end of the inverted-J trend are due to the absence of a high degree of rock/water interaction.

Therefore, the dLMC meteoric cement, which is depleted in $\delta^{13}C$ relative to marine calcite and for which the $\delta^{18}O$ values are relatively invariant, defines the water-dominated (high water/rock ratio) portion of the inverted-J trend (Fig. 5.1). In the water-dominated system, due to dissolution-precipitation reactions in shallow diagenetic settings, where $\delta^{13}C$-depleted fluids (derived from the influx of soil-gas derived CO_2) are prevalent, the final isotopic signature of dLMC meteoric cement shows highly variable $\delta^{13}C$ and relatively invariant $\delta^{18}O$ (Fig. 5.1). The isotopic composition of reactive marine carbonates (marine well-preserved fossils) is at the highest oxygen and carbon isotope values of this trend and demonstrates the origin of this secondary diagenetic cement. Hence, this distinctive inverted-J trend of isotopic values of dLMC meteoric cement results from the evolution of pore water due to the reaction of CO_2-charged meteoric fluids with metastable marine components (e.g., aragonitic gastropods).

In conclusion, Tortachilla Limestone dLMC meteoric cements have a narrow range of $\delta^{18}O$ value, from -3.8 to -4.8‰, and a wide range of $\delta^{13}C$ values, from -3.85 to -7.80‰. All of these cement samples are depleted in $\delta^{18}O$ and $\delta^{13}C$ relative to marine calcites (Pecten and Terebratellidae brachiopoda). The isotopic composition of Tortachilla Limestone dLMC meteoric cement represents an isotopically light composition (highly depleted) relative to the isotopic composition of marine calcite (Figs 5.1, 5.2). This suggests that seawater had no significant contribution to the formation of this cement. On the contrary, the isotopic value of the studied cements is close to values reported for calcite precipitated from modern coastal and island meteoric water in similar latitude (51.5°) by several workers (cf. Hay and Grossman 1992). This inverted-J pattern, extends from fossil samples with original marine compositions (average $\delta^{18}O$ -0.75‰) to the coarse calcite cements, reflecting precipitation from the groundwater system with varying degrees of buffering from the host rock ($\delta^{18}O_{cement}$ = -3.52 to -4.85‰), and is characteristic of freshwater recrystallisation of marine limestone and stabilisation of metastable marine minerals in meteoric environments (e.g., Meyers and Lohmann 1985; Banner and Hanson 1990).

5.3. Gull Rock Member:

The stable isotope composition of dLMC cements from the Gull Rock Member (See Fig. 1.4) is plotted in Fig. 5.3. Also shown are the ranges of average isotopic composition of marine equilibrium calcite (Terebratellidae brachiopoda and corrected values of aragonitic Turritella for its mineralogy after converting to calcite) from this unit, which are used as a proxy for seawater isotopic composition. The overall isotopic composition of this cement shows heavy values, compared to the dLMC cement from the Tortachilla Limestone (Fig. 5.1). The enriched $\delta^{18}O$ values in this cement can be ascribed to two factors. Firstly, the late Late Eocene time interval was a time of climatic deterioration and global cooling event. This world-wide cooling event had an influence on the St.Vincent Basin, as low bottom temperatures caused lower terrestrial temperatures. This is recorded in the enriched $\delta^{18}O$ values of the Gull Rock Member dLMC cement. This low terrestrial temperature is compatible with the high paleolatitude of the St.Vincent Basin at that time (about 50°S). Secondly, the heavy values of $\delta^{18}O$ could have been produced by cement precipitated from a diagenetic fluid which formed by mixing of meteoric water and the remaining trapped seawater in the sediments. This theory is consistent with the observation that heavy $\delta^{18}O$ in this cement is associated with enriched $\delta^{13}C$ values (Fig. 5.3). The $\delta^{18}O$ of dLMC cement is overlain on an equilibrium fractionation diagram which relates calcite $\delta^{18}O$ (PDB) values to temperature for a range of isotopic compositions of diagenetic fluids (SMOW). Considering the lower diagenetic temperatures for this unit compared to the Tortachilla Limestone (about 20 to 25°C), diagenetic fluids with $\delta^{18}O$ values of -1.0 to +1.0‰ (SMOW) results (Fig. 5.4). As shown, almost a single curve (δ_W = 0‰) can account for the entire range of cement compositions within the permitted temperature values, which probably indicates the average $\delta^{18}O$ values of the diagenetic fluids.

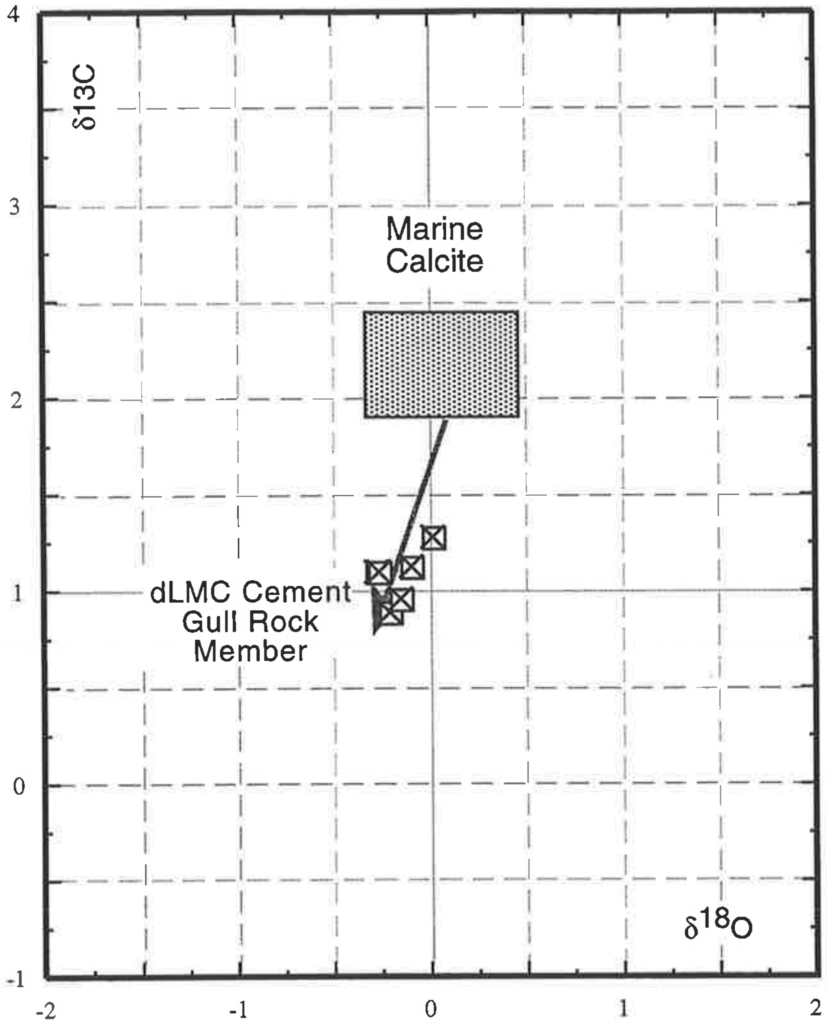


Fig. 5.3. The pattern in the isotopic composition of the dLMC meteoric cement of the Gull Rock Member. The original marine isotopic composition is the average isotopic composition of the Turritellidae (corrected for its aragonitic mineralogy) and brachiopoda which are close to equilibrium values (Rahimpour-Bonab et al. 1997b). The isotopic composition of meteoric dLMC cement in this unit is abnormally high and close to marine values, which probably demonstrates seawater-meteoric water mixing.

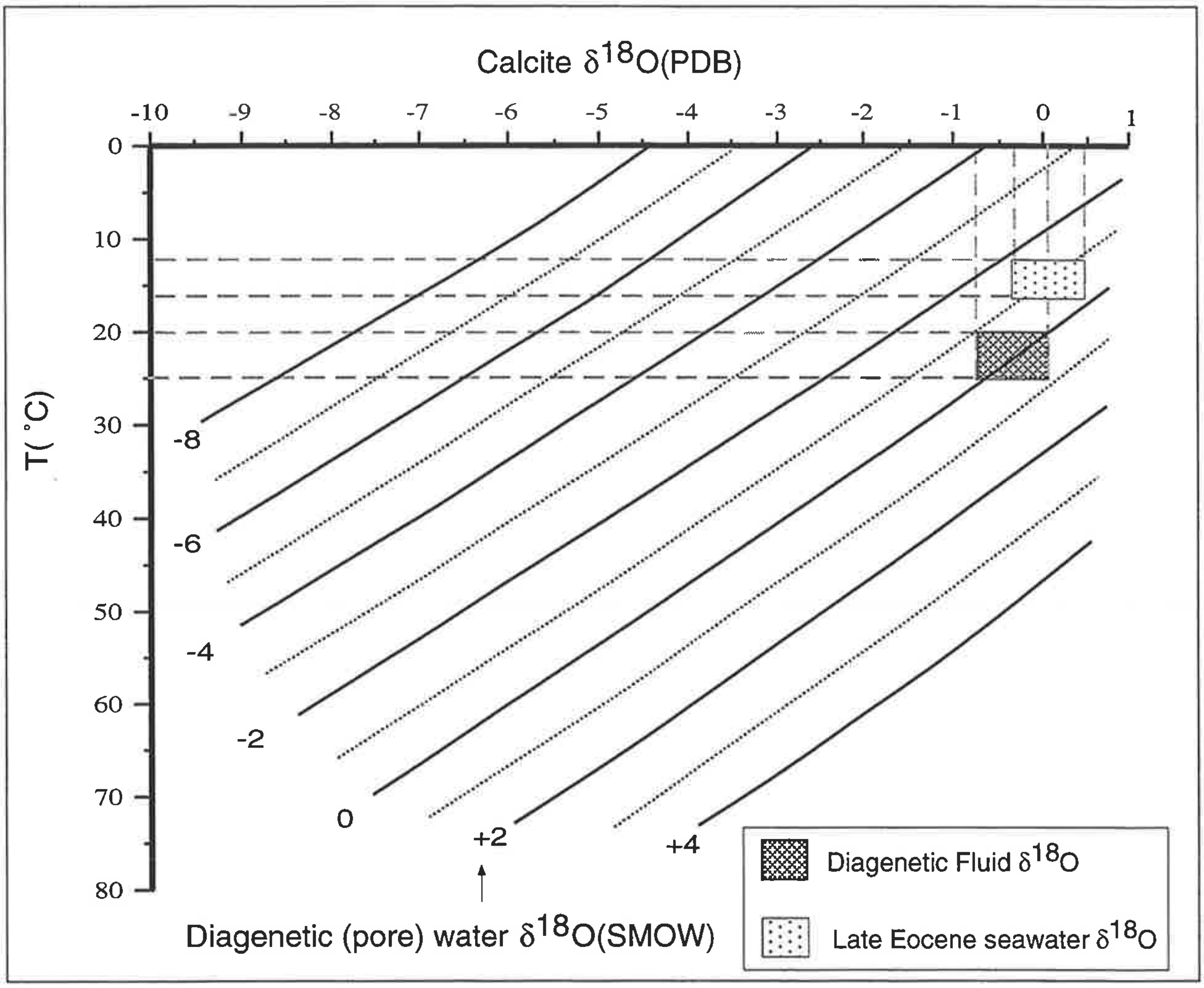


Fig. 5.4. The calculated $\delta^{18}O$ composition of calcite precipitated at equilibrium from waters of various compositions over a range of temperatures, using the calcite-water oxygen isotope fractionation equation of Friedman and O'Neil (1977). The range of possible water compositions from which the dLMC cement of the Gull Rock Member could have been precipitated is defined by the curves which pass through the stippled box between the 20 to 25°C temperatures, in this case, about +1.0 to -1.0‰ SMOW. Only a single curve ($\delta w = 0‰$) can account for the entire range of cement composition within the permitted temperature values.
The seawater isotopic composition of the Late Eocene at temperatures of 12 to 16°C, which was the range of the bottom water temprature for that high latitude basin is also shown (about 0 to -2‰ SMOW).

The oxygen isotope value of seawater is constrained by using $\delta^{18}O$ values of marine calcites and the temperature range of 12 to 16°C (See Fig. 6.2), which results in $\delta^{18}O_{seawater}$ values of about -0.2 to -2.0 (SMOW). The $\delta^{13}C$ value of seawater in the Late Eocene interval can be constrained from equilibrium marine calcite, as well. Using the average $\delta^{13}C_{marine\ calcite}$, and applying a fractionation factor of 2.3‰ for calcite-dissolved bicarbonate, $\delta^{13}C_{DIC}$ values of +0.1 to -0.5‰ for seawater result.

The petrographic and XRD studies reveal a coarse blocky equant texture for this cement with LMC mineralogy. The cement is void filling and crystals are growing toward the centre of the pore spaces. All of these characteristics are indicating formation in a meteoric diagenetic setting (Fig. 5.5). Therefore, this cement is probably formed by diagenetic fluids of meteoric origin which were partly modified by seawater contamination, as recorded by its enriched $\delta^{18}O$ value. However, these enriched $\delta^{18}O$ values are probably partly produced by lower terrestrial temperature of Late Eocene/Early Oligocene time, due to global cooling event. The $\delta^{13}C$ values of diagenetic fluids calculated from the $\delta^{13}C_{meteoric\ cement}$ are about -1.15 to -1.5‰, which demonstrates possible mixing of meteoric and seawater during cement precipitation. However, the contribution of seawater in producing diagenetic fluids was not greatly significant, because as mentioned earlier, the high rate of seawater contribution in diagenetic fluids would lead to undersaturation with respect to carbonates and consequent dissolution of body fossils, which is contrary to the well-preserved aragonitic and calcitic fossils of this unit.

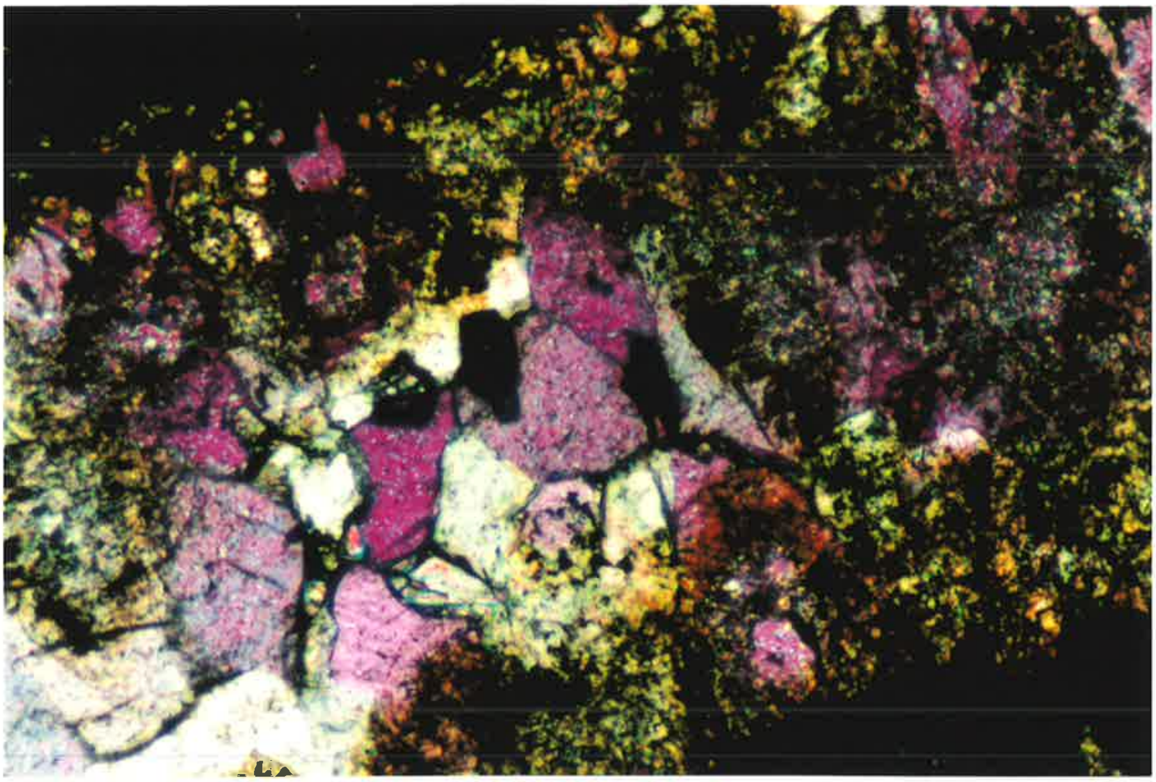


Fig. 5.5. Blocky, equant void-filling meteoric LMC cement from Gull Rock Member (Polarised Light, field of view 2 mm).

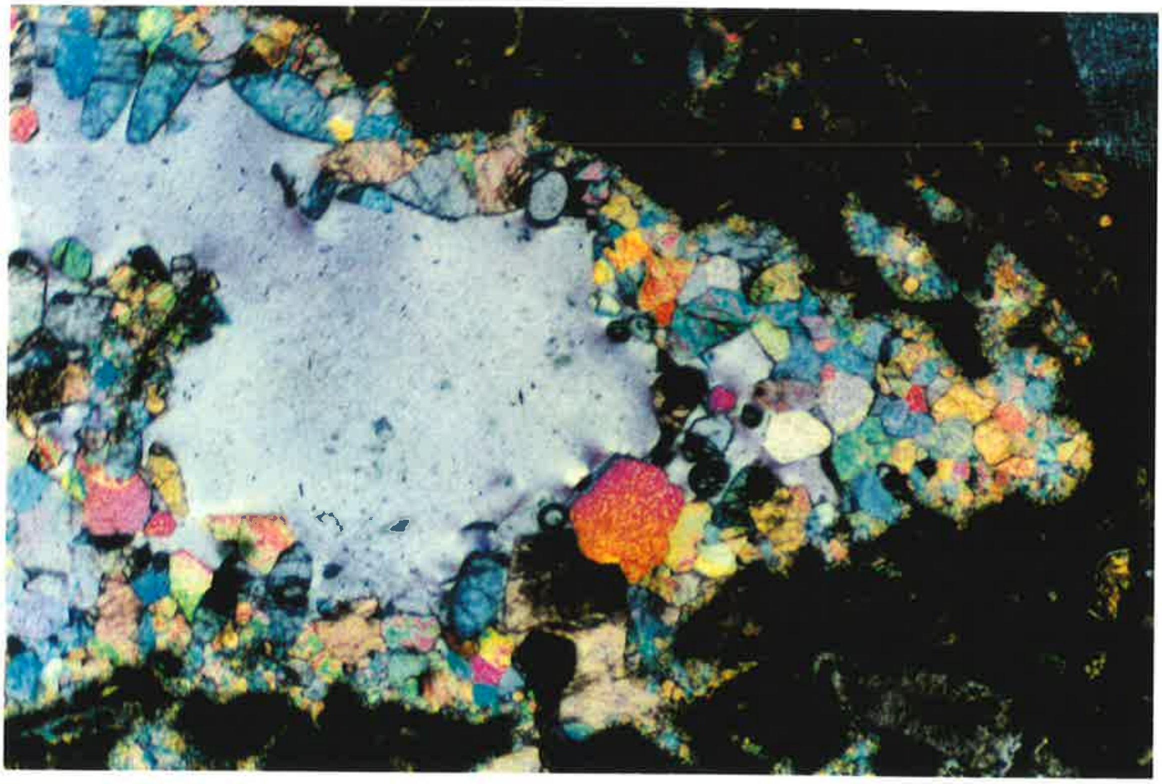


Fig. **5.6.** Blocky, equant void-filling LMC meteoric cement from Mannum Formation, which here partially fill the mould of a Turritellidae gastropoda (Polarised Light, field of view 5 mm).

5.4. Mannum Formation:

The dLMC meteoric cement in the Mannum Formation, which is a coarse grained meteoric cement (Fig. 5.6), shows enriched $\delta^{18}O$ isotopic values associated with depleted $\delta^{13}C$ values (Fig. 5.7). The overall isotopic composition of the dLMC cement ranges between -0.55 to -1.2‰ for oxygen and -0.7 to -1.25‰ for carbon. Whereas the $\delta^{13}C$ values of this cement are on average about 2.6‰ lighter than the equilibrium marine calcites, the $\delta^{18}O$ value of this cement is in the range of the marine calcite with a tendency toward even heavier values (Fig. 5.7).

In Fig. 5.8, the $\delta^{18}O$ range of this dLMC cement is overlain on an equilibrium fractionation diagram which relates calcite $\delta^{18}O$ (PDB) to temperature for a range of diagenetic fluid isotopic composition (relative to SMOW). Considering a temperature range of 20 to 30°C for diagenetic environment of this cement (which is a reasonable estimate for such a shallow burial diagenetic setting), diagenetic fluids with $\delta^{18}O$ values of +1.0 to -1.5‰ (SMOW) result. The isotopic compositions of marine fossils in the Mannum Formation were utilised for determination of the seawater isotopic composition of Late Oligocene time and considering a temperature range of 16 to 19°C (See Fig. 6.2), which gives a $\delta^{18}O_{seawater}$ of about -1.0 to -3.0‰ (SMOW).

The carbon isotopic composition of seawater in the Late Oligocene is constrained by utilising the $\delta^{13}C$ values of equilibrium marine calcites (considering a 2.3‰ calcite-bicarbonate fractionation), which gives values of -0.2 to -1.1‰ (PDB) for $\delta^{13}C_{DIC}$.

Fig. 5.8 demonstrates that the most negative $\delta^{18}O$ values of diagenetic pore fluids which could have been produced the dLMC meteoric cement of the Mannum Formation, were -1.5‰. This value is significantly heavier than observed $\delta^{18}O_{meteoric\ water}$ in a modern coastal setting for 50.5° latitude (cf. Hays and

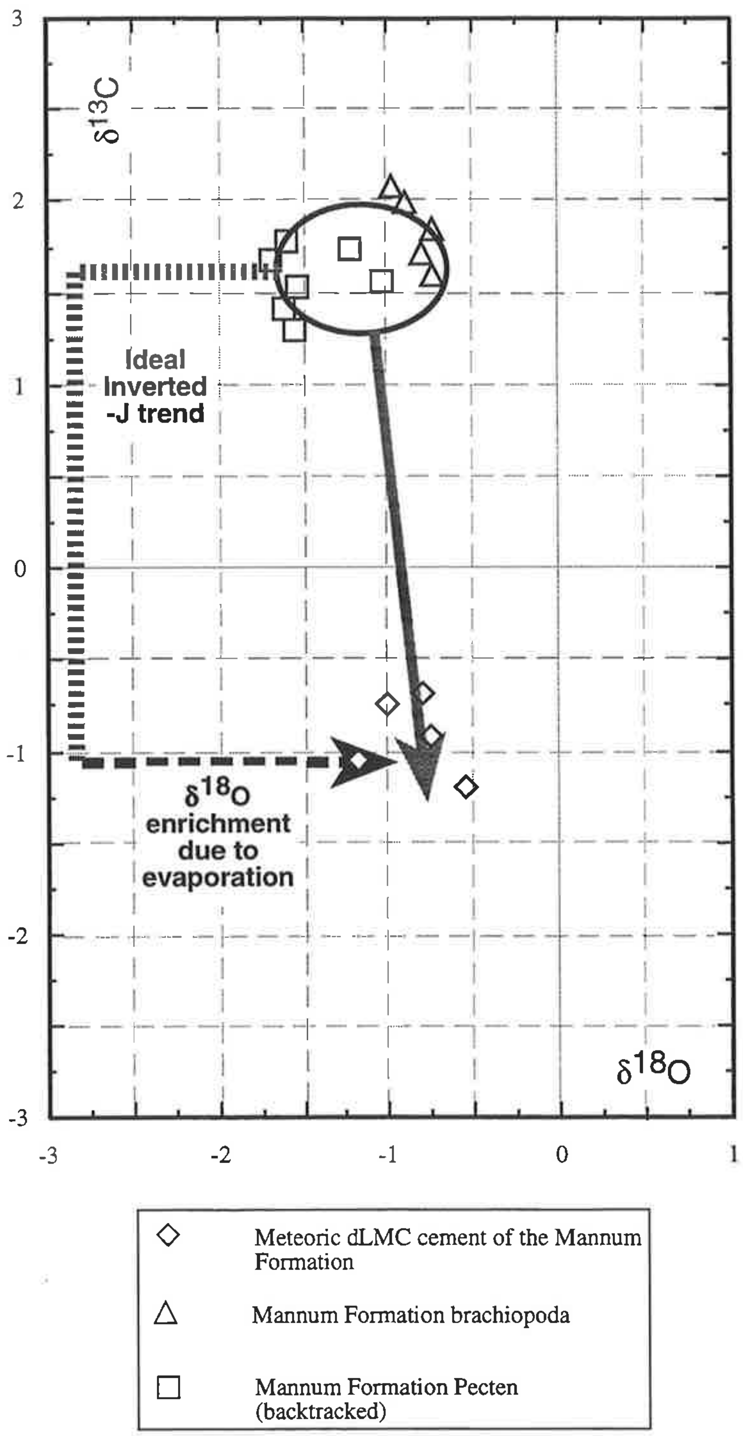


Fig. 5.7. The trend in the isotopic composition of the dLMC meteoric cement of the Mannum Formation from a location distal to the soil/calcrete zone. The original marine isotopic composition is the average isotopic composition of the Pecten and brachiopoda which are close to equilibrium values (Rahimpour-Bonab et al. 1997b). The $\delta^{18}O$ values of this cement show some diversion from the ideal Inverted-J pattern, probably due to evaporative enrichments.

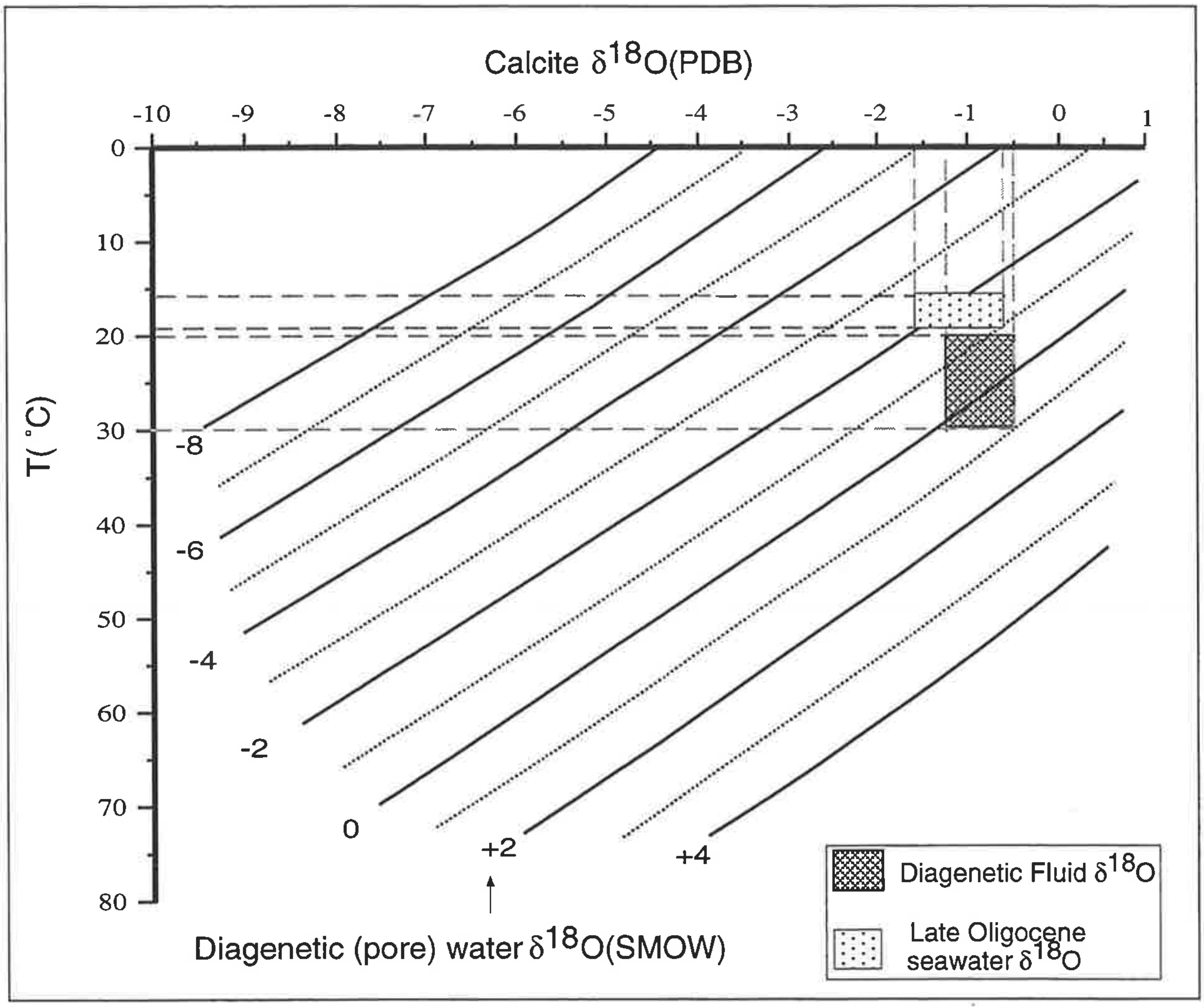


Fig. 5.8. The calculated δ^{18}O composition of calcite precipitated at equilibrium from waters of various compositions over a range of temperatures, using the calcite-water oxygen isotope fractionation equation of Friedman and O'Neil (1977). The range of possible water compositions from which the dLMC cement of the Mannum Formation could have been precipitated is defined by the curves which pass through the stippled box between the 20 to 30°C temperatures, in this case, about +1 to -1.5‰ SMOW. The seawater isotopic composition of the Late Oligocene at temperatures of 16 to 19°C, which was the possible range of the bottom water temperature for that high latitude basin is also shown (about -1 to -3‰ SMOW).

Grossman 1992), which is about -8‰ SMOW. Moreover, the heavier $\delta^{18}O$ value of this dLMC cement indicates meteoric water $\delta^{18}O$ values of up to +1.0‰ (SMOW) even heavier than the seawater values (about -1‰) (Fig. 5.8). The heavy $\delta^{18}O$ values of this meteoric cement, which is associated with relatively depleted $\delta^{13}C$ values, suggest that the $\delta^{18}O$ enrichment could have been produced by $\delta^{18}O$ evaporative enrichment in meteoric water prior to cementation. The warm climatic conditions recorded for this time interval in the Murray Basin and in other geologic locations in the world (Shackelton et al. 1984a, b), are consistent with relatively intensive evaporation of meteoric waters prior to meteoric cementation.

The mixing of meteoric water with marine water can not account for this heavy $\delta^{18}O_{\text{calcite cement}}$ signature, because these heavy $\delta^{18}O$ values are associated with light $\delta^{13}C$ value, which demonstrates formation by soil-derived CO_2 charged meteoric waters (Fig. 5.7).

Therefore, the isotopic composition of the Mannum Formation dLMC cement shows some diversion from the ideal trend of an inverted-J pattern, which is due to evaporative enrichment of $\delta^{18}O$. However, the $\delta^{13}C$ value of this cement is consistent with this inverted-J trend that indicates meteoric origin of this cement and a soil-derived-CO_2 contribution in the $\delta^{13}C$ signature (Fig. 5.7). The moderately low $\delta^{13}C$ value of this cement reflects relatively decreasing water-rock exchange as primary marine metastable aragonitic components were diagenetically stabilised. In conclusion, this distorted inverted-J trend of the isotopic values of dLMC meteoric cements results from the evolution of meteoric diagenetic water due to the reaction of soil-derived CO_2-bearing meteoric waters with the metastable marine components, while the concomitant evaporation process led to $\delta^{18}O$ enrichment of the meteoric waters.

In the Mannum Formation, in pristine Pecten fossil samples collected from samples sites close to the soil/calcrete horizons, the $\delta^{13}C$ values of fossils show abnormally depleted values. Petrographic studies reveal that this depleted $\delta^{13}C$ signature (up to -3.85‰) is due to contamination of the fossil Pecten samples with other types of cement which is fine grained vadose cements formed by soil-derived CO_2-charged meteoric waters in vadose zone (See Fig. 4.8). The $\delta^{18}O$ signature of these vadose cements, which are a mixture of marine $\delta^{18}O$ values and meteoric cement $\delta^{18}O$ value is in the range of marine values (heavy) and even shows some heavier values, which demonstrates the influence of evaporative enrichment on the total $\delta^{18}O$ signature of this fine grained vadose cement (See Fig. 4.13).

5.5. Lower Morgan Limestone:

The microscopic texture and isotopic composition of dLMC meteoric cement from the Lower Morgan Limestone are displayed in Figs 5.9 and 5.10. The original marine isotopic values are represented here by the isotopic composition of the well-preserved marine fossil samples of this unit. The $\delta^{18}O$ values of dLMC meteoric cement range from -1.85 to -0.9‰, while $\delta^{13}C$ values range from 0.20 to 0.55‰. The overall isotopic composition of this meteoric cement is depleted compared to marine values, as the $\delta^{13}C$ of this cement is about 1.85‰ and $\delta^{18}O$ is about 1.25‰ lighter than marine values.

The $\delta^{18}O$ range of this meteoric cement which is overlain on an equilibrium fractionation diagram, relates $\delta^{18}O_{calcite}$ (PDB) to temperature for a range of diagenetic fluid isotopic compositions (SMOW) (Fig. 5.11). In the temperature range of 20 to 30°C, which was prevailing in these shallow burial diagenetic settings, the $\delta^{18}O$ values for diagenetic fluids responsible for this cement are

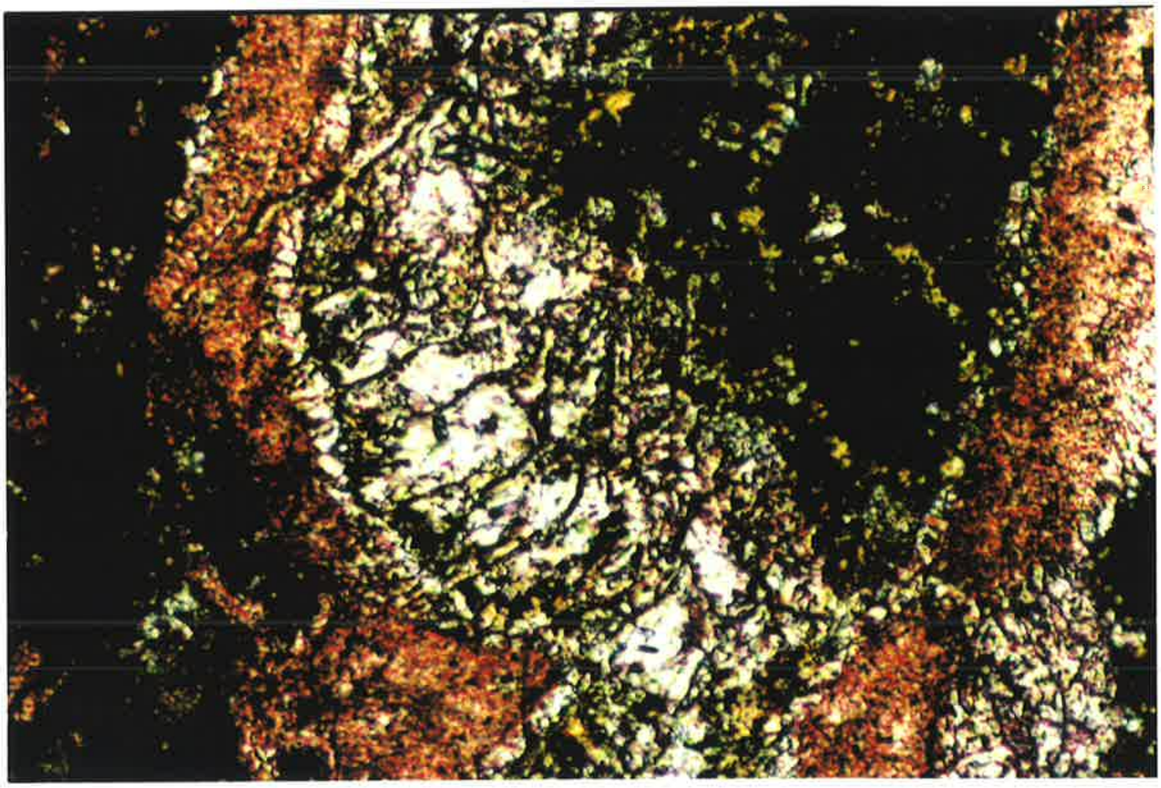


Fig. 5.9. The void-filling, circumgranular sparry calcite meteoric cement from the Lower Morgan Limestone. The pinkish colour of the calcite cement is due to staining (Normal Light, field of view 2 mm, stained thin section).

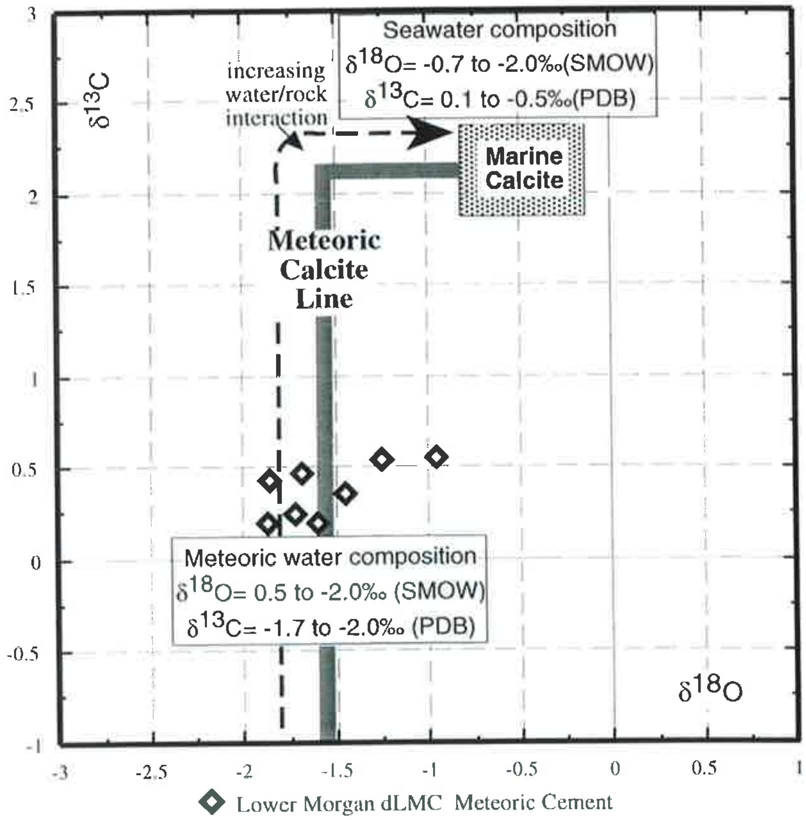


Fig. 5.10. The Inverted-J pattern in the isotopic composition of the dLMC meteoric cement of the Lower Morgan Limestone. The original marine isotopic composition is the average isotopic composition of the Pecten and brachiopoda, which are close to equilibrium values (Rahimpour-Bonab et al. 1997b).

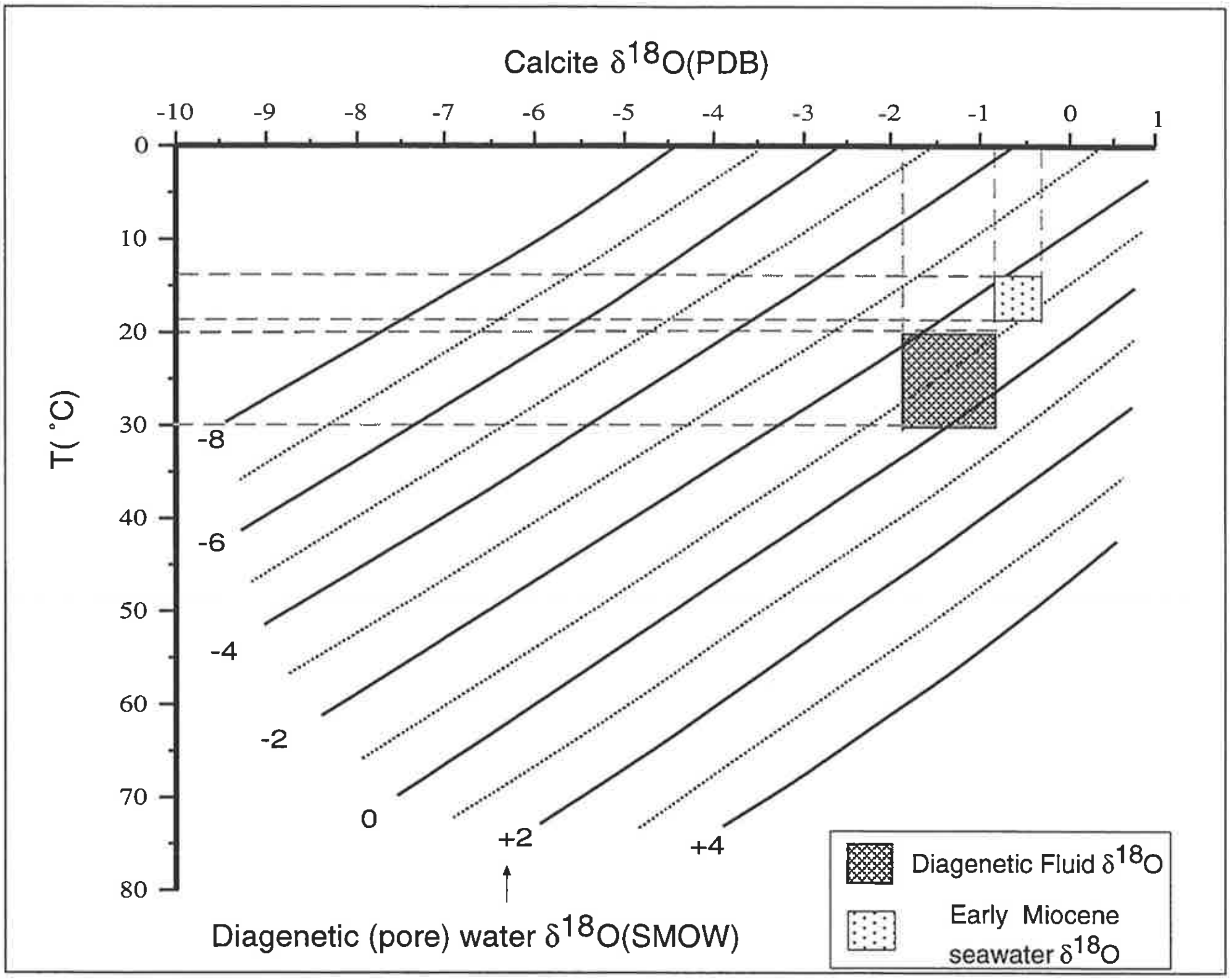


Fig. 5.11. The calculated $\delta^{18}O$ composition of calcite precipitated at equilibrium from waters of various compositions over a range of temperatures, using the calcite-water oxygen isotope fractionation equation of Friedman and O'Neil (1977). The range of possible water compositions from which the dLMC cement of the Lower Morgan Limestone could have been precipitated is defined by the curves which pass through the stippled box between the 20 to 30°C temperatures, in this case, about +0.5 to -2‰ SMOW. Only a single curve ($\delta w = -1‰$) can account for the entire range of cement composition within the permitted temperature values.
The seawater isotopic composition of the Late Oligocene at temperatures of 14 to 18°C, which was the range of the bottom water temperature for that high latitude basin, is also shown (about -0.5 to -2‰ SMOW).

about 0.5 to -2.0‰ (SMOW). Using marine calcite for calculation of the $\delta^{18}O$ of the Early Miocene seawater, in a temperature range of 14 to 18°C (See Fig. 6.2), values of -0.7 to -2.0‰ (SMOW) result.

The $\delta^{13}C_{DIC}$ of diagenetic fluids, considering the $\delta^{13}C_{dLMC\ cement}$ and 2.3‰ fractionation for calcite-bicarbonate, gives values of about -1.7 to -2‰ (PDB), while $\delta^{13}C_{DIC}$ value of seawater was about +0.1 to -0.5‰ (PDB), which is in the range of values for modern seawater.

The most negative $\delta^{18}O$ values of the diagenetic fluids which could have produced the dLMC cement of the Lower Morgan Limestone, were about -2‰ (SMOW), which is significantly heavier than the observed $\delta^{18}O_{meteoric\ water}$ in a modern coastal setting for similar latitude (about 50° - See Fig. 6.3) (cf. Hays and Grossman 1992), which is about -7‰ (SMOW).

The relatively heavy $\delta^{13}C$ and $\delta^{18}O$ values in this cement demonstrate formation in a horizon far from the influence of soil-derived CO_2, in diagenetic waters and higher rock/water interaction, and probably some contribution by seawater trapped in the sediments (Fig. 5.9). As observed in the other units, the prevalence of a meteoric regime in this unit is evident by the wholesale dissolution of metastable skeletal material. Therefore, the diagenetic fluids originally had a light $\delta^{18}O$ value, but this was altered (enriched) by progressive water/rock interaction prior to the dLMC cementation, thus leading to precipitation of cement with a relatively heavy isotopic signature. Evaporation cannot account for these observed heavy isotopic values, as the heavy $\delta^{18}O$ signature is associated with heavy $\delta^{13}C$ which is not indicative evaporative enrichment. In conclusion, the dLMC cement isotopic composition of the Lower Morgan Limestone plots in the upper parts of the inverted-J trends which is indicative of meteoric diagenetic conditions with high water/rock interaction and a low/water rock ratio in horizons far from soil-zones.

5.6. Cadell Marl:

The isotopic composition of the dLMC cements and the average values of marine calcite from Cadell Marl are shown in Fig. 5.12. The dLMC cement shows relatively less variable $\delta^{18}O$ (about -1.1 to -2.8‰) than the $\delta^{13}C$ (about -0.2 to -2.8‰) values. The overall isotopic composition of the dLMC is much lighter than the average values of marine calcite (Fig. 5.12).

The $\delta^{18}O$ range of the dLMC cement and marine calcite is used to calculate the isotopic composition of diagenetic fluids and seawater (late Early Miocene/early Middle Miocene). By constraining the temperature of formation of the dLMC cement in this shallow burial diagenetic setting to between 20 to 30°C, diagenetic fluids with $\delta^{18}O$ values of 0.1 to -3.0‰ (SMOW) result (Fig. 5.13). The $\delta^{18}O_{seawater}$, utilising average equilibrium marine calcites and a temperature range of 12 to 16°C (See Fig. 6.2), gives values of 0.0 to -2.2‰ (SMOW).

The $\delta^{13}C$ values of dLMC cement in this unit is utilised to constrain the $\delta^{13}C$ values of diagenetic fluids resulting in values between -2.5 to -5.0‰ (PDB). The relatively highly depleted $\delta^{13}C$ value of this dLMC cement is probably indicative of the introduction of soil-derived CO_2 during percolation of meteoric water through the soil zone. The alternative for light $\delta^{13}C$ is diagenesis in an open system causing exchange with atmospheric CO_2, which has $\delta^{13}C$ values of about -8‰.

The $\delta^{13}C_{DIC}$ of seawater in this time interval is constrained from the $\delta^{13}C$ value of the equilibrium marine calcites of this unit, which gave average values of 0.8 to -0.1‰.

The general isotopic composition of this dLMC cement is indicative of a meteoric origin and its overall isotopic pattern is comparable with the ideal inverted-J pattern of meteoric calcites (Fig. 5.12). This isotopic pattern demonstrates a

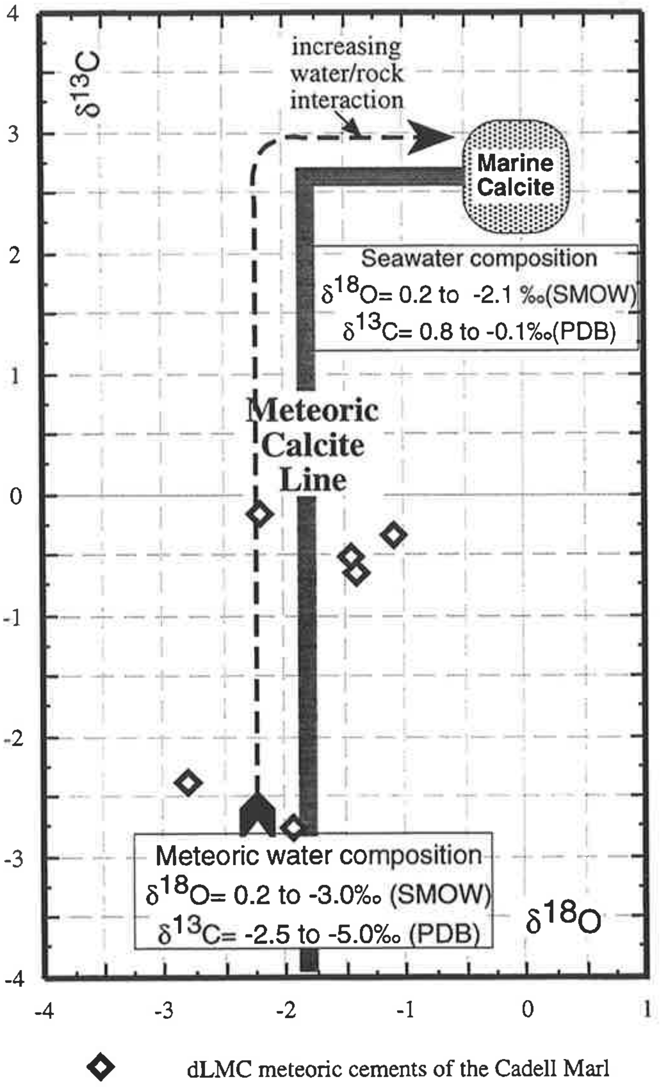


Fig. 5.12. The Inverted-J pattern shown by the isotopic composition of the dLMC meteoric cement of the Cadell Marl. The original marine isotopic composition is the average isotopic composition of the Pecten and brachiopoda, which are close to equilibrium values (Rahimpour-Bonab et al., in press). Estimated isotopic composition of meteoric water is based on the fractionation equation of Friedman and O'Neil (1977) (Fig. 5.2) using average $\delta^{18}O$ values of dLMC meteoric cement at 25°C. The carbon isotopic composition is based on the most negative values of dLMC cement and applying a fractionation factor of 2.3‰ for calcite-bicarbonate (Turner 1982). The oxygen isotope of seawater is also constrained by that equation (Fig. 5.2) using $\delta^{18}O$ value of marine calcite at 12 to 16°C and the carbon isotope values from the average $\delta^{13}C$ values of marine calcite, after 2.3‰ correction.

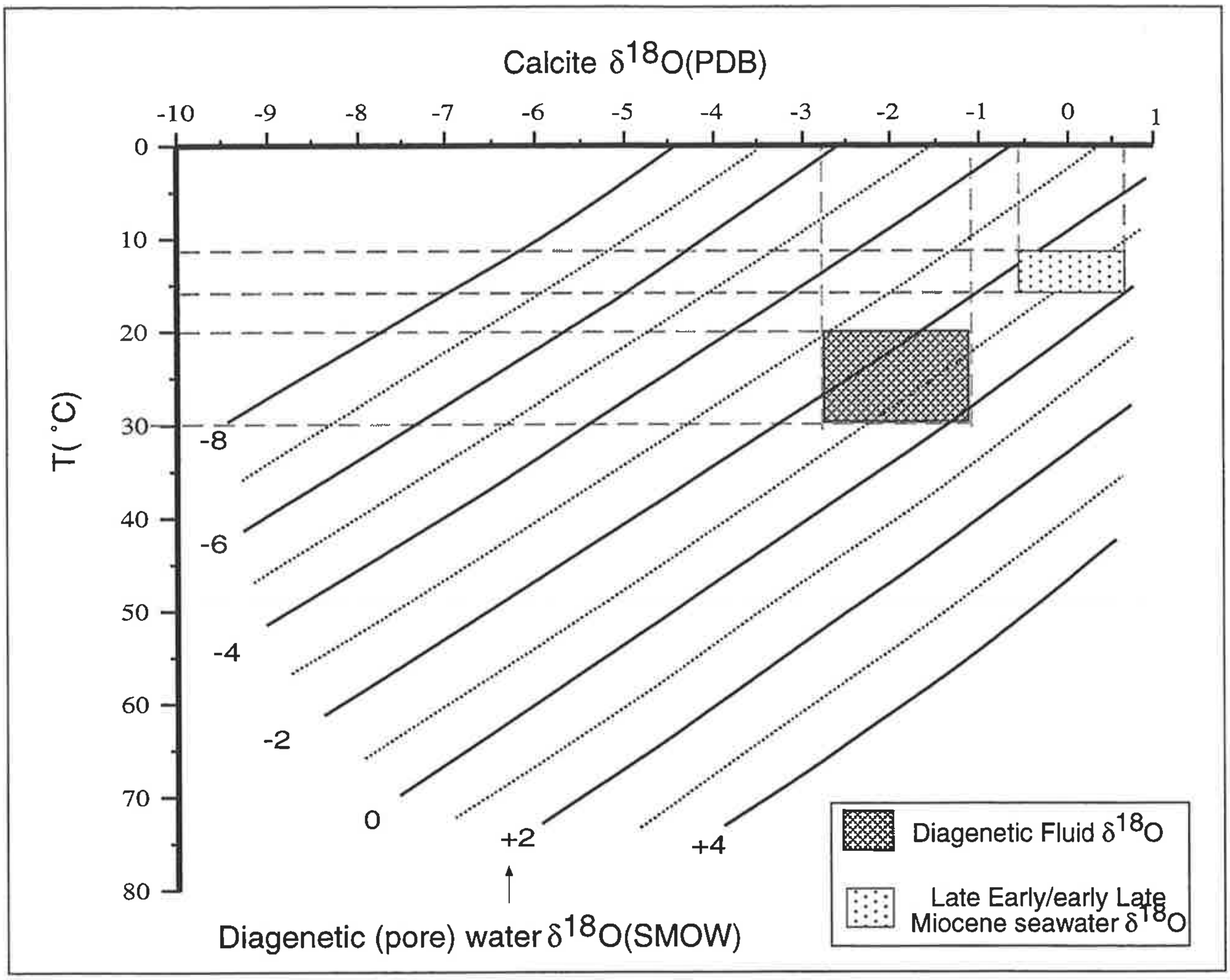


Fig. 5.13. The calculated $\delta^{18}O$ composition of calcite precipitated at equilibrium from waters of various compositions over a range of temperatures, using the calcite-water oxygen isotope fractionation equation of Friedman and O'Neil (1977). The range of possible water compositions from which the dLMC cement of the Cadell Marl could have been precipitated is defined by the curves which pass through the stippled box between the 20 to 30°C temperatures, in this case, about +0.2 to -3.0‰ SMOW. Only a single curve (δw= -2‰) can account for the entire range of cement composition within the permitted temprature values.
The seawater isotopic composition of the late Early to early Middle Miocene at temperatures of 12 to 16°C, which was the range of the bottom water temperature for that high latitude basin, is also shown (about -2.1 to 0.2‰ SMOW).

meteoric coastal system with $\delta^{18}O_{\text{meteoric water}}$ values of -3.0 to 0.1‰ (SMOW), with some contribution from seawater, which caused relatively heavy carbon and oxygen isotopes. In addition, the relatively heavy isotopes are indicative of a relatively high rock/water interaction and low/water rock ratio.

5.7. Upper Morgan Limestone:

The microscopic texture and isotopic composition of dLMC meteoric cement from Upper Morgan Limestone are shown in Figs 5.14 and 5.15. The isotopic composition of this meteoric cement shows highly variant $\delta^{13}C$ associated with less variable $\delta^{18}O$ value, while both isotopes are lighter than the average of the marine calcites of this unit. The overall isotopic composition of this cement ranges between 1.9 to -3.55‰ for carbon and -0.4 to -3.2‰ for oxygen. The isotopic composition of the diagenetic fluid that precipitated this cement is constrained in Fig. 5.16, by using meteoric cement oxygen isotope values at a temperature range of 20 to 30°C, resulting in values between +1.0 to -3.5‰ (SMOW). The oxygen isotope composition of seawater is also constrained by using the marine calcite oxygen isotope values at a temperature of about 8 to 14°C (See Fig. 6.2), which gives $\delta^{18}O_{\text{seawater}}$ values about -1.2 to +0.6‰ (SMOW). The temperature range of seawater for the Middle/Late Miocene time interval was the lowest in the studied Tertiary record due to climatic deterioration.

The carbon isotopic composition of seawater of the Middle/Late Miocene is constrained by the $\delta^{13}C$ values of the marine calcite and by applying appropriate corrections for fractionation between seawater and equilibrium calcite, which result in values of about -0.2 to -1.0‰ (PDB). The $\delta^{13}C_{\text{dLMC cement}}$ is also used to constrain the $\delta^{13}C_{\text{DIC}}$ of the diagenetic fluids, resulting in highly variable values of about -0.4 to -5.85‰ (PDB).

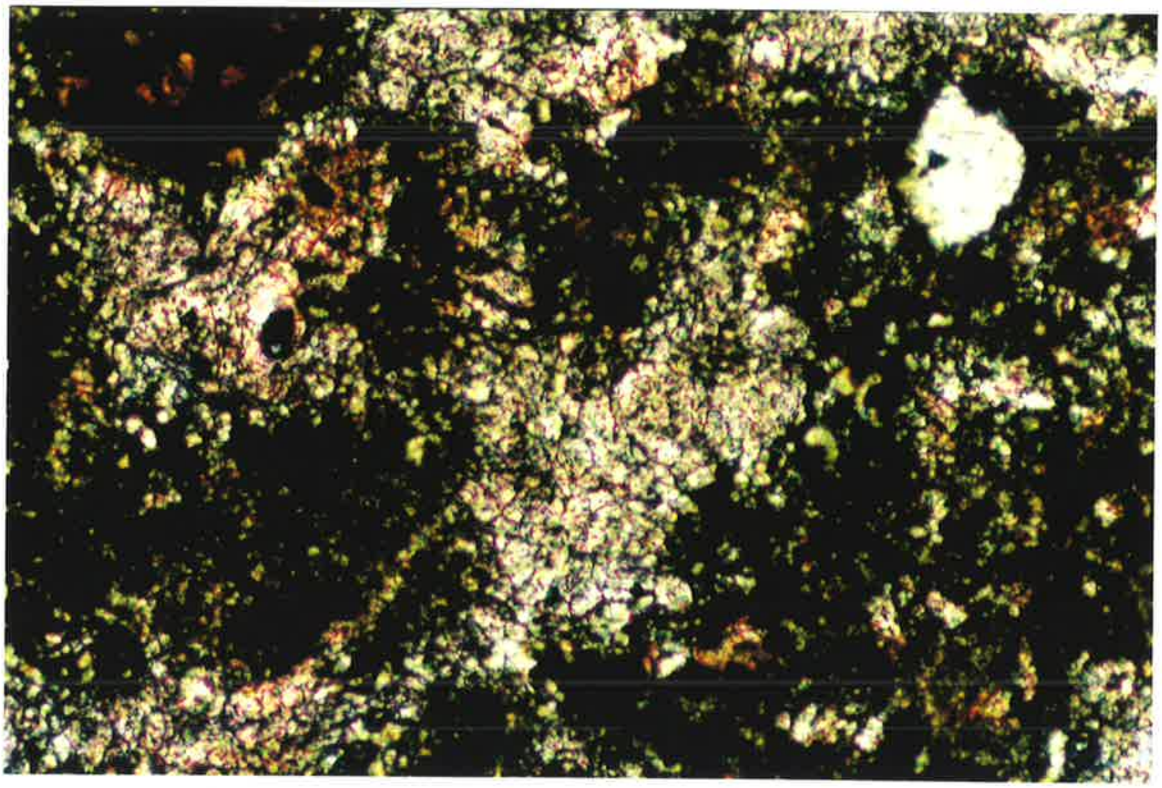


Fig. 5.14. The fine grained void-filling sparry calcite meteoric cement from Upper Morgan Limestone. The pinkish colour of the calcite cement is due to staining (Normal Light, field of view 2 mm, stained thin section).

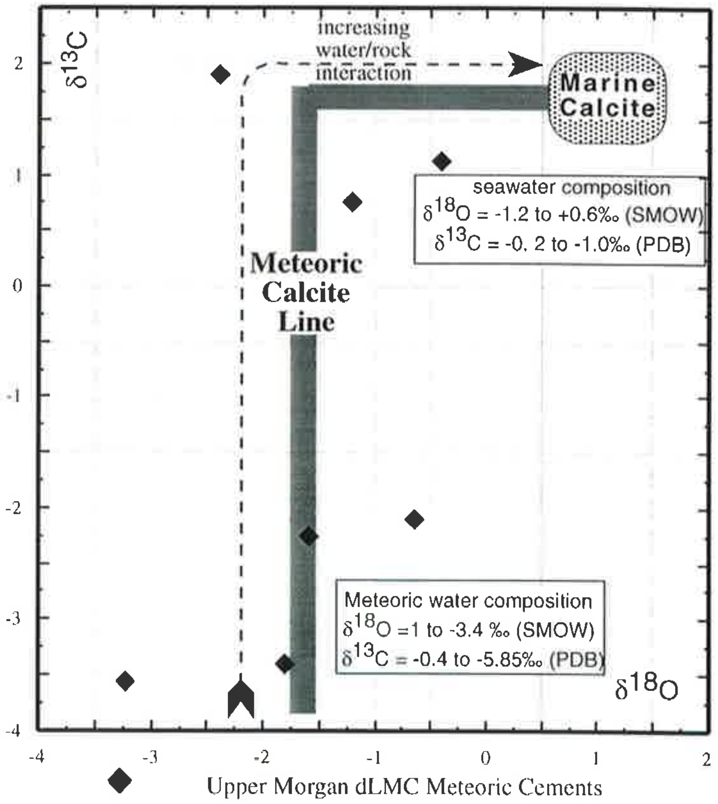


Fig. 5.15. The Inverted-J pattern shown by the isotopic composition of the dLMC meteoric cement of Upper Morgan Limestone. The original marine isotopic composition is the average isotopic composition of the Pecten which is close to equilibrium values (Rahimpour-Bonab et al. 1997b). Estimated average isotopic composition of meteoric water is based on the fractionation equation of Friedman and O'Neil (1977) at 25°C. Carbon isotopic composition is based on the most negative values of the dLMC cement and by applying a fractionation factor of 2.3‰ for calcite-bicarbonate (Turner 1982). The oxygen isotope of seawater is also constrained by using $\delta^{18}O$ marine calcite in that equation at 8 to 14°C (Fig. 5. 16) and the carbon isotope is calculated from the average $\delta^{13}C$ marine calcite after a 2.3‰ correction.

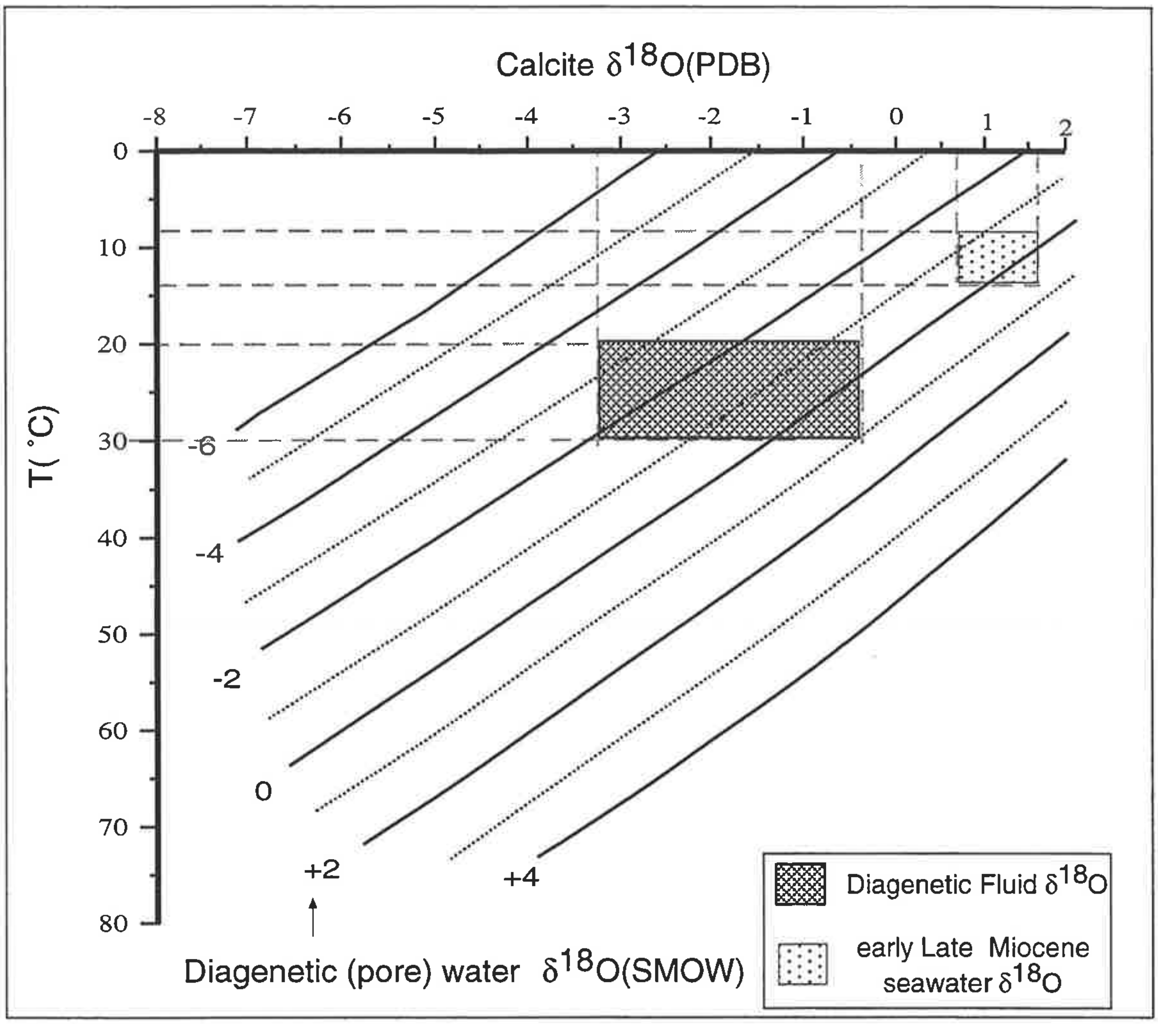


Fig. 5.16. Th calculated $\delta^{18}O$ composition of calcite precipitated at equilibrium from waters of various compositions over a range of temperatures, using the calcite-water oxygen isotope fractionation equation of Friedman and O'Neil (1977). The range of possible water compositions from which the dLMC cement of the Upper Morgan Limestone could have been precipitated is defined by the curves which pass through the stippled box between the 20 to 30°C temperatures, in this case, about +1 to -3.4‰ (SMOW).

The seawater isotopic composition of the early Late Miocene at temperatures of 8 to 14°C, which was the range of the bottom water temperature for that high latitude basin, is also shown (about -1.2 to +0.6‰ SMOW).

The cement (and thus diagenetic fluids) shows highly variable $\delta^{13}C$ values, whereas its $\delta^{18}O$ value is much less variable. This suggests a meteoric origin for the cement, as the general distribution pattern is comparable with the inverted-J trend of meteoric cements (Fig. 5.15). However, the heavy values of some cements suggest a contribution of seawater during the formation of the diagenetic fluids. This observation is consistent with the fact that the heaviest $\delta^{18}O$ values of diagenetic fluids are close to the seawater isotopic composition (Fig. 5.16). On the other hand, and consistent with this observation, the most enriched $\delta^{13}C_{dLMC\ Cement}$ (and thus the diagenetic fluids) shows values close to the marine calcites (and seawater) (Fig. 5.15). Therefore, the dLMC cement of this unit is produced by meteoric fluids in a coastal diagenetic setting which was influenced by seawater influx (or trapped seawater in sediments), as shown by the heaviest isotopic values of this cement.

5.8. Conclusion:

Carbonate sediments exposed in meteoric systems undergo post-depositional alterations which eventually result in stabilisation of the metastable components and precipitation of diagenetic calcites as cement. The isotopic composition of these meteoric cements is influenced by the isotopic composition of the original marine calcites and the meteoric fluids. Therefore, the isotopic composition of the diagenetic fluids is related to, and can be estimated from, that of the cement. These estimates provide essential constraints for evaluating the nature of secular changes in the ocean chemistry as well as meteoric water composition with time. The diagenetic setting and processes evolved in formation of these cements are also recognisable from the isotopic composition of these cements.

The isotopic composition of seawater can also be estimated by using the well preserved fossil material and constraining relevant bottom water temperatures. With the assumption of changing $\delta^{18}O$ value of seawater (the ultimate source of the meteoric water) through geologic time, the observed variations in the $\delta^{18}O$ values of the studied calcite cements suggest formation of such cement from different $\delta^{18}O_{\text{meteoric-water}}$, which reflect the northward drift of Australia during the Cenozoic and thus continued $\delta^{18}O_{\text{meteoric water}}$ variations with time.

CHAPTER SIX

PALEOENVIRONMENTAL INTERPRETATION OF THE TERTIARY OF SOUTH AUSTRALIA

6.1. Introduction:

In the middle 1970s, Savin et al., (1975) and Shackelton and Kennett (1975a and b) in their pioneering works, assumed that, before Middle Miocene time (15 Ma), there were no significant continental ice sheets. However, Matthews and Poore (1980) and Matthews (1984) challenged that theory and proposed that ice caps were established earlier in the Cenozoic. They contended that tropical seasurface temperatures were similar to today, major ice accumulation occurred in the Paleogene and that cooling of bottom waters occurred throughout the Cenozoic. They proposed that because previous investigators compared Tertiary isotopic records to the modern ocean, they thereby calculated surprisingly cool temperatures for the tropical seasurface. Matthews and Poore (1980) proposed that Tertiary data should be compared with average Late Pleistocene temperatures, assuming a constant tropical seasurface temperature. By this approach, they suggested that the earth had been partially glaciated at least since the Eocene and perhaps even through much of Cretaceous time. Thus, by comparison of the Tertiary data and average Late Pleistocene data and assuming a constant tropical seasurface temperature, they contended that a major glaciation event occurred at 38 to 40 m.y. ago, rather than at 12 to 17 Ma, which had been assumed by previous workers. Therefore, assumptions about the existence and size of ice sheets at various times during the Tertiary had a significant effect on the interpretation of isotopic data. Shackelton et al., (1984a, b) noted that the model presented by Matthews and Poore (1980) leads to the unlikely conclusion that "there was actually slightly more ice on the globe at the warmest part of the Middle Miocene than there is today".

Then, Hus (1984) discovered evidence of the Late Eocene glaciation in the Ross Sea. Next, Barron et al., (1989) reported the existence of sea-level ice sheets at Prydz Bay, Antarctica, from at least the earliest Oligocene and possibly since late Middle Eocene (42.5 Ma). Finally, Shackelton himself (1986), by studying benthic foraminifera records, suggested three glacial phases in the Oligocene. Nowadays, the existence of ice sheets since the Early Tertiary, associated with a strong positive $\delta^{18}O$ shift of about 1‰, is accepted by most investigators (e.g., Adams et al. 1990; Berggren and Prothero 1992). The general trend in $\delta^{18}O$ value of seawater and foraminifera shows an increase from Early Eocene time to the Recent (indicating a decrease in seawater temperature). In the Eocene, the $\delta^{18}O$ values increased in two steps: (1) an increase between 52 and 48 Ma (Early/Middle Eocene boundary) of about 1‰ in benthic foraminifera and (2) an increase of 0.5 to 0.7‰ in the late Middle Eocene (45 to 40 Ma) (Miller et al. 1987a, b). From this evidence, they believe an ice-free world existed before the Early Eocene, which is supported by the presence of terrestrial plants in high latitudes.

The differences in $\delta^{18}O$ values between glacial and interglacial periods result from two effects. First, an ice effect which is due to the locking up of ^{16}O-rich water in polar ice caps and consequently a corresponding enrichment of $\delta^{18}O$ in seawater. Second, a temperature effect which is related to the growth of organisms in colder water during glaciation. Generally, at comparable geographical latitudes an oxygen isotope difference of about 1.6‰ is observed between glacial and interglacial periods (Shackelton 1977). Shackelton (1967) and Shackelton and Opdyke (1973) suggested that two thirds of the isotopic variations from interglacial to glacial periods are due to ice storage effects on $\delta^{18}O_{seawater}$, and just one third of this change is because of the temperature effects. Most investigators now agree on this issue. Mix (1987), for example, concluded that up to 30% of the $\delta^{18}O$ variations in carbonates during the Tertiary are due to temperature effects. The overall Cenozoic stable oxygen isotope variation in calcitic benthic foraminifera is about a 4 to 5‰ increase from ice-free conditions to the glacial times. These isotopic changes reflect the evolution of the climate through growth of continental ice caps and subsequent cooling of the deep ocean water (e.g., Emiliani 1955; Savin et al. 1975; Shackelton and Kennett 1975a, b; Keigwin and Corliss 1986; Berggren and Prothero 1992).

The carbon isotopic records of foraminifera also reflect variations during the Cenozoic of about 2‰ (Shackelton et al. 1984b). Although there is an overall trend from the Palaeocene to the Pleistocene toward positive $\delta^{18}O$ values, no long-term parallel trend has been perceived in the $\delta^{13}C$ record of this time interval, and $\delta^{13}C$ variations are recorded as relatively shorter cyclic events. The global changes in carbon isotope records, that occur over periods longer than the residence time of carbon in the ocean, can only arise as a result of long term changes in the global rate of storage as the inorganic form of carbon rather than as carbonate (e.g., Adams et al. 1990). This rate of storage is related to sea-level, climate, the composition of the atmosphere and the accumulation of global coal and oil reservoirs.

Benthic organisms has advantages over planktonic ones for $\delta^{13}C_{DIC}$ (dissolved inorganic carbon) studies, because, as Shackelton et al., (1985) suggested, the average chemistry of the oceans is better represented at the seafloor than close to the surface. The surface waters are more exposed to external factors such as runoff and precipitation and so are more liable to chemical changes. Whereas recognisable oscillations in the stable isotope records of the foraminifera have been extensively utilised for paleoenvironmental studies in different basins, there has been little attempt to use the isotopic signatures of the invertebrate macrofossils to interpret the history of paleoenvironmental events, especially during the Cenozoic. Two reasons come to mind. First, in many cases, macrofossils are partially or even completely altered and thus their original composition is masked by diagenesis. Second, macrofossils are abundant in shallow water environments in marginal basins, and these marginal basins are frequently under the influence of nearby continents or atmospheric precipitation. However, by taking appropriate precautions and using unaltered fossils, it is possible to differentiate marine chemical signatures from mixed marine-freshwater signatures and utilise the geochemical records of marine invertebrates for interpretation of their paleoenvironment. Then, these data can be employed for study of the global isotopic changes caused by different processes such as the waxing and waning of ice-sheets.

In the study areas, Tertiary limestones of the St.Vincent and Murray Basins of South Australia that contain abundant well-preserved fossil samples, providing an opportunity for paleoenvironmental reconstruction and for tracing secular seawater chemistry changes during this period. A detailed petrographic and isotopic study has been carried out to differentiate pristine fossil materials from the altered ones in different units and where fossil samples were altered, their original isotopic signatures were retrieved by the backtracking process (Chapter Four).

The $\delta^{13}C_{DIC}$ of the ambient seawater is reflected in the $\delta^{13}C$ value of its inhabitants which are preserved as fossils. The important point is the effect of metabolic fractionation (the vital effect) that may mask the original seawater isotopic composition and which usually results in light $\delta^{13}C_{DIC}$ values. To prevent this problem, the organisms that present the lowest metabolic effects over their isotopic composition, should be employed for paleoenvironmental studies and geochemical reconstruction. Accordingly, geochemical studies on the neighbouring Holocene temperate carbonate environment has produced extensive information about the nature of carbonate production by different carbonate-secreting organisms and its geochemical implications (Bone and James, 1997; Rahimpour-Bonab et al. 1997a, b). Therefore, in this study, only fossil samples which showed that they precipitated their calcareous shells in isotopic equilibrium with their ambient waters, have been utilised for paleoenvironmental interpretations.

The objectives in this chapter are (1) to present the isotopic variations of these marginal basins during different Tertiary times (excluding the Pliocene); (2) to establish $\delta^{18}O$ and $\delta^{13}C$ variation curves for this period, based on molluscan and brachiopods samples; (3) to disentangle the regional and global seawater chemistry changes in this area and their effects on these isotopic records; (4) to compare the isotopic composition of well-preserved macrofossils of the study area with well-studied foraminifera from different parts of the world; and (5) to substantiate the importance of macrofossils for such studies.

6.2. Oxygen Isotopic Records of the Tertiary

6.2.1. Late Eocene to Early Oligocene:

Paleotemperature investigations utilising the $\delta^{18}O$ value of skeletal carbonates of fossil material was pioneered by Urey (1947) and Epstein and Lowenstam (1953). This is now a major technique in paleoenvironmental studies (e.g., Hudson and Anderson 1989; Marshall 1992). The method is based on the fact that the ratio of the two stable isotopes of oxygen ($^{16}O/^{18}O$), when precipitated in carbonate in an equilibrium state from the ambient waters, is temperature dependent (e.g., Marshall 1992). In his pioneering work in Australia, Dorman (1966, 1968) estimated the paleotemperatures of the Tertiary using different molluscs. However, because he assumed a constant $\delta^{18}O_{SW}$ during the Tertiary and because he failed to carry out petrographic studies to determine the diagenetic alteration of his fossil samples, his results are dubious.

In this study, paleotemperature values for different fossils were calculated using equations (1) and (2) from Chapter Two. To calculate an accurate paleotemperature using the $\delta^{18}O$ value of fossils, a precise knowledge of $\delta^{18}O_{SW}$ is of paramount importance. However, estimating $\delta^{18}O_{SW}$ is indecisive because of several factors:

(1) In modern oceans the surface seawater $\delta^{18}O$ values vary by about 1.5‰ between low and high-latitudes in open oceans (Broecker 1989) and by as much as 3.0‰ between open oceans and marginal seas (Fairbanks 1982; Fairbanks et al. 1992). These variations in the $\delta^{18}O_{SW}$ are produced by the combined effects of evaporation, precipitation, Rayleigh distillation and atmospheric vapour transport. Isotopically depleted water vapour is continuously transported from the subtropics towards the poles during these processes, leading to $\delta^{18}O$ enrichment in seawater in the subtropics and depletion in high-latitudes.

(2) The average $\delta^{18}O_{SW}$ has changed through geological time because of the waxing and waning of glaciers and because of temperature variations. Therefore, in order to calculate paleotemperatures from the $\delta^{18}O$ values of the calcareous fossils, the mean oxygen isotopic composition of seawater ($\delta^{18}O_{SW}$) must be constrained by adjusting the $\delta^{18}O$ values of all fossils for long term shifts in the mean isotopic composition of the paleoceans due to changes in global ice volume.

Hambrey et al., (1991) and Zachos et al., (1994), using the glaciomarine ice-rafted debris (IRD) record of Antarctica as a major sign of glaciation, distinguished the ice-free world from the glaciated world in the Paleogene. According to these researchers, prior to the Late Eocene, the world was ice-free, with $\delta^{18}O_{SW}$ values of about -0.96‰ (SMOW) and therefore the $\delta^{18}O$ variations in the ice-free world are attributed to the temperature variations. Zachos et al., (1994) suggested that in most of the Late Eocene, ephemeral continental ice sheets existed but that they had only slight effects on the $\delta^{18}O_{SW}$. They suggested that in the Late Eocene and the Early Oligocene the $\delta^{18}O_{SW}$ values were about -0.8 and -0.5‰, respectively. Zachos et al., (1994) added that the times of full continental glacial activity were the earliest Oligocene and the Middle Oligocene. Correspondingly, for the Late Oligocene and the Early Miocene a $\delta^{18}O_{SW}$ value of -0.96‰, for the Middle Miocene $\delta^{18}O_{SW}$ value of -0.8‰ and for the Late Miocene $\delta^{18}O_{SW}$ value of -0.5‰ are used in this study, which are consistent with ice volume increases during these times. These values are presented by different workers (e.g., Shackelton et al. 1984 a, b; Shackelton 1986; Breza and Wise 1992; Zachos et al. 1994). These mean $\delta^{18}O_{SW}$ values of the world's ocean are in the range or close to the calculated values of $\delta^{18}O_{SW}$ from marine fossil of the study area (Chapter Five).

Conspicuous ocean temperature changes have occurred from the Paleogene to the Holocene. Seasurface temperatures (SST) during the Late Paleocene were about 9 to 11°C warmer than today, and so by the Early Eocene, southern SST exceeded 14 to 16°C (Zachos et al. 1994). The warm SST conditions lasted for at least two m.y. (Barrera and Huber 1991) but by the Early/Middle Eocene, the SST decreased about 5 to 6°C, resulting in a low SST (about 3 to 6°C) in the Southern Ocean, during the Late Eocene (Breza and Wise 1992; Zachos et. al. 1992, 1994). Another cooling event that occurred at the Eocene/Oligocene boundary, showed a decline of about 1 to 2°C (e.g., Zachos et al. 1994).

Bottom water temperatures during the Late Paleocene were between 7 to 10°C and during the Early Eocene about 10 to 14°C. Along with high-latitude SST, the bottom water temperatures decreased about 8 to 10°C over the Late Eocene and the Early Oligocene and in the Late Eocene bottom water temperatures ranged from 4 to 8°C. By the Late Eocene and the Early Oligocene, in high-latitudes a conspicuous cooling event occurred that caused about an 8°C decrease in SST from the Early Eocene, which is contemporary with the cooling event in the tropical SST, but to a much lesser extent.

The lightest foraminiferal $\delta^{18}O$ value of the Cenozoic is recorded in Early Eocene time (e.g., Shackelton and Kennett 1975a, b; Miller et al. 1987a; Miller 1992), which is interpreted as an ice free world by Miller et al. (1987a, b). The $\delta^{18}O$ content increased from the Early Eocene to the earliest Oligocene which represents a changeover from the "greenhouse world" to a glaciated "icehouse world" (Miller et al. 1991). The $\delta^{18}O$ increase during this time interval occurred in three stages:

(1) The first increase in the $\delta^{18}O$ values is by about 1.0‰ which occurred close to the Early/Middle Eocene boundary (Miller et al. 1987a, in the Atlantic; Miller et al. 1987b in the Pacific).

(2) The second $\delta^{18}O$ increase of approximately 1.0‰ occurred near the Middle/Late Eocene boundary (e.g., Oberhansli et al. 1984; Keigwin and Corliss 1986; Miller et al. 1987a in the Atlantic; Shackelton and Kennet 1975a and b; Miller 1992 in the Pacific). The time of this $\delta^{18}O$ increase is not well-constrained.

(3) The third $\delta^{18}O$ increment in this period of about 1.0-1.5‰ happened in the latest Eocene/earliest Oligocene (Shackelton and Kennett 1975 a, b; Savin et al. 1975; Corliss et al. 1984; Miller et al. 1987a, b; Miller 1992).

In the study area, no isotopic data is available to examine the possibility of $\delta^{18}O$ increase at the Early/Middle Eocene boundary, because, in the St.Vincent Basin the oldest Tertiary unit in the Willunga-Noarlunga Embayment, is the North Maslin Sand which is of Middle Eocene age and contains no fossil material suitable for paleotemperature measurements. The second stage of the $\delta^{18}O$ increment that occurred at the Middle/Late Eocene boundary, is partially recorded in different fossils of the Tortachilla Limestone (40-37 Ma - early Late Eocene). The Pecten fossils of this unit show $\delta^{18}O$ values with an average of -0.60‰. The $\delta^{18}O$ values of Terebratellidae brachiopods are also recorded with an average of -0.75‰. The backtracked $\delta^{18}O$ values of the Turritellidae are between -0.40 to 0.6‰. As shown in Fig. 6.1, the paleotemperature of the bottom waters of the St.Vincent Basin at this time ranged between 19 and 13°C, which may reflect summer and winter temperature oscillations. Obviously, because these fossils are the oldest fossil samples from the study area which were analysed for their isotopic signature, it is not possible to estimate the possibility of $\delta^{18}O$ increase at this stage.

The third stage of the $\delta^{18}O$ increase that occurred in the latest Eocene (35.8 Ma) as seen in the $\delta^{18}O$ values of benthic foraminifera, is an increase of almost 1‰ associated with an increase in high latitude planktonic foraminifera. Terebratellidae brachiopods of the Gull Rock Member (middle Late Eocene) show almost an 0.60‰ increase in the $\delta^{18}O$ values compared with the older brachiopods of the Tortachilla Limestone (early Late Eocene - Figs. 6.1 and 6.2). A similar $\delta^{18}O$ increase is shown by the other fossils. This $\delta^{18}O$ increase in the Late Eocene records of the study area probably caused by the inception of glaciation in Antarctica, and is consistent with the world-wide $\delta^{18}O$ increase of that time (e.g., Miller et al. 1987; Miller 1992). It is indicative of mid-high latitude cooling beginning in the Early/Middle Eocene (Chrons C22N-C21N) with a positive $\delta^{18}O$ shift of up to 1‰ at the Middle/Late Eocene (Chrons C18N-C17N equivalent to the Tortachilla Limestone and the Gull Rock Member) and in the earliest Oligocene (Chrons C13N - Berggren and Prothero 1992). This cooling event resulted in the establishment and evolution of a major temperature gradient between low and high latitudes. The bottom water temperature decreased from about 12-13°C in the

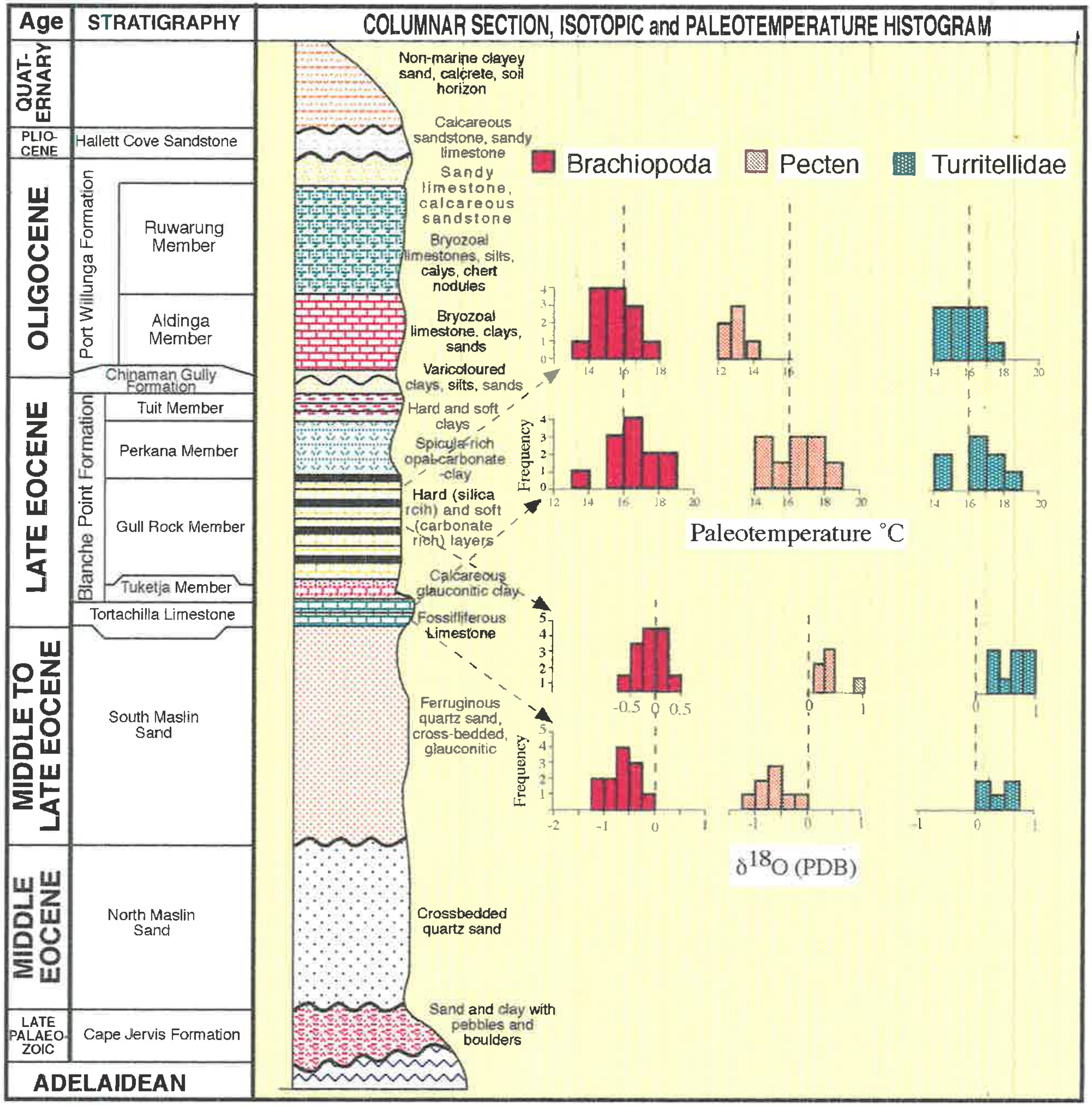


Fig. 6.1. Generalised stratigraphic column (modified from McGowran 1979), isotopic and paleotemperature histograms of the Tertiary units, Maslin-Aldinga area (not to scale). The δ18O values increase from the Tortachilla Limestone to the Gull Rock Member which is synchronous with a temperature decrease.

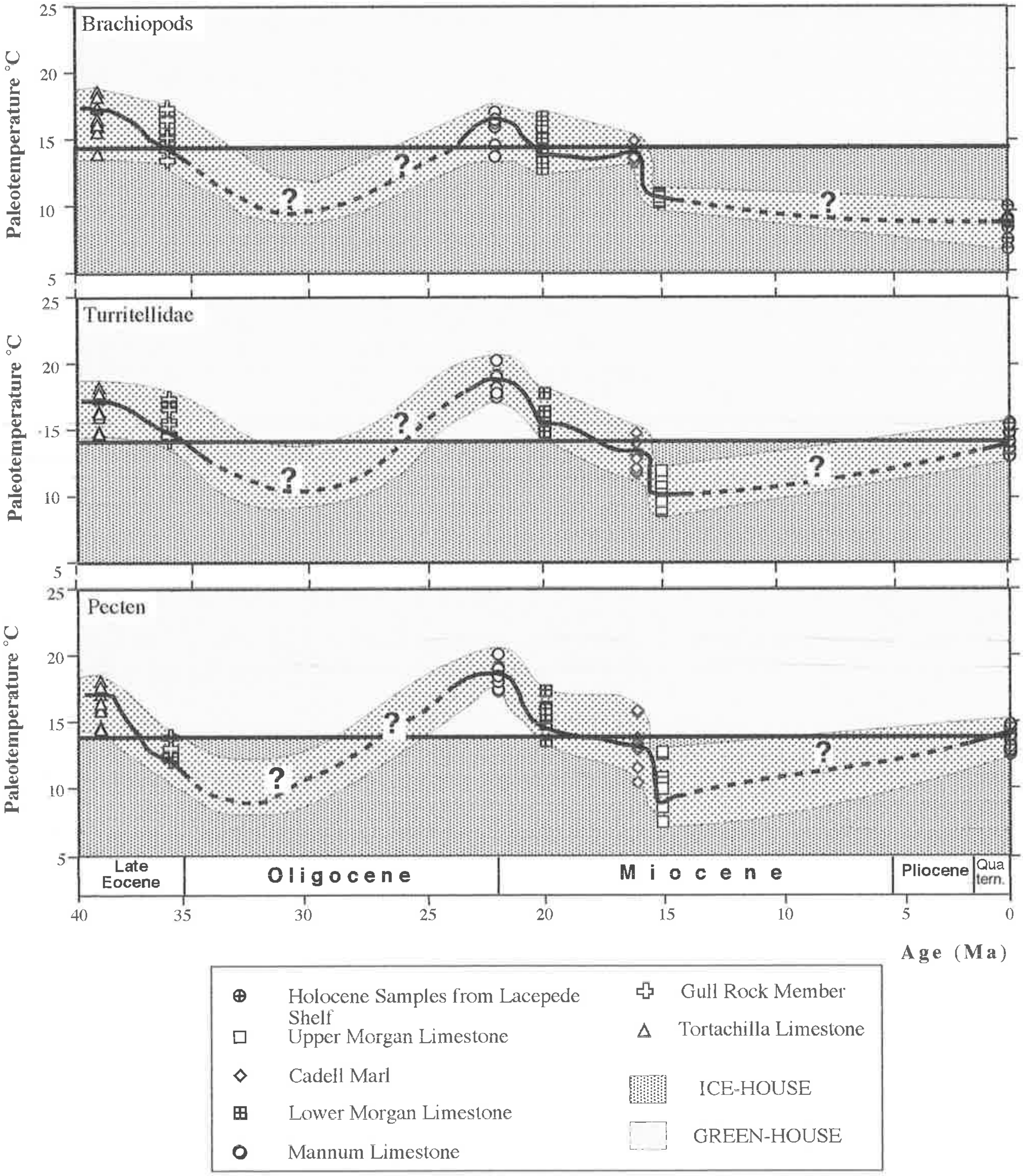


Fig. 6.2. The paleotemperature variations with time resulting from different fossils of diverse Tertiary ages from the study area. The Holocene brachiopods show some inconsistency in recording temperature which is due to some influence of metabolic effects on their $\delta^{18}O$ values (Rahimpour-Bonab 1997b).

Early Eocene to about 8-9°C in the Late Eocene. However, the amount of this increase in $\delta^{18}O$ values of the studied fossil brachiopods is less than that of the deep sea benthic foraminifera. The backtracked isotopic composition of the Pecten samples of the Gull Rock Member shows about a 1.0‰ increase in the $\delta^{18}O$ values, compared to the $\delta^{18}O$ of the Tortachilla Limestone Pecten (Figs 6.1, 6.2, 6.3). Moreover, the $\delta^{18}O$ value increase of the middle Late Eocene (36 Ma) is also recorded in the Turritellidae of the Gull Rock Member, with about an 0.6‰ increase, compared with the backtracked isotopic values of Turritellidae from the Tortachilla Limestone (Figs 6.1, 6.2, 6.3). Shackelton (1986) suggested that the cause of the isotopic changes ($\delta^{18}O$ increase) of the Late Eocene to Early Oligocene was a reduction in deep-water temperature by about 4°C. The age of this isotopic event is introduced by Berggren et al. (1985) as about 35.9 Ma, using the magnetic anomaly timescale. This is almost the same age as the Gull Rock Member (36 Ma). This sharp $\delta^{18}O$ increase at 36-35 Ma (immediately after the Eocene/Oligocene boundary) indicates the inception of glaciation in Antarctica (Miller et al. 1987a, b). Apparently, this third stage of the $\delta^{18}O$ increase was induced by ice sheet build-up in Antarctica and a subsequent decrease in bottom-water temperature (e.g., Miller 1992).

The average paleotemperature records (calculated) of the diverse fossils of the Tortachilla Limestone of the St.Vincent Basin (early Late Eocene) are 16.5°C for Turritellidae, 16.4°C for brachiopods and 16.2°C for Pecten, considering $\delta^{18}O_{SW}$ values of -0.8‰ (Figs. 6.1, 6.2). To calculate the paleotemperature record of the Gull Rock Member (middle Late Eocene) the $\delta^{18}O_{SW}$ values of -0.5‰ is considered for that time as the consensus is that there was more ice in Antarctica in the middle Late Eocene than the early Late Eocene. By this assumption, the average $\delta^{18}O$ values of the Turritellidae of the Gull Rock Member give a temperature of 15.5°C, compared with 15.3°C for brachiopods and 12.8°C for Pectens (Fig. 6.1). This declining trend of about 1.4°C in the average

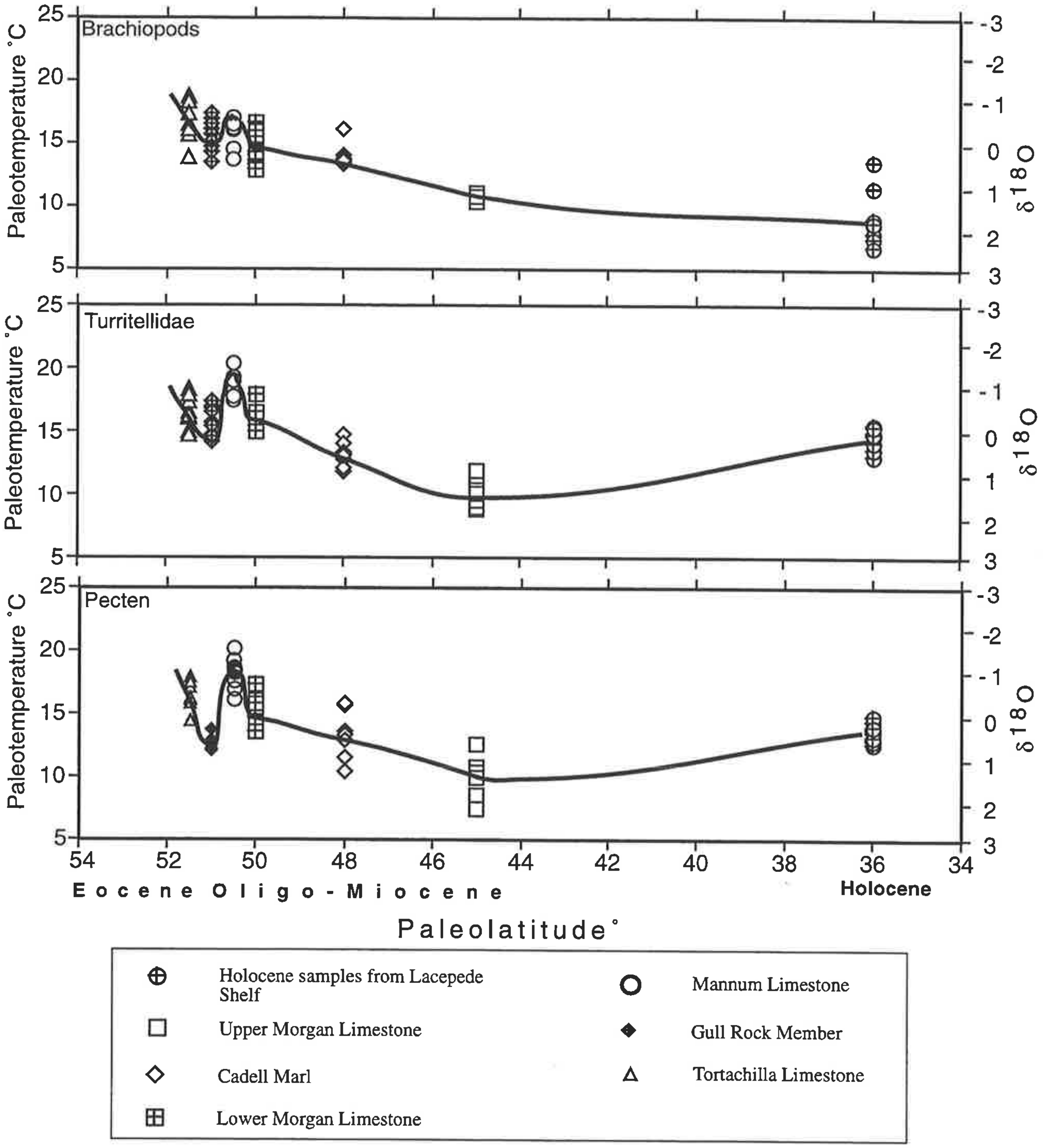


Fig. 6.3. The bottom water temperature variations in the study area accompanying the northward drifting of the Australian continent during Cenozoic time (paleolatitudes from Smith et al. 1981). The $\delta^{18}O$ seawater variations during the Cenozoic, recorded by different fossils, are also shown.

paleotemperature records reflects the cooling event intensification toward the Eocene/Oligocene boundary as seen in the benthic foraminiferal records of DSDP (e.g., Miller et al. 1988b; Zachos et. al. 1994) and is in the range of the temperature offset (1 to 2°C) presented by many DSDP workers, such as Zachos et al., (1994). Meanwhile, a comparison of benthic paleotemperature records of this study with bottom water temperatures shows a higher temperature in the St.Vincent Basin, which was shallower at that time. Therefore, it is more reasonable to compare temperature records of this study with intermediate and surface dwelling planktonic foraminifera that live in different depths from the surface to 300 m.

Moreover, the faunal assemblage of these Tertiary units in comparison with their Holocene cool-water counterparts of southern Australian continental shelves, supports the idea that normal oceanic conditions prevailed during most of the Tertiary period in the studied basins. As the results of this study show, the calculated temperature from different fossil groups within the same stratigraphic unit are reasonably consistent, indicating the credibility of paleotemperature results and the equilibrium precipitation of fossil carbonates used in this study, which leads to a precise recording of the ambient seawater paleotemperatures. Small discrepancies in paleotemperature values among different fossils could be ascribed to microhabitat-related geochemical variations.

The northward drifting of the Australian continent during Tertiary time facilitated higher temperature variations as the continent passed through different geographical zones. This also led to terrestrial paleoclimatological changes. As shown in Figs 6.2 and 6.3, all fossil assemblages of the different Tertiary units of the study area reflect the paleotemperature and $\delta^{18}O$ oscillations during this northward continental drift.

Therefore, the major increase in the $\delta^{18}O$ values in the Late Eocene towards the beginning of the Early Oligocene, that are interpreted as a major cooling event accompanied by the initiation of glacial activities in Antarctica, is reflected in the isotopic temperature of the Tortachilla Limestone and the Gull Rock Member biota. They indicate about a 1.4°C decrease in the overall paleotemperature records during this time interval. The time of maximum glacial build-up traced by ice-rafted deposits in Antarctica is the earliest Oligocene and Middle Oligocene, but the pristine fossils from these time periods were not available in study area for analysis.

6.2.2. Late Oligocene to Late Miocene:

In the Oligocene epoch (25 to 35 Ma) a climatic transition occurred from the warm periods of the early Cenozoic to the cold periods of the later Cenozoic. The thermal maximum of the Early Eocene was followed by a significant cooling at 40 - 50 Ma, which may have caused the faunal turnover of 38 to 40 Ma (Corliss et al. 1984; Raup and Sepkowski 1986). Ciesielski et al., (1988), Barron et al., (1989) and Schlich et al., (1989), from drilling projects in the Southern Ocean, and Barrett et al., (1987), from drilling projects around Antarctica, confirmed that an intermittent continental ice sheet existed on Antarctica, between the Early Oligocene and the Early Miocene (Miller et al. 1991). The peculiar features of the Oligocene ocean were relatively low carbonate sedimentation rates and lower productivity (Berger 1981; James and Bone, 1992).

The $\delta^{18}O$ values of Miocene benthic foraminifera indicate that deep waters warmed from the Late Oligocene/earliest Miocene (about 24 Ma) and reached their maximum values near the Early/Middle Miocene boundary (17 and 15 Ma) (Wright et al. 1992). This event is recorded in the $\delta^{18}O$ signatures of the different fossils in the Murray Basin, e.g., the Mannum Formation and Lower Morgan Limestone, show high average bottom water temperatures of 17.5°C and 16°C, respectively (Figs 6.2, 6.3, 6.4 and 6.5).

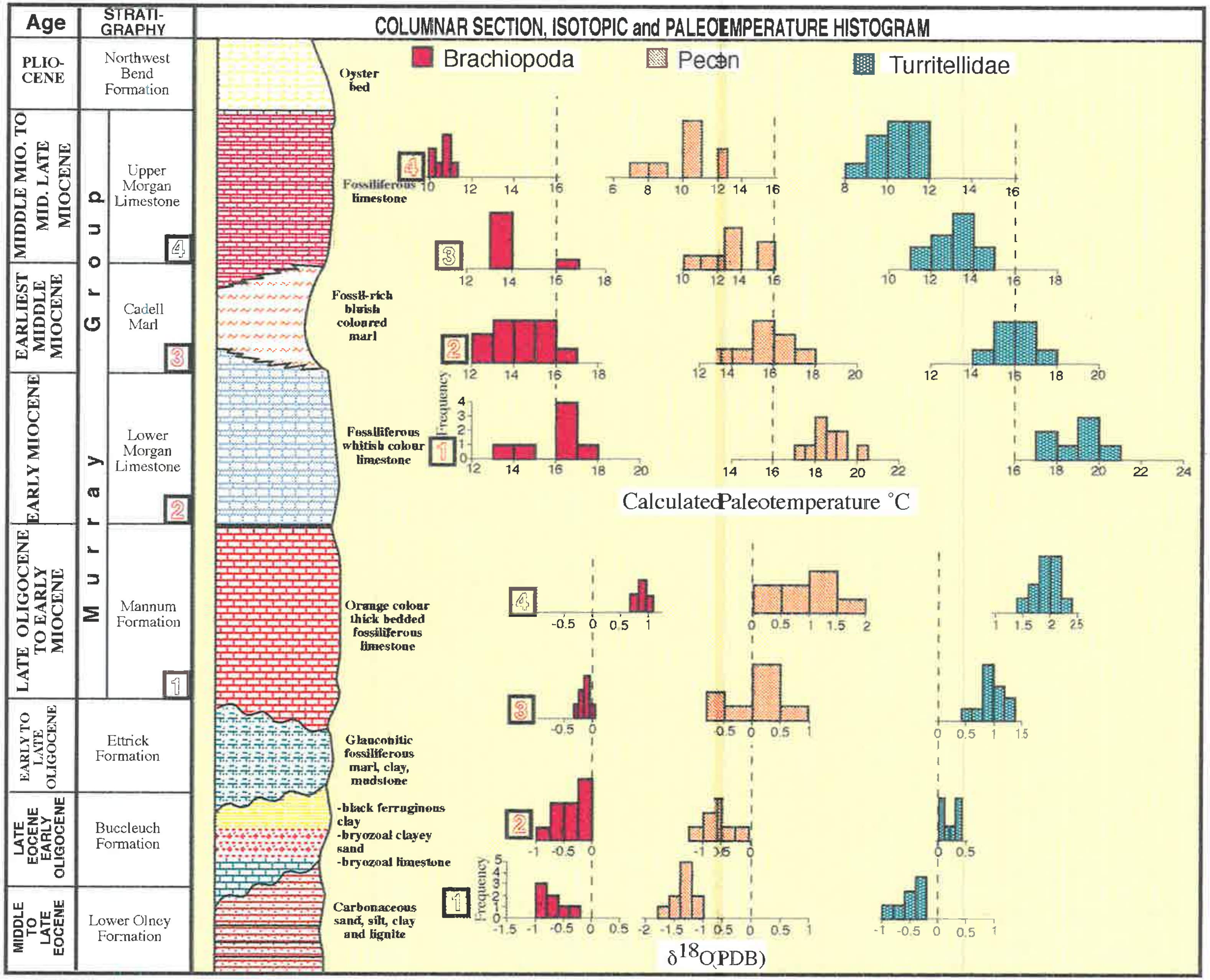


Fig. 6.4. Generalised stratigraphic column of the Murray Basin (not to scale) (modified from Alley and Lindsay 1995) and isotopic paleotemperature histograms derived from different fossils of the Tertiary units (1 to 4) of the Murray Basin in the Morgan area. The paleotemperatures show a declining trend from Late Oligocene to Late Miocene.

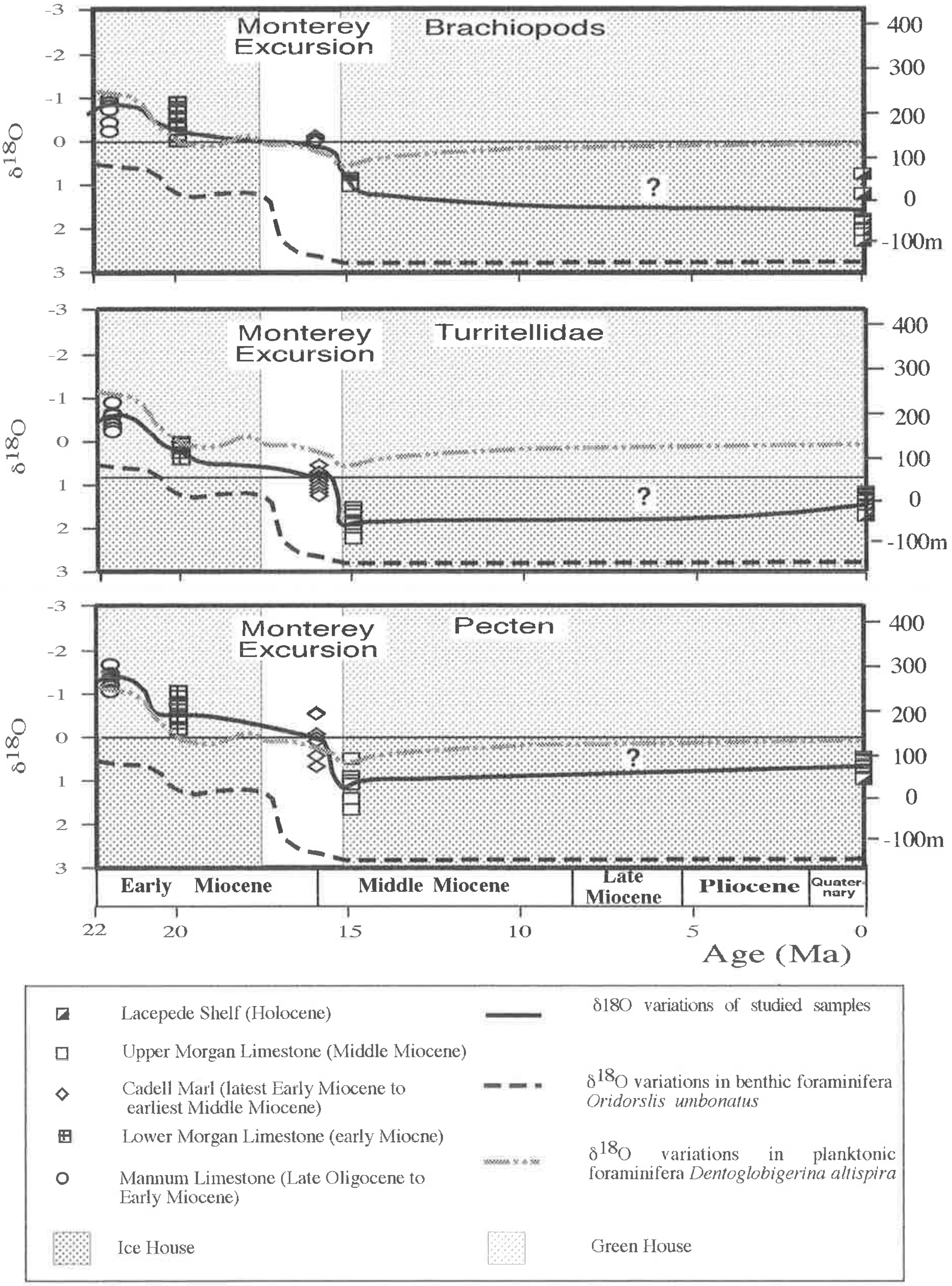


Fig. 6.5. The δ ^{18}O variations versus age in different fossils from the Murray Basin. The influenece of the Monterey Excursion on the oxygen isotopic composition of different mid-Miocene calcareous organisms is also shown. Generalised d18O variation curves of the benthic and planktonic foraminifera from Vincent and Berger (1985) which are consistent with curves resulting from other foraminifera, are shown for comparison. The approximate degree of sea-level fluctuations, as calculated from oxygen isotope composition of fossils (after appropriate corrections), is shown on the right.

The warmer temperatures of the Late Oligocene/Early Miocene (17 to 20 Ma) did not persist for all of the Miocene. A significant climatic change occurred between 10 and 17 Ma (Middle Miocene), which caused a large $\delta^{18}O$ increase at 17 to 15 Ma (Figs 6.2, 6.3, 6.4 and 6.5). This abrupt increase in the $\delta^{18}O$ values was first interpreted by Shackelton and Kennett (1975a, b) as the first Antarctic glaciation, but then it was ascribed to a deep-water cooling event (4 to 5°C) with some ice cap growth (Miller et al. 1987a; Moore et al. 1987). These latter authors suggested that expansion of the Antarctic ice sheet could have caused sea-level lowering at 10 to 11 Ma. Therefore, apparently there was an extensive ice cap on Antarctica by about 10 Ma, of which significant parts had existed since 40 Ma. This climatic deterioration is recorded in the Cadell Marl and the Upper Morgan Limestone fossil assemblages, and is consistent with foraminifera from other parts of the world (Fig. 6.5).

Accordingly, during the mid-Miocene, the low latitude planktonic foraminifera recorded an average increase of 0.8‰ in $\delta^{18}O$ values and the benthic foraminifera an average increase of about 1.3‰ (Wright et al. 1992). In the Murray Basin, the $\delta^{18}O$ values show an average increase of about 0.8‰ in the Pecten samples and the Turritellidae samples from the Lower Morgan Limestone (Early Miocene) to the base of the Cadell Marl (latest Early Miocene to earliest Middle Miocene). An average increase of about 0.5‰ in $\delta^{18}O$ values of the Terebratellidae brachiopods is also recorded. The average bottom water temperature of the Cadell Marl is calculated about 13.4°C with a minimum of 10°C, which represents a decline of about 3.5°C compared with the average temperature values of the Mannum Formation and the Lower Morgan Limestone (Figs 6.2 and 6.3). This temperature decline during the Middle Miocene recorded by fossils of the study area, is close to the temperature offset (4 to 5°C) observed by Miller et. al., (1987a, b) and Moore et. al., (1987) in benthic foraminifera of different DSDP sites at this time interval.

Therefore, the long term trend in the Miocene was a gradual increase in the $\delta^{18}O$ values from the earliest Miocene to the early Middle Miocene with an abrupt increase in the $\delta^{18}O$ around 17-16 Ma. This depicts warm conditions in the Early Miocene with relatively small ice caps in Antarctica and then the onset of colder conditions (caused by the intensification of glaciation) and deepwater cooling in the Middle Miocene.

The temperature variations calculated from the $\delta^{18}O$ content of the different fossil taxa from the Murray Basin are presented in Figs 6.6, 6.7 and 6.8. Almost all fossil samples present linear variations between their $\delta^{18}O$ content and temperature which indicates equilibrium precipitation of their shell carbonates. Moreover, their linear variations are mainly parallel to the standard paleotemperature curve of Friedman and O'Neil (1977) which again manifests the equilibrium isotopic composition, and the accuracy of the paleotemperature measurements, of these fossil samples.

The mainly narrower range of $\delta^{18}O$ values for the molluscan shells of the modern cool-water carbonate environment of the Lacepede Shelf compared to the Tertiary fossil samples of the study area (See Figs 4.1 to 4.15), probably indicates the higher summer and winter temperature differences in the bottom waters of the St.Vincent and Murray Basins, which, in turn reflects the shallower depths of these basins during the Tertiary. These relatively shallow ancient basins rendered themselves more susceptible to climatic variations, such as higher temperature fluctuations of bottom waters, whereas in the Holocene environment of the Lacepede Shelf, most deeper water samples show variations in the bottom water temperature of smaller magnitudes. These relatively high $\delta^{18}O$ variations in the fossil samples also may indicate the higher variations in the seawater isotopic composition of these Tertiary basins.

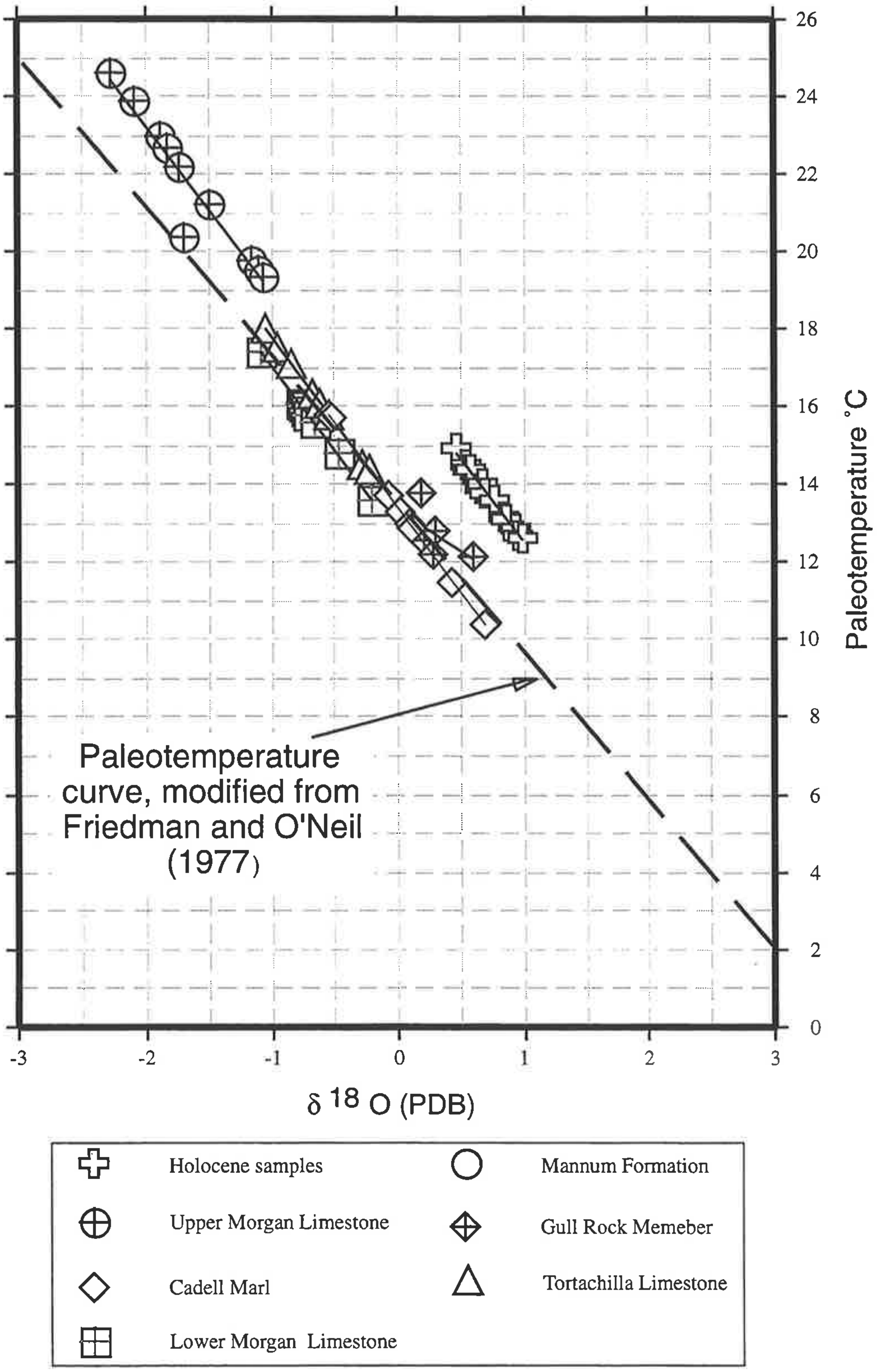


Fig. 6.6. The relationship between the $\delta^{18}O$ values of Pecten and paleotemperature in the fossil and Holocene samples. The paleotemperature standard curve of Friedman and O'Neil (1977) is shown for comparison, and regression lines are also presented. The regression lines for Pecten samples from diverse ages are parallel and are also compatible with the standard paleotemperature curve.

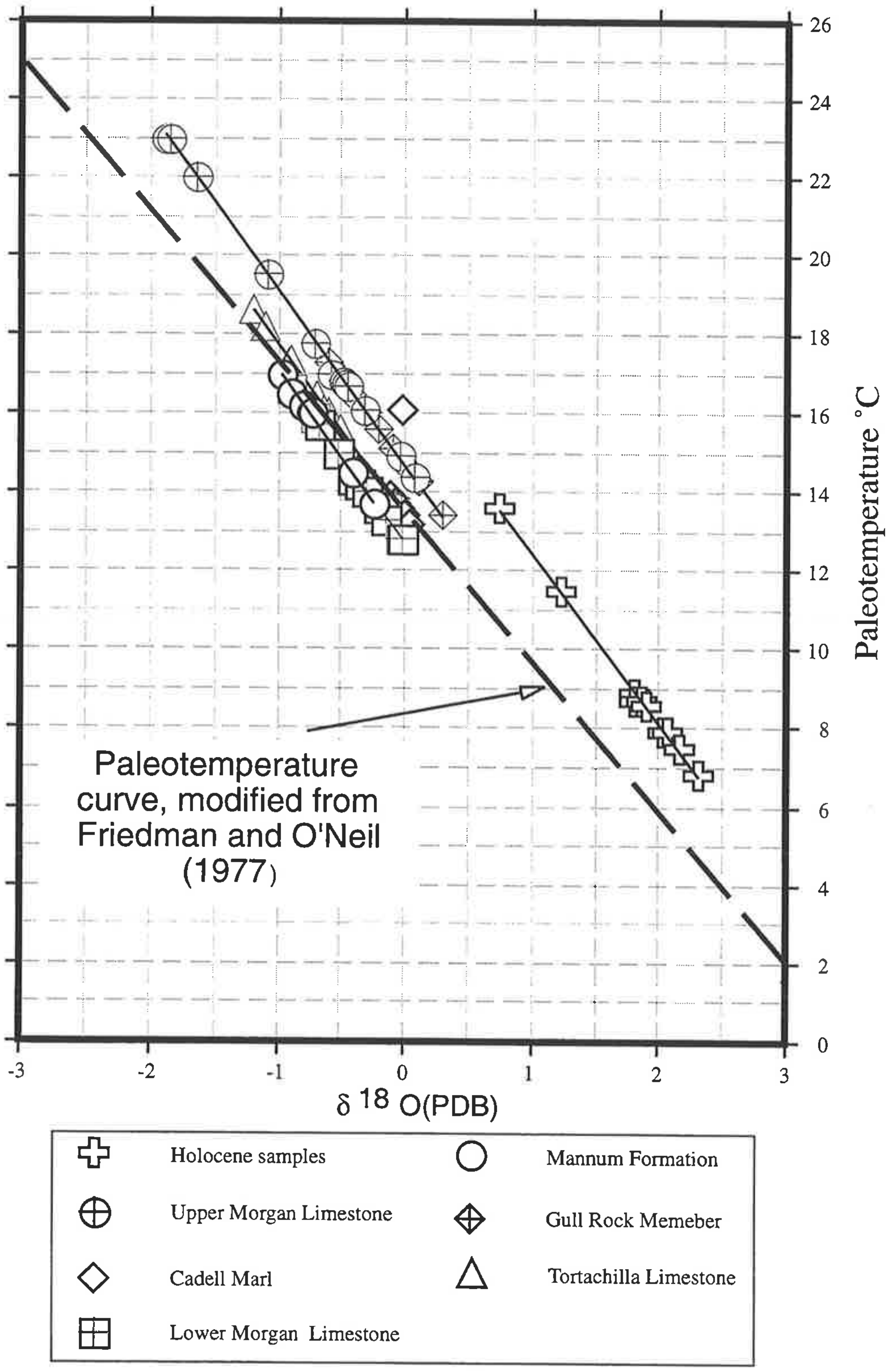


Fig. 6.7. The relationship between the $\delta^{18}O$ values of Terebratellidae brachiopods and paleotemperature in the fossil and Holocene samples. The paleotemperature standard curve of Friedman and O'Neil (1977) is shown for comparison, and regression lines are also presented. The regression lines for Terebratellidae brachiopods samples from diverse ages are parallel and are also compatible with the standard paleotemperature curve.

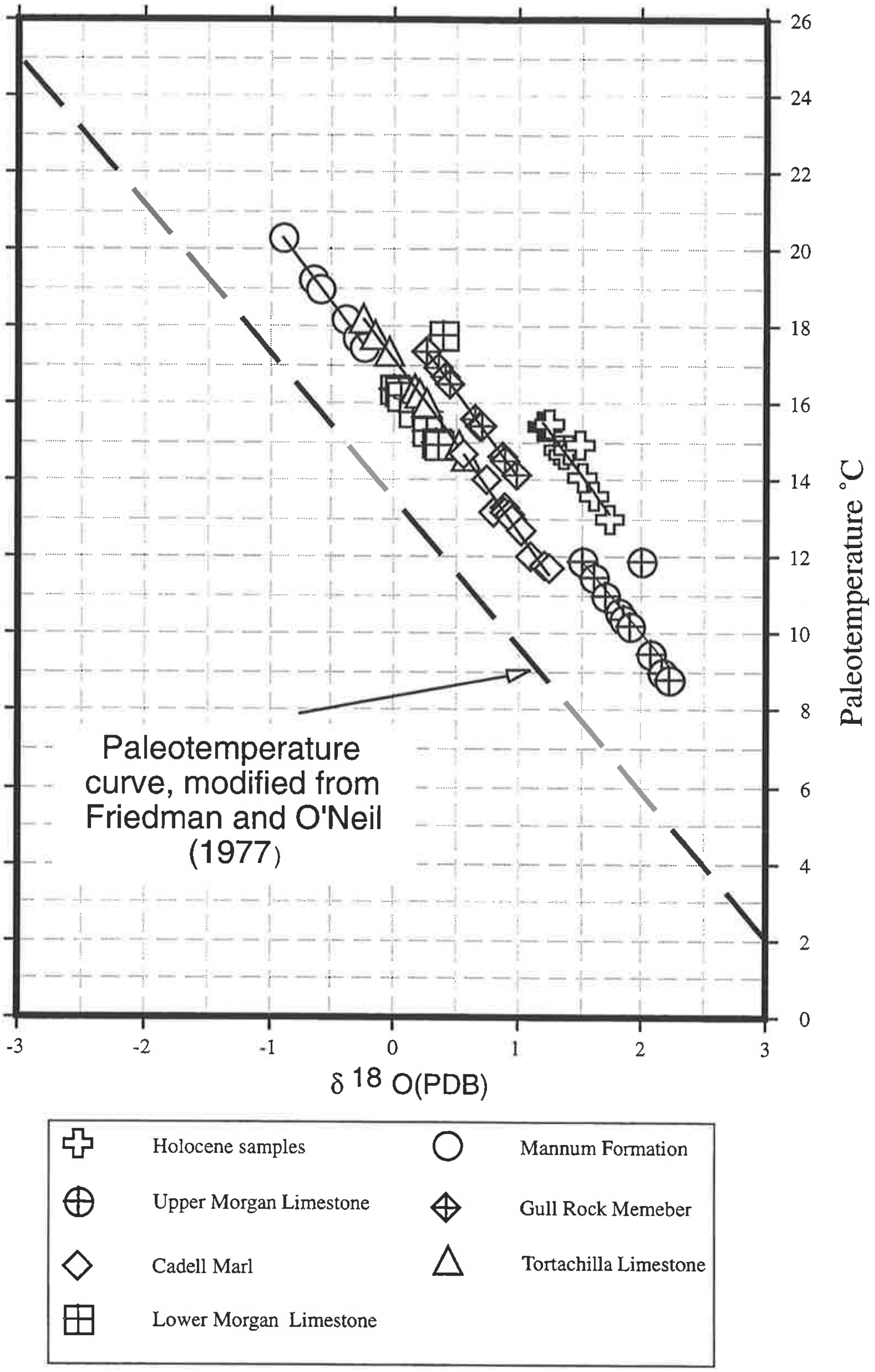


Fig. 6.8. The relationship between the $\delta^{18}O$ values of Turritellidae and paleotemperature in the fossil and Holocene samples. The paleotemperature standard curve of Friedman and O'Neil (1977) is shown for comparison, and regression lines are also presented. The regression lines for Turritellidae samples from diverse ages are parallel and are also compatible with the standard paleotemperature curve.

6.3. Carbon Isotopic Records of the Tertiary:

The organic matter production by phytoplanktons in the photic zone and its subsequent oxidation in deeper waters is one of the main controls on the $\delta^{13}C_{DIC}$ of the oceans (e.g., Broecker 1982; Berger et al. 1989). Hence, changes in the $\delta^{13}C_{DIC}$ value of the shallow water basins (photic zone), which are recorded in the $\delta^{13}C$ content of different fossils, reflect periods of high and low productivity in the shelf waters. The $\delta^{13}C$ oscillations recorded by the isotopic profiles of fossils (Chapter Nine) indicate the paleoproductivity variations due to influx of nutrient-rich upwelling currents in the shelf edge area, as seen in the Holocene cool-water carbonate environments of the Bonney and Lacepede Shelves. In general, the $\delta^{13}C_{DIC}$ of seawater on the carbonate platforms can be changed by several factors such as evaporation, dilution by fresh water, carbon transfer, the rate of photosynthesis and invasion of organic material (e.g., Broecker and Tahahashi 1966; Morse et al. 1984; Lazar and Erez 1992). The ability of these factors to influence the $\delta^{13}C_{DIC}$ of basin seawaters also depends on the depth and size of the basin, degree of restriction, and pattern of water circulation in the basin. Considerable ^{13}C depletion exists in the freshwater of atmospheric or continental provenance (rain, runoff, ground water), and $\delta^{13}C$ values of these waters are close to -7.0‰, which is a reflection of the composition of atmospheric CO_2. A more pronounced depletion in the $\delta^{13}C$ records of the fossils may reflect additional organic carbon input into the basin waters (e.g., from soil CO_2, humus, etc.). Thus, the freshwater flux into closed or semi-closed basins from the surrounding land, or directly from the atmosphere, can largely alter the isotopic composition of the water mass.

Furthermore, there are some differences in the $\delta^{13}C_{DIC}$ content of surface and deep seawaters ($\Delta\delta^{13}C_{DIC}$) and the amount of these differences reflects the productivity and circulation within the oceans. A positive $\delta^{13}C_{DIC}$ excursion is interpreted as either an increase in organic productivity, or as an intensified organic carbon deposition in shelf sediments during oceanic onlaps. Negative shifts in the $\delta^{13}C_{DIC}$ content might be interpreted as a ^{12}C return from the biomass to DIC due to changes in productivity rates. Moreover, sealevel lowering is accompanied by erosion of organic rich shelf sediments which add to the influx of organic carbon to the seawater and thus enhance a negative excursion of $\delta^{13}C_{DIC}$. Therefore, the $\delta^{13}C$ content of oceanic DIC ($\delta^{13}C_{DIC}$) is also controlled by the fluxes of ^{13}C-depleted (reduced) carbon and ^{13}C-enriched (oxidised) carbon into and out of the ocean and by the oxidation and reduction of organic matter within the ocean.

6.3.1. Early Oligocene to late Middle Miocene:

The $\delta^{13}C$ records of the Tertiary display several global cyclic variations. These $\delta^{13}C$ global variations at a given site reflect (1) the climatically induced global organic carbon inventory changes that involve carbon transfer between ocean water DIC and the organic reservoir of terrestrial biomass and shelf sediments; (2) the changes in abyssal circulations; (3) the regional oceanic heterogeneity; and (4) local changes in productivity, especially on continental shelves (Curry and Lohmann 1982; Sarnthien et al. 1982; Ku and Luo 1992). The latter include local factors that influence the $\delta^{13}C_{DIC}$ content of seawater such as source of continental runoff and its organic content (runoff from vegetated areas or from arid lands), surface productivity, basin openness and its morphology, that constrains seawater circulation.

In general, three major $\delta^{13}C$ cycles have been recorded in Oligocene to Miocene times in the benthic and planktonic foraminifera of the Atlantic, Pacific and Indian oceans at different DSDP sites (e.g., Miller and Fairbanks 1983, 1985; Shackelton et al. 1984a, b; Vincent and Berger 1985). These $\delta^{13}C$ cycles indicate global changes in the $\delta^{13}C_{DIC}$ content of mean ocean water. The intervals with major

$\delta^{13}C$ fluctuations occurred at about 37-33 Ma (Late Eocene/Early Oligocene), 25-22 Ma (across the Oligocene/Miocene boundary) and 18-14 Ma (across the Early/Middle Miocene boundary). These cycles had periods of 7-12 m.y. and amplitudes of about 0.5 to 1.0‰ (Mix and Fairbanks 1984).

The first $\delta^{13}C$ cycle lasted about 12 m.y. (from 37 to 24.5 Ma), the second about 8.5 m.y. (from about 24.5 to 16 Ma) and the third about 7 m.y. (from about 16 to 8 Ma - e.g., Miller and Fairbanks 1985). The boundaries of these global cycles of $\delta^{13}C$ were chosen as the most enriched $\delta^{13}C$ interval, i.e. 37, 24.5, 16, and 8 Ma (See Figs 4.1 to 4.3; Fig. 6.9).

The first global ^{13}C cycle is recorded in the isotopic signatures of fossils samples from the St.Vincent Basin, while the second and third global carbon cycles are recorded in the isotopic signature of fossils from the Murray Basin.

6.3.1.1. First Global Carbon Cycle:

The first $\delta^{13}C$ global cycle of the Late Eocene/Early Oligocene (37 to 24.5 Ma) is partially correlated with the Gull Rock Member. The Terebratellidae brachiopods of this unit show the heavier $\delta^{13}C$ values (between 1.5 to 3.31‰) in comparison with the Tortachilla Limestone brachiopods (See Fig. 4.2). The aragonitic Turritellidae gastropod of this unit also exhibits heavier $\delta^{13}C$ values (2.91 to 3.25‰) (See Fig. 4.3, 4.11 and 4.12). The $\delta^{13}C$ values of Turritellidae are less scattered than those of the brachiopods. Obviously, the heavier $\delta^{13}C$ values of Turritellidae in comparison with Terebratellidae brachiopods are due to their aragonitic mineralogy (Chapters Two and Three). Calculated $\delta^{13}C$ isotopic values for the Pecten fossils of the Gull Rock Member show an average of 1.5‰ (See Fig. 4.1, 4.11 and 4.12). Different fossils of this unit all show distinct increase in $\delta^{13}C$ compared to their older counterparts in the Tortachilla Limestone (See Figs 4.1 to 4.15). The increases are 1.6, 0.9 and 1.0‰ respectively. In the case of the

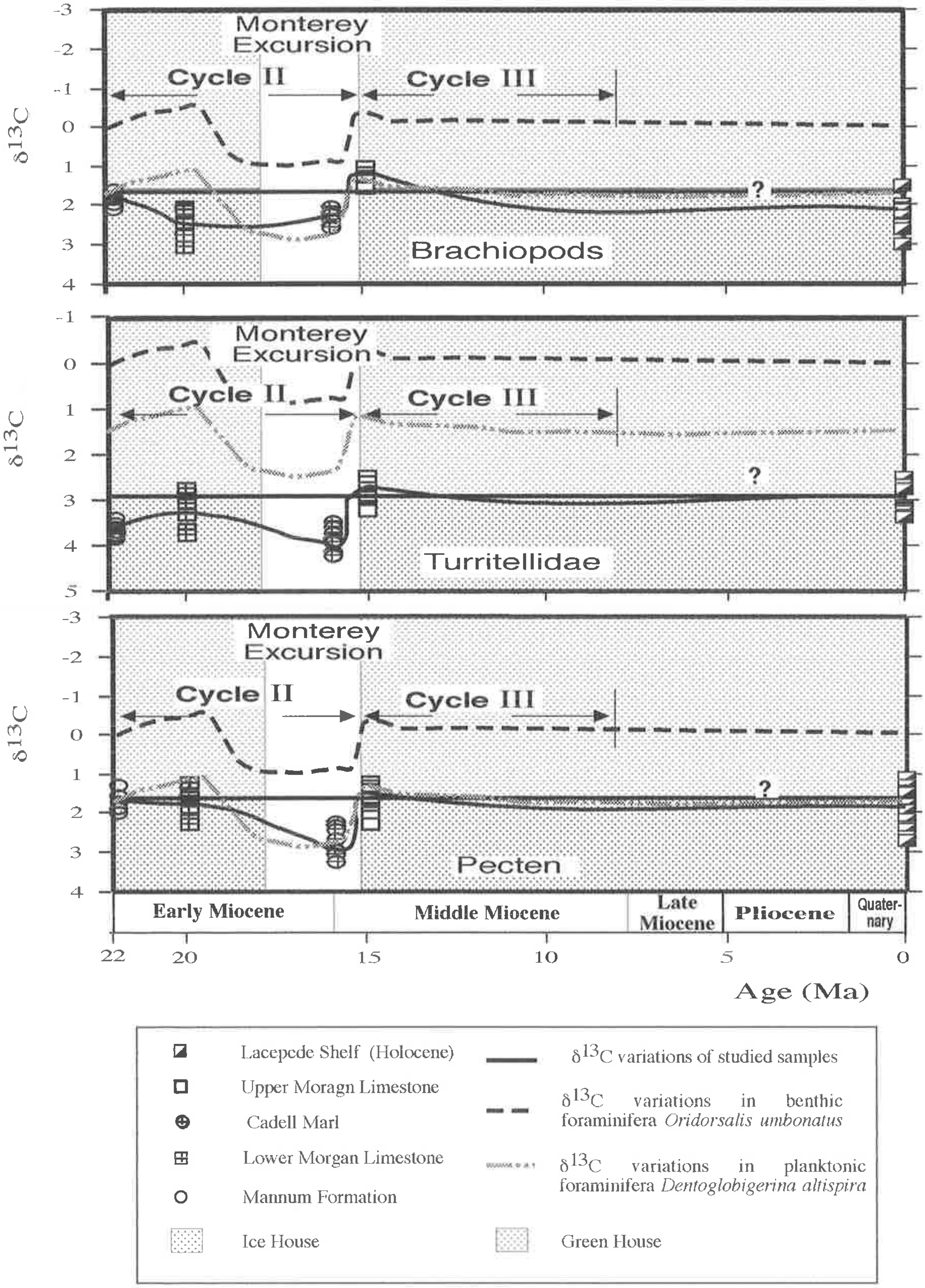


Fig. 6.9. The $\delta^{13}C$ variations in different fossils of the Murray Basin with age. The ^{13}C cycles, which are consistent with the second and third world-wide Tertiary carbon cycles (worldwide Tertiary carbon Cycles from Miller and Fairbanks 1985) are also shown. The positive carbon excursions in 16 Ma was due to the Monterey Excursion. Generalised $\delta^{13}C$ variation curves of the benthic and planktonic foraminifera from Vincent and Berger (1985) are also shown for comparisons.

t $\delta^{13}C$ values from the Gull Rock Member are higher
ıes from the Tortachilla Limestone. These $\delta^{13}C$
t fossils at this time in the study area are compatible
ents recorded in different benthic foraminifera (Miller
ent with the first global carbon cycle.

bon Cycle:

The second ^{13}C global cycle (the Late Oligocene/Early Miocene, 24.5-16 Ma) in the Murray Basin is partly recorded in the Terebratellidae brachiopod fossils of the Mannum Limestone. Brachiopods of this unit show $\delta^{13}C$ values with an average of 2‰. The backtracked values of the Pecten and Turritellidae fossils of this unit have average $\delta^{13}C$ values of 1.6‰ and 3.75, respectively (Fig. 6.9). The younger part of this cycle, namely the Early Miocene, is recorded in the brachiopods and Pecten fossils of the Lower Morgan Limestone. The $\delta^{13}C$ of brachiopods of this unit show heavy $\delta^{13}C$ values, with an average of 2.6‰, which on average is even more enriched than the Mannum Limestone brachiopods (See Fig. 4.2; Fig. 6.9). The Pecten fossils of the Lower Morgan Limestone also display heavy $\delta^{13}C$ values with an average of 2.1‰ (See Fig. 4.1; Fig. 6.9). Turritellidae samples of this unit, because of their aragonitic mineralogy are not preserved, but their backtracked isotopic values can be calculated from the Pecten fossils. which occur with them. These show heavy average $\delta^{13}C$ values of 3.35‰ (Fig. 6.9).

The terminal part of this $\delta^{13}C$ cycle, according to the data of different workers (e.g., Savin et al. 1981: Miller and Fairbanks 1983, 1985; Keigwin and Keller 1984) exhibits the highest $\delta^{13}C$ values of these three global $\delta^{13}C_{DIC}$ cycles. This event is recorded in the remarkably well-preserved Cadell Marl fossils, with the heaviest $\delta^{13}C$ values in the studied Tertiary samples (16 Ma). This is synchronous with the global Monterey Excursion, first described in the Monterey of California

(Vincent and Berger 1985), and resulted in heavy carbon and oxygen isotopes in the Murray Basin in the Middle Miocene (Chapter Seven).

6.3.1.3. Third Global Carbon Cycle:

The third ^{13}C-rich cycle, that lasted from 16 to 8 Ma (Middle/Late Miocene) in the Murray Basin, is not as well-recorded as the second cycle. The only rock record of this age is the Upper Morgan Limestone, which contains Terebratellidae brachiopods and Pecten fossils. These fossils show lighter δ^{13}C values, with an average of -0.4 and -0.5‰, respectively. The average δ^{13}C decrease of these fossils compared to the Cadell Marl is about 2.6 and 3.2‰ in the brachiopods and Pecten samples, respectively. This δ^{13}C negative excursion followed the positive δ^{13}C excursion recorded by the Cadell Marl fossils. Seemingly, such a large δ^{13}C offset (between 2.6 to 3.2‰) in the studied fossils of this unit is not consistent with the global δ^{13}C offset of this time (about 0.5 to 1.0‰). These light δ^{13}C values of the Lower Morgan Limestone are probably produced by the combined effects of global and regional/local conditions.

I. Global Effects: During the early Middle Miocene (beginning of the third cycle), the maximum δ^{13}C values were 1.4 to 1.8‰, as recorded by foraminifera (Woodruff and Savin 1985). Their lowest δ^{13}C values for that time are still heavier than the δ^{13}C values of Pecten samples from the Upper Morgan Limestone (between 0.35 to -1.45‰). This δ^{13}C negative excursion in unaltered Pecten fossils of the Upper Morgan Limestone is so large (up to -3‰) that it can not be explained simply by the global carbon budget changes induced by the waxing and waning of ice-caps. Furthermore, the maximum fluctuation in the δ^{13}C values of foraminifera from glacial to interglacial time, generally, is up to 1.0‰, and thus such a large decrease in the δ^{13}C values of the brachiopods and Pecten fossils of the Upper Morgan Limestone can not be ascribed entirely to the global δ^{13}C decline. The range of the δ^{13}C offset recorded in the Middle/Late Miocene is between 0.5 to 1.0‰ reflecting changes in the global carbon budget (e.g., Haq et al. 1980; Vincent et al. 1980; Woodruff et al. 1981). Therefore, the $\delta^{13}C$ values of the different fossil samples of the Upper Morgan Limestone should be produced by the combined effects of the global and local conditions. The $\delta^{13}C$ negative excursion at this time is contemporary with a global $\delta^{13}C$ offset in the middle of the third cycle, after a peak of the $\delta^{13}C$ values in the beginning of this cycle (Cadell Marl).

Glacial events had a great impact on the $\delta^{13}C$ content of DIC of seawater during geological times by influencing sea-level, which itself, influences the $\delta^{13}C_{DIC}$ of seawater. During sealevel highstands, large volumes of $\delta^{13}C$-depleted organic material were deposited and preserved on the continental shelves. Therefore ^{12}C-enriched organic materials were removed from seawater and this them led to increased $\delta^{13}C_{DIC}$ values of seawater. Conversely, during sea-level lowstands, less organic material was buried on the narrow continental shelves, and seawater $\delta^{13}C_{DIC}$ decreased correspondingly. In addition, the former highstand continental shelf sediments, which were enriched in organic materials, would have been exposed to weathering and erosion. Consequently, these would have been transferred to the ocean by runoff from the land, and subsequently would have induced further $\delta^{13}C_{DIC}$ depletion. Thus, sealevel fluctuations critically influenced the delivery of organic material to the seawater, and consequently, indirect causes led the $\delta^{13}C_{DIC}$ of seawater. Therefore, the $\delta^{13}C$ depletion in different fossils of the Upper Morgan Limestone, partially reflects the ice cap growth at that time in Antarctica. This ice-cap build up and consequent sea-level fall, led to changes in the global carbon budget. This sea-level fall indicated by the isotopic composition of the Upper Morgan Limestone fossils was contemporaneous with the global sea-level fall of 15 Ma (e.g., Miller and Fairbanks 1985). Therefore, these long term fluctuations of the $\delta^{13}C_{DIC}$ values at the global scale are caused by organic carbon transfer between the open ocean and continents (Shackelton 1986), or between the open ocean and continental shelves and estuaries (Broecker 1982), or between deep basins of the oceans (Kroopnick 1974). These carbon isotopic variations also indicate significant climatic changes which were generated by glacial transgression and its influences on the transfer of continental biomass to the oceans.

II. Regional/Local Effects: In the modern North Pacific Basin, oxidation of organic matter in deep-sea waters causes progressive enrichment in the ^{12}C with increasing depth and age of the water mass, which results in $\delta^{13}C_{DIC}$ values as low as -0.5‰ for seawater (Patterson and Walter 1994). On the other hand, the average $\delta^{13}C$ values of Pecten fossils from the Upper Morgan Limestone are also about -0.5‰, which, considering about a 2.3‰ fractionation between dissolved inorganic carbon (DIC) and calcite (e.g., Turner 1982; Romanek et al. 1992), results in an average of -2.8‰ for the $\delta^{13}C_{DIC}$ of the ambient seawater during the time of the Pecten mineralization (Middle/Late Miocene). This is even lower than the measured values of the deep old waters of the North Pacific Basin presented by Patterson and Walter (1994).

Patterson and Walter (1994) also suggested that the $\delta^{13}C_{DIC}$ depletion in the seawater in Florida Bay is related to seawater residence time on the platform. Accordingly, water bodies with a low circulation rate have a higher residence time, and would therefore present lighter $\delta^{13}C_{DIC}$ values. Patterson and Walter (1994) also presented $\delta^{13}C_{DIC}$ variations with salinity in Florida Bay, Great and Little Bahamas Banks and the Atlantic Reef Tract. There, $\delta^{13}C$ values of normal salinity seawater are close to the predicted equilibrium values. However, at salinities both higher or lower than normal, the $\delta^{13}C_{DIC}$ values becomes increasingly depleted. These depletions in $\delta^{13}C_{DIC}$ can be produced by two different sets of conditions. Firstly, the $\delta^{13}C_{DIC}$ depletion in salinities higher than normal values can be considered in evaporitively concentrated waters. During evaporation, depletion in the ^{13}C can be caused by progressive carbonate precipitation or intensive photosynthesis (as the water mass ages - Herczeg and Fairbanks 1987; Lazar and Erez 1992). Secondly, the $\delta^{13}C_{DIC}$ depletion in low-salinity waters can result from CO_2 input from terrestrial organic material.

During carbonate precipitation, the heavy ^{13}C is precipitating as $CaCO_3$ more rapidly than ^{12}C (the concept of fractionation between bicarbonate and calcium carbonate). Thus seawater would be depleted in the $\delta^{13}C_{DIC}$, especially in a semi-restricted water masses for which recharging of the depleted seawater by new normal DIC-content ocean waters is limited. However, because of pH changes, only less than half of $\sum CO_2$ could be removed by rapid carbonate precipitation. Assuming isotopic enrichment of 2.7‰ relative to water during the precipitation of aragonite, and 1.0‰ during calcite precipitation (e.g., Romanek et al. 1992), the residual DIC would be depleted in ^{13}C at most by about 1‰. During photosynthesis, phytoplankton preferentially take up ^{12}C-rich DIC and thus cause $\delta^{13}C_{DIC}$ enrichment in shallow seawater. However, intensive photosynthesis, such as seen in microbial mat communities by Lazar and Erez (1992), and fast consumption of DIC by these organisms, produces a deficit of DIC in water. This provokes invasion of isotopically light CO_2 ($\delta^{13}C = -8$‰) from the atmosphere into the water (brine). Thus, this newly generated DIC is depleted in $\delta^{13}C$ and impels precipitation of $\delta^{13}C$-depleted carbonates.

If the $\delta^{13}C$ depletion in seawater is induced by high rates of evaporation, an $\delta^{18}O$ enrichment, which is the simultaneous effect of evaporation, should also be observed. However, on the contrary, the $\delta^{13}C$ depletion in fossils of the Upper Morgan Limestone not only is not accompanied by $\delta^{18}O$ enrichment, but there is actually some depletion in $\delta^{18}O$ values of these fossils (See Figs 4.1 and 4.2). Therefore, the $\delta^{13}C$ depletion in the fossil samples by intensive evaporation can not be regarded as the cause of the observed light $\delta^{13}C$ values in the Upper

Morgan Limestone. Furthermore, Stiller et al. (1985) proposed that in intensive evaporation in closed basins, heavy-carbon enrichment (heavy $\delta^{13}C$ values) can be achieved through non-equilibrium gas-transfer isotope fractionation. Additionally, there is no sign of such extreme chemical conditions in this basin (high salinity or intensive photosynthesis by algal mats). Hence, seawater dilution by the influx of land derived organic materials, which is accompanied by $\delta^{18}O$ depletion (mixing of seawater by light $\delta^{18}O$ freshwater) is a more reasonable explanation for the $\delta^{13}C$ depletion of these fossil samples. Additionally, this depletion could partly be attributed to the input of isotopically light ^{13}C-CO_2 from biotic respiration in the ambient waters.

The lower $\delta^{13}C$ values in some well-preserved Terebratellidae brachiopods and Pecten fossils of the Upper Morgan Limestone could also be caused by a decrease in the $\delta^{13}C$ of the ambient DIC at the time of shell mineralization caused by (1) deepening of the basin below the photic zone, (2) stagnation, and (3) influx of land-derived organic matter.

(1) A deepening of the basin and entry to the aphotic zone would diminish the activities of phytoplanktons, which use mainly ^{12}C-rich DIC and cause enrichment in $\delta^{13}C_{DIC}$ of photic zone water. In the Upper Morgan Limestone there is no evidence of such depth and this limestone, as mentioned before, is formed in a shallow carbonate platform that represents a sea-level fall and shoaling, which was concomitant with global sea-level lowering.

(2) The stagnation would cause a reducing environment and its manifestation would be the extensive formation of pyrite, which is not discerned in this unit. Moreover, in a stagnant basin, because of the low oxygen content, such invertebrate fauna can not survive, yet there are abundant and diverse fossils in this formation. The presence of clastic particles in this limestone is another reason for a non-stagnant and dynamic basin.

(3) A land-derived low ^{13}C-content organic material influx from neighbouring areas by runoff also can lead to some depletion in $\delta^{13}C_{DIC}$ during oxidation of organic matter. Correspondingly, low $\delta^{13}C$ values in the Upper Morgan Limestone fossils could also be ascribed to the relatively nearshore position of their sedimentary carbonate environment. Keith and Parker (1965) pointed out that $\delta^{13}C$ values of nearshore samples could be lower than those of offshore samples. This is possibly because nearshore shells contain same carbon derived from land plants, which are characterised by light $\delta^{13}C$ values even lower than those of marine vegetation. In addition, land derived CO_2 dissolved in fresh water runoff can cause $\delta^{13}C_{DIC}$ depletion in marginal environments. Lloyd (1964) also showed that on the Florida Platform, shells of modern molluscs exhibit $\delta^{13}C$ depletion with increasing environmental restriction and influx of land derived organic matter. Land-derived organic matter is introduced by freshwater runoff that itself leads to lowering of salinity, and these low salinity waters are usually themselves lower in $\delta^{13}C$ as well as in $\delta^{18}O$ (Anderson and Arthur 1983), resulting in lower $\delta^{13}C$ and $\delta^{18}O$ values of carbonates.

The $\delta^{18}O$ value of these fossil Pecten and brachiopods from the Upper Morgan Limestone (16-10 Ma), contrary to the expectation of a glacially induced $\delta^{18}O$ increase contemporary with sea-level fall, are slightly lighter (between -1 to -2‰). This $\delta^{18}O$ depletion was produced by a temporary (at a geologic time scale) restriction of the Murray Basin and a higher freshwater influx that led to some dilution in the overlying seawater of this shallow carbonate platform. This $\delta^{18}O$ depletion was accompanied by about 3‰ depletion in $\delta^{13}C$, which again indicates the influx of land-derived organic material by freshwater runoff to the semi-restricted basin. This basin was only temporarily and intermittently restricted, because the isotopic signature is only partially affected by light values of fresh water invasion, i.e. it is far heavier than the typical freshwater $\delta^{18}O$ signature which is usually less than -8.0‰ (See Figs 4.1 and 4.2). Solar heating of the shallow-water depositional environment of the Lower Morgan Limestone samples might have caused water temperature to increase and thus induced lighter $\delta^{18}O$ values in the fossil carbonates.

Comparisons of studied fossil samples with their modern counterparts, surprisingly, show that the $\delta^{18}O$ values of the ambient water at 16-10 Ma ago (glacial) was about -2.5 ‰ lighter than today (interglacial). Again, this supports the idea of a fresh water influx at that time. In summary, the overall trend of the $\delta^{13}C$ of this unit is consistent with the seawater negative secular shifts of carbon-13 from the Middle Miocene towards the Pleistocene, and even to the Recent, although the magnitude of the $\delta^{13}C$ offset is greater than average. This $\delta^{13}C$ depletion is coincident with sea-level lowering, the phenomenon which many workers used for justification of this event (e.g., Tappan 1968; Scholle and Arthur 1980; Woodruff and Savin 1985; Berger and Vincent 1986). Contrary to the general positive shifts of $\delta^{18}O$ in marine carbonate from the Middle Miocene to the Pleistocene and Recent, the $\delta^{18}O$ values of this unit exhibit negative shifts, probably because of freshwater contamination. This observation also indicates that the Murray Basin at that time was a semi-restricted shallow water basin with low circulation which was intermittently diluted by freshwater with a high organic material content. The restriction was imposed by a progressive sea-level fall, starting at about 16 Ma, due to the initiation of extensive ice sheets in Antarctica.

6.4. Sea-Level Fluctuations Recorded in the Stable Isotope Signature of Fossils:

The amount of seawater removed from the oceanic reservoir and deposited in ice sheets, besides causing a drop in sea-level is reflected by an increase in the $\delta^{18}O$ of the remaining seawater (e.g., Williams 1988). Accordingly, considering the significant effects of temperature on the $\delta^{18}O$ values of carbonates (up to 30%, Mix 1987), the $\delta^{18}O$ value of seawater that is preserved in fossils of certain ages can be utilised to establish a sea-level fluctuation curve.

Studies of continental margins exhibit dramatic sealevel fluctuations during the Tertiary. The $\delta^{18}O$ values of fossil carbonates from different locations are used to reconstruct the sea-level fluctuations during the Tertiary. One of these important fluctuations is a sea-level lowering in the Oligocene (Vail and Hardenbol 1979; Olsson et al. 1980). Vail and Hardenbol (1979) suggested that the greatest sea-level fall of the Cenozoic occurred about 29 Ma, but Olsson et al., (1980) found that a large sea-level lowering occurred prior to 32 Ma. In this regard, Matthews and Poore (1980) suggested that large abrupt fluctuations in sea-level on a global scale are due to the growth and decay of ice-caps.

In the St.Vincent Basin, the sea-level fall of the Oligocene was initiated in the Late Eocene by glacial activity and ice-sheet growth, and is indicated by the increasing positive trend of $\delta^{18}O$ in the Tortachilla Limestone and the Gull Rock Member (Fig. 6.1). Although no isotopic data are available for this major sea-level fall of the Oligocene, the sedimentary records of this time consist of shallow water and clastic sediments, such as the Chinaman Gully Formation and the Port Willunga Formation in the St.Vincent Basin (e.g., McGowran 1989, 1991) and the Olney Formation in the Murray Basin (e.g., Alley and Lindsay 1995. Generally, the St.Vincent Basin was more marine-dominated than the Murray Basin in Late Eocene time. The marine-dominated carbonate units of the Tortachilla Limestone and the Gull Rock Member were deposited containing copious marine fossils. The sea-level regression of the Oligocene in the St.Vincent Basin began with the deposition of the regressive unit of the Chinaman Gully Formation, which consists of sand, silt and clay. It was deposited in a terrestrial to very shallow marginal environment and contains calcareous lenses in places. This Early Oligocene regression continued with deposition of the basal gravelly sands of the Aldinga Member of the Port Willunga Formation, which disconformably overly the Chinaman Gully Formation (Lindsay 1967). This rapidly changes to a marine environment, with the deposition of bryozoan calcarenites (Ruwarung Member), which demonstrates the world-wide Late Oligocene transgression.

Sea-level fall during this time interval, as recorded by $\delta^{18}O$ values of studied fossil samples, is about 130 m, considering 30% temperature effects on $\delta^{18}O$ signatures (Mix 1987). However, the total sea-level fall was greater than this, because this data is merely showing the initial part of the sea-level fall. Moreover, as Keigwin and Keller (1984) suggested, at times during the Early Cenozoic, the growth of ice-sheets was not accompanied by an increase in $\delta^{18}O_{SW}$ values equal to that of the Quaternary, or ice accumulation on the continents was not as enriched in ^{16}O. Because it seems most likely that ice accumulated in the polar regions and because the $\delta^{18}O$ values of precipitation are at least partly a function of the temperature of precipitation (Dansgaard 1964), then it follows that with a pole-to-equator gradient of air temperature lower than today, sufficient ice had been stored to cause larger sea-level changes with smaller seawater composition changes (i.e., smaller increase in $\delta^{18}O_{seawater}$ values due to ice growth). Savin et al., (1975) suggested that the planetary temperature gradient was less in pre-Quaternary time. Therefore, the maximum $\delta^{18}O$ positive shifts of 29 m.y. ago (which is not as high as predicted) could really reflect a very much greater sea-level fall. Hence, smaller seawater isotopic changes occurred due to isotopically heavier continental ice sheets (Keigwin and Keller 1984). In summary, continental ice was probably more enriched in $\delta^{18}O$ than it is today, possibly because of a lower planetary temperature gradient, thus accounting for relatively smaller $\delta^{18}O$ changes and larger sea-level changes.

In the Murray Basin, sea-level fluctuations extracted from oxygen isotopic composition of diverse fossils of different ages, with the application of the appropriate corrections for the effects of temperature variations on the $\delta^{18}O$ values, are shown in Fig. 6.5. The first sea-level fall apparently occurred about 22 Ma, with a magnitude of about 80m. This is shown by the decrease in the $\delta^{18}O$ values of the fossils from the Lower Morgan Limestone, compared with the Mannum Formation fossils.

By the late Early Miocene, due to intensification of the ice-cap build up in Antarctica, another sea-level fall occurred that is recorded in the Cadell Marl fossils. This $\delta^{18}O$ positive shift (about 16 Ma) was on average about 0.9‰ (See Figs. 4.1 to 4.15; Figs 6.3 to 6.5). The $\delta^{18}O$ increase continued into the Upper Morgan Limestone, due to an increase in ice-cap growth in Antarctica, which led to a further sea-level fall of about 120 m during the Middle Miocene-early Late Miocene. The Murray Basin was restricted and had limited access to the open ocean. This restricted circulation led to the deposition of the Upper Morgan Limestone, with isotopic signatures that exhibit significant fresh-water influx.

Miller and Fairbanks (1985), by comparing their inferred glacio-eustatic data with carbon cycles, concluded that there was no consistent response of carbon isotopes to sea-level changes during the Tertiary, because:

(1) Against all predictions, the $\delta^{13}C_{DIC}$ global increases that took place at the beginning of the Late Eocene and the Early Oligocene (about 35 Ma) and near the Oligocene/Miocene boundary (about 25 Ma) were associated with $\delta^{18}O$ increases that are interpreted as sea-level falls and glacial build-ups.

(2) The inferred glacio-eustatic lowering of 31-28 Ma is not associated with a change in $\delta^{13}C_{DIC}$.

(3) The global $\delta^{13}C$ positive shift inception at 18 Ma is associated with a major $\delta^{18}O$ increase. Therefore, this inconsistent relationship prevents the inference of a simple causal relationship between sea-level changes and the $\delta^{13}C$ cycles. To challenge this contention, the geochemical data from this study are compared with the conclusions reached by Miller and Fairbanks (1985).

In the St.Vincent Basin, the $\delta^{18}O$ increase in the fossil Turritellidae, Pecten and brachiopods of the Gull Rock Member is associated with an increase in the $\delta^{13}C$ values of these fossils (during the first $\delta^{13}C$ cycle in the Late Eocene/Early Oligocene, 35 Ma). Thus, in this time interval, all $\delta^{13}C$ increases were associated with $\delta^{18}O$ increases, as contended by Miller and Fairbanks (1985).

Comparisons of the $\delta^{13}C$ values of the different fossils from parts of the second $\delta^{13}C$ global cycle showed that:

(1) brachiopods of the Lower Morgan Limestone also exhibit some increase in average $\delta^{18}O$ values, in comparison with the brachiopods from the Mannum Formation. Pecten fossils of the Lower Morgan Limestone also show some $\delta^{18}O$ increase compared to of the Mannum Formation.

(2) The world-wide $\delta^{13}C$ increase at 16 Ma (mid-Miocene) is clearly recorded by different fossils of the Cadell Marl. In this unit, large positive $\delta^{13}C$ shifts of about 1.2‰ in Pecten fossils are associated with an increase in $\delta^{18}O$ of about 1‰. Turritellidae samples of this unit also show simultaneous increases in $\delta^{13}C$ and $\delta^{18}O$ values, of about 0.7 and 0.5‰, respectively.

No isotopic data are available from the study area for the time interval of 31-28 Ma to compare with the data presented by Miller and Fairbanks (1985), which showed that the $\delta^{18}O$ increase is not associated with changes in $\delta^{13}C$.

In summary, as far as data from the study area show, the contention of Miller and Fairbanks (1985) that the relationship between sea-level changes, $\delta^{18}O$ value variations and the $\delta^{13}C$ cycles are inconsistent, is correct.

6.5. Conclusion:

The stable isotopic study of different fossil samples revealed that the $\delta^{13}C$ variations in carbonates are mainly reflecting secular variations in $\delta^{13}C_{DIC}$ of seawater during the Tertiary period, and are neither facies-controlled nor (unexpectedly) influenced by diagenetic alterations. The $\delta^{18}O$ data of different fossil carbonates of the study area have been used for the reconstruction of sea-level fluctuations and estimations of paleotemperature.

The Monterey Event caused deposition of the Cadell Marl with a conspicuous isotopic signature, in the earliest Middle Miocene. The Middle/Late Miocene intensification of ice-sheet growth in Antarctica led to a global sea-level fall and climatic deterioration, which itself imposed some restrictions in the Murray Basin and led to a light isotopic signature of fossil carbonate in the Upper Morgan Limestone, by increasing fresh-water runoff.

The general trend in the $\delta^{18}O$ value of seawater, which shows an increase from the Early Eocene to the Holocene, is reflected in the isotopic composition of different foraminifera and is also recorded by the studied macrofossils. The contention of this study is that the marginal marine carbonate environments and their ancient counterparts deserve more attention with regard to secular geochemical variations during geologic time as they can provide additional information on the geochemical imprint of the transgression-regression events than the traditionally used deep-sea foraminifera. Moreover, the advantage of geochemical studies in the marginal basins is that, because they are more susceptible to sea-level fluctuations than deep-sea basins, sometimes they can better record sea-level fluctuation and transgression-regression events, than deep-sea foraminifera, providing diagenetic resets and terrestrial influxes are taken into consideration.

CHAPTER SEVEN

THE MONTEREY EXCURSION IN SOUTHERN AUSTRALIA;

EVIDENCE FROM STABLE ISOTOPES OF TERTIARY SEQUENCES

7.1. Introduction:

The Monterey Formation crops out near Monterey along the coastal regions of California (Vincent and Berger 1985) and its equivalents are found all around the North Pacific region. These late Early to early Middle Miocene rocks contain considerable siliceous material within especially organic-rich mudstones, phosphatic rocks and authigenic carbonates. The Monterey Formation has been the focus of several studies because of its importance as a source rock and reservoir for petroleum. The large amounts of organic carbon sequestration in these sediments were the main cause of the $\delta^{13}C_{DIC}$ (DIC = Dissolved Inorganic Carbon) positive excursion. In fact, the initial $\delta^{13}C$ enrichment resulted in a rapid extraction of organic carbon from the ocean-atmosphere system and deposition in the form of organic-rich sediments on continental shelves, resulting in rocks such as the Monterey Formation (Vincent and Berger 1985) and the phosphorite deposits of the southern United States (Compton et al. 1990, 1993). The $\delta^{13}C$ increase occurred in both planktonic and benthic foraminifera, indicating an external major influence on the $\delta^{13}C$ composition of seawater.

The main isotopic feature of the Monterey Formation is an exceptional positive $\delta^{13}C$ excursion of about 1‰ which is associated with some $\delta^{18}O$ enrichment

(Vincent and Berger 1985; Compton et al., 1990, 1993). This positive $\delta^{13}C$ excursion reflects episodic large-scale changes in organic carbon deposition relative to carbonate sedimentation (Woodruff and Savin 1991; Flower and Kennett 1994). In the Monterey Formation, the $\delta^{13}C$ enrichment is associated with phosphatic sediments, which themselves are synchronous with the onset of strong coastal upwelling. This led to a surge of nutrients into shelf waters and flourishing productivity of both benthic and planktonic organisms. This increased biological activity in nutrient-rich waters caused the removal of ^{12}C-enriched organic matter, which led to a positive excursion of $\delta^{13}C_{DIC}$. On the other hand, the sea-level rise near the Early/Middle Miocene boundary (16.5 Ma) created more accommodation space on shelf areas for the deposition and accumulation of organic-rich Monterey type sediments, which itself impelled $\delta^{13}C_{DIC}$ positive shifts (Vincent and Berger 1985). However, from 16.5 to 13.5 Ma, sea-level dropped in response to ice-cap build-ups in Antarctica, thus bringing to a close the enriched seawater.

Foraminifera analyses indicate that this $\delta^{13}C$ increase was a world-wide excursion (e.g., Savin et al. 1981; Miller and Thomas 1985; Keigwin and Keller 1984; Vincent and Berger 1985; Miller and Fairbanks 1985) and has been termed the Monterey Excursion (Vincent and Berger 1985). The $\delta^{13}C$ enrichment, which was initiated about 17.5 Ma and lasted for 4 m.y., resulted in a global $\delta^{13}C$ increase of about 1‰ in surface and deepwater dwelling organisms. Since 13.5 Ma, the $\delta^{13}C$ values have decreased by about 1‰, i.e., they are now the same as they were about 18 Ma, before Monterey Excursion.

The purpose of this study is to present geochemical and sedimentological evidence indicating the influence of the Monterey Excursion within the Oligo-Miocene sediments of the Murray Basin, along the continental margin of southern Australia.

7.2. Monterey Paleoceanographic Event, Evidence from the Cadell Marl:

The Miocene period in the Murray Basin of South Australia was a time of extensive carbonate sedimentation that resulted in the formation of the Murray Group fossiliferous limestones. However, in some parts of the basin, sudden changes in lithology from the Lower Morgan Limestone to the highly fossiliferous unit of the Cadell Marl occur. Evidently, the formation of the Cadell Marl in this basin is a result of a variety of controls including local basin topography, global glacio-eustatic sea-level and regional variations in biotic paleoproductivity that caused an abrupt change in the local sedimentation regime. This change in the sedimentation regime which occurred in the latest Early Miocene to the earliest Middle Miocene (about 16 Ma) coincided with the global climatic and paleoceanographic evolution of this period, which in the Northern Pacific region is recorded as the Monterey Excursion (Vincent and Berger 1885).

The global climatic deterioration as a function of rapid ice-cap buildup in Antarctica in mid-Miocene time. It led to an increasingly steep pole-to-equator thermal gradient and consequent acceleration of atmospheric circulation which itself led to intensification of oceanic circulation and upwelling. These increase in the nutrient-rich upwelling currents led to an increase in oceanic productivity and higher biological activity in coastal areas. The evidence for this paleo-upwelling current invigoration is the high density and diversity of fossil taxa in the Cadell Marl, which is remarkably higher than in either of the enclosing units. These upwelling currents are recorded in the stable isotopic profiles of the Cadell Marl fossils. The high rates of organic activity caused higher rates of organic carbon sequestration into the sediments and thus the lowering of the atmospheric CO_2 level. This led to ice-house effects (Vincent and Berger 1985).

The time interval of the Monterey Excursion is 17.5 to 13.5 Ma. The peak of this event is recorded in the Cadell Marl, however, its inception is recorded in the stable isotopic composition of the Lower Morgan Limestone (21 Ma) fossils which show relatively heavy carbon and oxygen isotopic values (Fig. 7.1; See Figs. 6.4 and 6.9). Based on paleontological studies, McGowran and Li (1994) suggested that the Monterey Excursion in the Murray Basin was initiated earlier in the upper parts of the Mannum Formation (23-21 Ma). The termination of this excursion is manifested by the Upper Morgan Limestone, with light $\delta^{13}C$ and $\delta^{18}O$ values (Fig. 7.1; See Figs. 6.4 and 6.9).

Contrary to the Monterey Formation, which was deposited under the influence of biologically productive surface waters with low-oxygen bottom waters (anaerobic conditions - e.g., Isaacs 1983; Vincent and Berger 1985), the Cadell Marl was deposited in a well-oxygenated environment. Such an environment is necessary for the dense population of diverse benthic organisms.

The positive excursion of $\delta^{13}C$ in the different fossils of the Lower Morgan Limestone and the Cadell Marl units is contemporary with the global $\delta^{13}C$ increase of the Middle Miocene (See Fig. 6.9). The average increase of 1.6‰ is even higher than the positive excursion reported from the Monterey Formation and its equivalents (about 0.9 to 1.0‰ by Vincent and Berger 1985; Flower and Kennett 1993). The heaviest $\delta^{13}C$ values of the studied Tertiary sections in South Australia are recorded by the fossil assemblages of the Cadell Marl (Fig. 7.1; See Fig. 6.9). The $\delta^{13}C$ composition of the Pecten fossils (n= 11) of the Cadell Marl, for example, show the heaviest $\delta^{13}C$ values in the studied Tertiary record, with a range of 2.0 to 3.3‰. The Turritellidae $\delta^{13}C$ composition displays heavy values between 3.6‰ to 4.2‰ (n= 16), which again is higher than the other older Turritellidae samples in the studied Tertiary section (Fig. 7.1). Terebratellidae

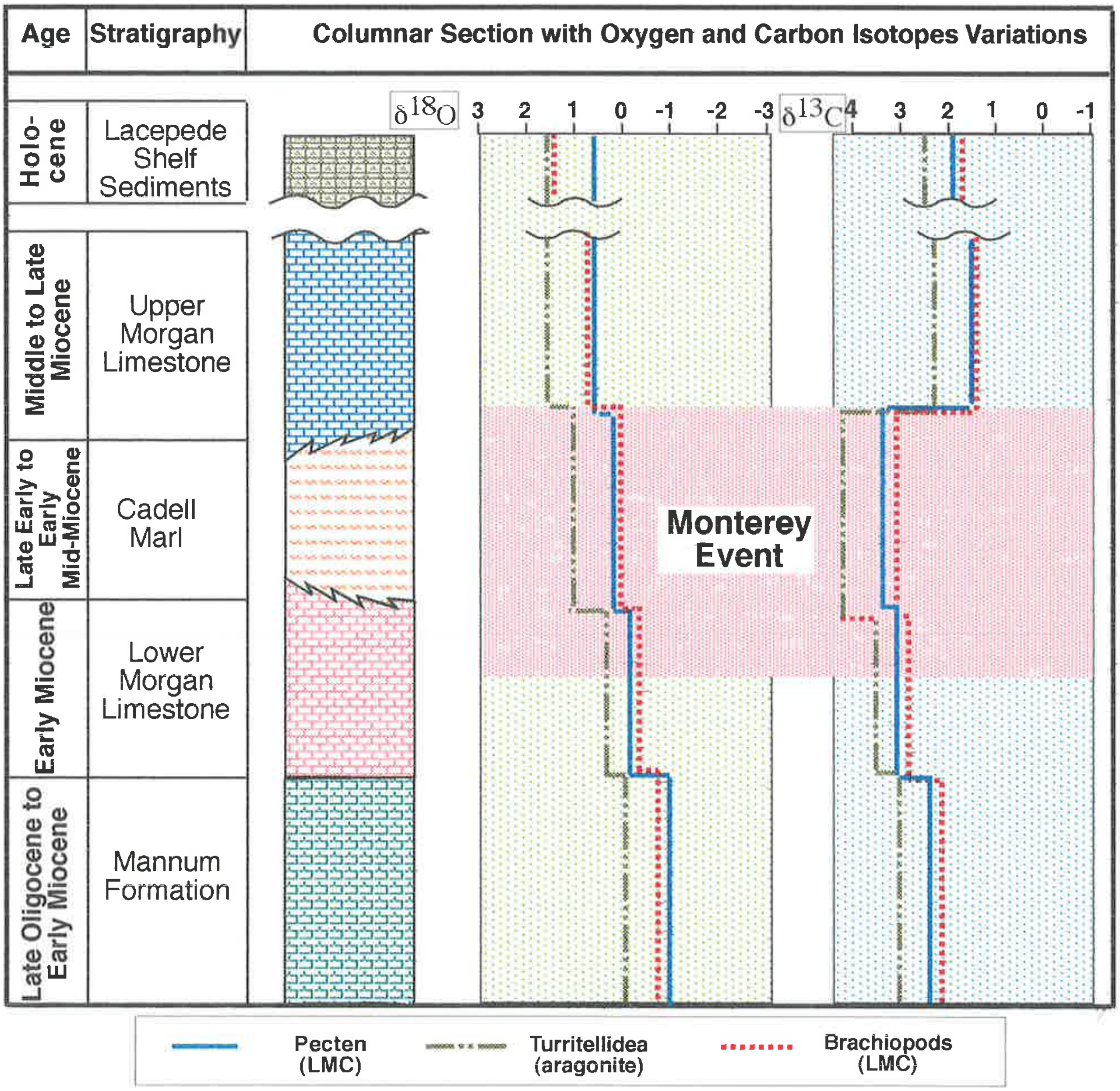


Fig. 7.1. The composite columnar stratigraphic section of the Murray Basins (not to scale). The variations of the average oxygen and carbon isotopic values in each unit are shown including the heavy carbon and oxygen isotope values of the Cadell Marl in Middle Miocene time (Monterey Excursion). The higher isotopic values of Turritellidae gastropods are due to their aragonitic mineralogy.

Brachiopoda of the Cadell Marl show $\delta^{13}C$ values with range of 2.0 to 2.5‰ (n= 11).

The important point in comparing the overall $\delta^{13}C$ values of the Cadell Marl fossils with fossils of other Tertiary units in the study area and also with Holocene samples, is that, not only are they usually heavier than their older counterparts, but they are even heavier than their modern counterparts. Results show a high $\delta^{13}C_{DIC}$ value for the Murray Basin at 16 Ma, which is concomitant with the global high $\delta^{13}C$ value known as the Monterey Excursion.

The $\delta^{18}O$ values recorded by the different fossils of the Cadell Marl, which are approximately the heaviest $\delta^{18}O$ recorded in the studied Tertiary section, are consistent with the heaviest $\delta^{18}O$ values presented by Wright et al., (1992) for this time interval by using foraminifera of different Deep-sea sites (See Fig. 6.4). The $\delta^{18}O$ global positive excursion at the early Middle Miocene denotes the cessation of the Early Miocene warming trend and the inception of high-latitude cooling, which coincides with ice cap build-up in Antarctica. The initiation of ice sheets in Antarctica was at 16.5 m.y., with the ice-sheets persisting until today. The storage of carbon in marginal basin sequences is postulated as a major cause of global cooling initiation during the Middle Miocene. Vincent and Berger (1985) suggested that the sequestration of organic carbon in the shelf sediments, enhanced the cooling process in Antarctica by inducing a decrease of the total carbon content in the ocean, and consequently a decrease in atmospheric CO_2 and a "cool-house effect". Raymo (1994) suggested that deposition of the organic-rich units of the Monterey Formation was the result of increased nutrient delivery to the ocean from the Himalayan episode of exhumation and weathering during this time. In this regard, DePaolo and Finger (1991) first recognised that a global increase in weathering preceded organic deposition and global cooling and that they may have been related events.

The initiation of a substantial build-up of ice in the early Middle Miocene resulted in a drop in sea-level by 13.5 Ma. Using a $\delta^{18}O$ sealevel calibration of 0.055‰ for every 10 m (Miller et al. 1987a, b) and considering an average $\delta^{18}O$ increase of 0.8‰ in the Cadell Marl fossils and a temperature correction of 30% (Mix 1987), a sea-level drop of about 95 m is resulted for the study area. This sea-level lowering continued and ended during deposition of the Upper Morgan Limestone and caused the restriction of the basin. The progressive drop in sea-level and an associated increase in the rate of freshwater influx to the basin waters led to the production of a light isotopic signature in this unit (See Fig. 6.4).

7.3. Conclusion:

The high $\delta^{13}C$ values of the Cadell Marl of the Murray Basin at 16 Ma, which are contemporary with global high $\delta^{13}C$ values in other parts of the world's oceans, demonstrate the influence of the Monterey Excursion on the $\delta^{13}C$ compositions of different biogenic carbonates. This observation indicates that the latest Early Miocene (16 Ma) was the period of heaviest $\delta^{13}C$ values in most of the Cenozoic, even heavier than present day values. Therefore, the $\delta^{13}C$ positive excursion in diverse fossils of the Cadell Marl represents a general correlation with $\delta^{13}C$ records of the Monterey Formation and deep-sea benthic records, which is also concomitant with the global organic-rich depositional regime of the Early to Middle Miocene. The transfer from the almost ice-free world prior to Middle Miocene time to a glaciated world of the Late Miocene to Holocene is clearly reflected in the carbon and oxygen isotopes of the studied Tertiary sediments.

CHAPTER EIGHT

CENOZOIC TERRESTRIAL ISOTOPIC PALEOCLIMATOLOGY OF SOUTH AUSTRALIA; DEDUCED FROM METEORIC CEMENTS AND MARINE FOSSILS

8.1. Introduction:

Paleotemperature investigations using oxygen isotope ratios in sedimentary minerals have developed over the past five decades (Urey 1947; Epstein and Lowenstam 1954; Hudson and Anderson 1989; Marshall 1992). Most attention has been concentrated on the marine biogenic carbonates for estimation of marine paleotemperatures for different geologic times. Accordingly, less attention has been paid to the potential of the isotopic composition of terrestrial carbonate minerals for paleotemperature reconstruction, and most of these few studies have involved biogenic skeletal material such as lacustrine invertebrates (e.g., Abell 1985).

The work of Hays and Grossman (1991) in reconstructing the terrestrial paleotemperatures using meteoric cements is the pioneering effort on this subject. They introduced an equation for paleotemperature calculation of near-surface diagenetic environments, using oxygen isotopic values of seawater and diagenetic meteoric calcite cement. The empirical and theoretical data on the $\delta^{18}O$ values of the meteoric cement show a negative trend versus decreasing paleolatitude.

On the other hand, the Australian continent has been moving northward during the Cenozoic era, thus sustaining a continuous variation in latitude during this time. In this chapter, firstly, using Hays and Grossman (1991) paleotemperature equation and the isotopic values of meteoric cement from different Cenozoic limestones of the St.Vincent and Murray Basins of South Australia, the terrestrial paleotemperatures of these areas during the Cenozoic have been calculated. Secondly, the marine paleotemperature for these basins during this time interval based on the isotopic composition of different marine fossils have been calculated. Finally, the paleotemperature results from the two different methods and materials are compared.

The different stratigraphic units in the study area, deposited in marginal marine basins, were influenced by different sea-level fluctuation events. The cements were precipitated in meteoric phreatic and vadose environments when these carbonate sediments were exposed to meteoric waters not long after deposition, as a result of the periodic lowering of sea-level. These sea-level fluctuations were climatically controlled. The limestones in the study area have only been buried to shallow depths, reflected in the type of cements, which are mainly meteoric phreatic and vadose cements.

Hays and Grossman (1991), by substituting the meteoric water $\delta^{18}O$ Vs temperature relation into the calcite $\delta^{18}O$ paleotemperature equation introduced an equation for paleotemperature based on the $\delta^{18}O$ values of (diagenetic) low-Mg-Calcite (dLMC) and the $\delta^{18}O$ values of seawater, assuming equilibrium precipitation in meteoric water. Their equation for coastal diagenetic environments is as follows:

$$T_{coastal} = 13.3 \pm 32.6\ [-0.231 - 0.0613\ (\delta^{18}O_{mcl} + \delta^{18}O_{SW})]^{1/2} \qquad \text{(A)}$$

where T is temperature °C, $\delta^{18}O_{mcl}$ is the oxygen isotope composition of meteoric cement and $\delta^{18}O_{SW}$ is the oxygen isotope composition of seawater.

Paleotemperature values for different fossils were calculated using equations (1) and (2) (Chapter Two).

8.2. Isotopic Variations of Meteoric Cements Versus Paleolatitude:

Most shallow-marine carbonate sediments are composed of metastable minerals of high-Mg-Calcite (HMC) and aragonite. These minerals, during reaction with freshwater (meteoric water), either dissolve or recrystallise and increase the concentration of Ca^{2+} and $CO_3^{2=}$ ions in any diagenetic fluids. Therefore, by reaching supersaturation in the fluid, these ions are precipitated as diagenetic Low-Mg-Calcite (dLMC) cement (James and Choquette 1984). The $\delta^{18}O$ values of this dLMC cement reflect the $\delta^{18}O$ value of the meteorically derived pore fluids, that were the sponsor of the dLMC cementation. The oxygen isotopic composition of this dLMC cement is mainly controlled by the ambient temperature and the isotopic composition of the local meteoric waters. In this regard, Meyers and Lohmann (1985) suggested that because of the relatively low stability of carbonate minerals at low, near-surface temperatures, high O_{water}/O_{rock} ratios are maintained near the recharge area, and so the rock contribution to oxygen isotope composition of meteoric cement is low, compared to the contribution of the oxygen isotope of the meteoric water in these cements. Consequently, the meteoric calcite cement $\delta^{18}O$ signature is mainly controlled by the ambient temperature and isotopic composition of local meteoric water, and thus reflects the climatic conditions of that time.

Since meteoric water $\delta^{18}O$ values decline with decreasing ambient temperature and increasing latitude, the $\delta^{18}O$ signature of meteoric calcite cement should exhibit a similar relation with latitude and be an indicator of continental paleotemperature (Hays and Grossman 1991). The isotopic composition of meteoric waters that have originated from marine waters during Rayleigh distillation processes varies due to:

(1) Variations in the composition of marine water, e.g., marine water isotopic composition changes due to glacial build-ups that lead to $\delta^{18}O$ variations (enrichment) in the source of the meteoric waters (i.e. seawater), and in meteoric waters and subsequently in meteoric cement.

(2) Distance from both the marine source and the equator, which means more evaporation-precipitation (higher Rayleigh effects) and so more fractionation and production of lighter $\delta^{18}O_{\text{meteoric water}}$. Hence, the $\delta^{18}O$ values of meteoric waters and resulting dLMC cements change with distance from their source and the equator due to the Rayleigh distillation effect. Dansgaard (1964) showed a latitudinal decrease in the $\delta^{18}O$ values of meteoric waters because of the Rayleigh effect. Correspondingly, the $\delta^{18}O$ value of meteoric water varies from about -2‰ (SMOW) near the equator (low latitude) to as low as -50‰ (SMOW) near the poles (high latitude). Hence, the resulting meteoric cements should reflect this latitudinal decrease (e.g., Hays and Grossman 1991). In this regard, Australia has a special significance because its northward drift during Cenozoic time led to latitudinal changes of the continent, which caused variations in the mean $\delta^{18}O$ values of rainfall precipitation through time. These $\delta^{18}O_{\text{meteoric water}}$ variations would have caused simultaneous variations in the $\delta^{18}O$ values of the meteoric cement resulting from these meteoric waters.

(3) Changes in climate and subsequently variations in mean annual temperatures during the Cenozoic time due to glacial waxing and waning induced changes in the isotopic composition of meteoric waters. In Australia, this climatic change has been complicated by the northward drifting of the continent through diverse climatic zones. Moreover, this drifting also led to marine paleoenvironmental variations in the marginal St.Vincent and Murray Basins which are reflected in the isotopic composition of different fossils in these areas.

In the study area, dLMC meteoric cements from different stratigraphic units within the Cenozoic have been sampled and their isotopic composition has been measured. The mean $\delta^{18}O$ values of the meteoric cements exhibit a negative correlation with paleolatitude (Fig. 8.1). Their general trend is parallel with the theoretical coastal cement regression line. However, some factors occasionally distorted or overlapped this general trend. These could be secondary diagenetic alterations of the original meteoric cements, contamination of meteoric waters with seawater, evaporation of the meteoric water prior to cementation and the orographic effect (e.g., Hays and Grossman 1991).

The oldest dLMC meteoric cement was extracted from the Tortachilla Limestone (39-38 Ma). This cement replaced aragonitic Turritellidae and now luminesces brightly under cathodoluminescence (CL). This cement exhibits the lightest $\delta^{18}O$ value among the different meteoric cements (Fig. 8.1). This light $\delta^{18}O_{\text{meteoric cement}}$ is consistent with the highest paleolatitude (geographic position) of the Tortachilla Limestone (St. Vincent Basin), during the early Late Eocene, at the southernmost location of the Australian continent at that time. Thus, this is compatible with the observation of Hays and Grossman (1991) and others that low $\delta^{18}O$ values are concomitant with high latitudes.

The $\delta^{18}O$ dLMC meteoric cement of the Late Eocene Gull Rock Member (36-35 Ma) also shows a negative relationship with paleolatitude. However, in comparison with the general trend of the $\delta^{18}O_{\text{meteoric cement}}$ Vs paleolatitude (Fig. 8.1), this cement is atypically enriched in $\delta^{18}O$, which may have been produced by evaporation of the meteoric waters prior to infiltration to sediments and cementation. An alternative explanation for this relatively anomalous heavy $\delta^{18}O_{\text{meteoric cement}}$ is contamination of the light-$\delta^{18}O$ content meteoric water with the heavy-$\delta^{18}O$ content of seawater during cementation leading to precipitation of meteoric cement with higher $\delta^{18}O$ values (in this case mixed meteoric-marine

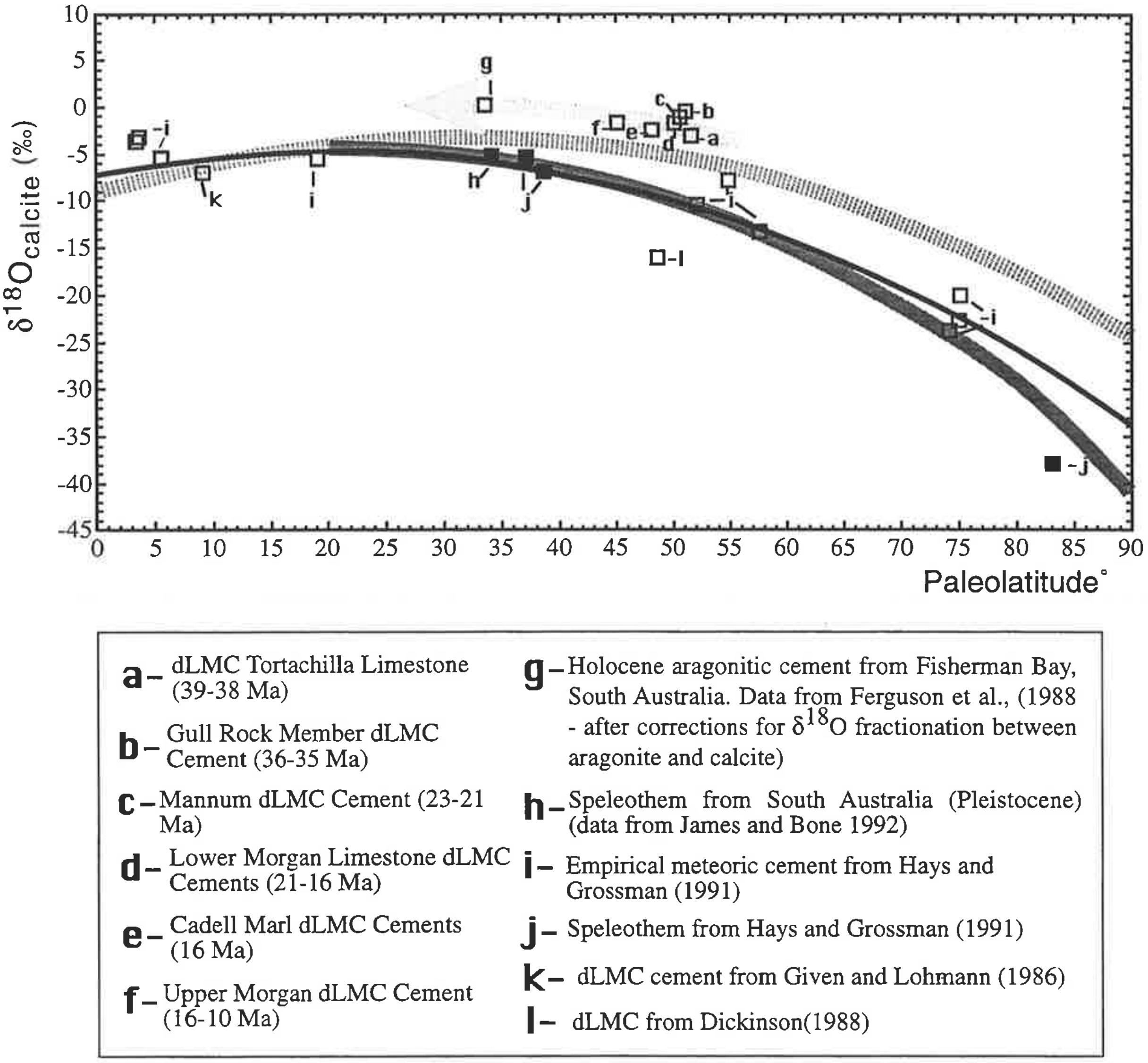


Fig. 8.1. The mean $\delta^{18}O$ variations of meteoric cements (open squares) and speleothem (crossed squares) as a function of paleolatitude. Second-order regression lines are defined for $\delta^{18}O$ values of empirical cement (thin line), theoretical coastal cement (dashed line), and theoretical inland cement (heavy line)(modified after Hays and Grossman 1991). Also shown (arrow), is the regional trend of $\delta^{18}O$ variations vs. paleolatitude observed in the study area. This Tertiary to Holocene trend is approximately compatible with the empirical and theoretical curves.

cement). Seawater percolation through carbonate sediments that have already been cemented by meteoric waters also can yield the same results. Another explanation for this $\delta^{18}O$ enrichment is temperature decrease at that time due to climatic deterioration. Indeed, this positive $\delta^{18}O$ shift is concomitant with the cooling event of the Late Eocene/Early Oligocene boundary, discussed in Chapter Six.

The dLMC meteoric cement of the Mannum Limestone (23-21 Ma) exhibits higher $\delta^{18}O$ values, with Australia drifting toward lower latitudes, which is consistent with the aforesaid model (equilibrium precipitation of this cement). The Lower Morgan (21-16 Ma) dLMC meteoric cement shows a slightly lower increase in $\delta^{18}O$ values with higher paleolatitude compared to the Mannum Limestone, but still demonstrates the general trend of $\delta^{18}O_{\text{meteoric cement}}$-increase with paleolatitude-decrease. The Cadell Marl (16 Ma) and Upper Morgan Limestone dLMC meteoric cements also exhibit this ideal trend, thus demonstrating their meteoric origin and equilibrium precipitation. Finally, the Holocene aragonitic meteoric cement from Fisherman Bay, South Australia (Ferguson et al. 1988), shows the heaviest $\delta^{18}O$ values among the different meteoric cements, which is consistent with its lowest latitudinal position and probably highest continental temperature of the area during the Cenozoic (considering an average $\Delta\delta^{18}O_{\text{aragonite-calcite}} = 0.8‰$ correction for fractionation between aragonite and calcite, e.g., Tarutani et al. 1969; Turner 1982).

The overall trend of $\delta^{18}O_{\text{meteoric-cement}}$ versus paleolatitude of the Cenozoic sediments from the study area (Fig. 8.1) is comparable with the second order regression of the global theoretical coastal cements (Hays and Grossman 1991) and shows the same negative correlation with paleolatitude. Moreover, the trend is also parallel with the empirical cement curve (Fig. 8.1). This indicates that the groundwater controlling the ultimate composition of meteoric cement in the study area, is derived predominantly from coastal recharge, a pattern that is still prevailing in the modern environment of the study area.

8.3. Paleotemperature Calculated from Meteoric Cements:

Coastal paleotemperature variations during the Cenozoic were calculated from the $\delta^{18}O$ values of meteoric calcite cements using Equation (A) and the average $\delta^{18}O$ values of meteoric cements from different stratigraphic units. However, as shown in this equation, for an accurate estimation of the paleotemperature, a precise knowledge of seawater $\delta^{18}O$ variation is necessary. In modern oceans, the surface seawater $\delta^{18}O$ values vary about 1.5‰ between low and high-latitude in the open oceans (Broecker 1989), and as much as 3.0‰ between the open oceans and the marginal seas (Fairbanks 1982; Fairbanks et al. 1992). These variations in the $\delta^{18}O_{SW}$ are produced by the combined effects of evaporation, precipitation, Rayleigh distillation and atmospheric vapour transport. During these processes, isotopically depleted water vapour is continuously transported from the subtropics towards the poles, leading to $\delta^{18}O$ enrichment in seawater in the subtropics and depletion in high-latitudes. Moreover, the average $\delta^{18}O_{SW}$ has changed through geological time because of glacial waxing and waning and temperature variations. Therefore, in order to calculate paleotemperatures from the $\delta^{18}O$ values of the carbonate fossils or cements, the mean oxygen isotopic composition of seawater ($\delta^{18}O_{sw}$) must be constrained by adjusting the $\delta^{18}O$ values of all fossils for long term shifts in the mean isotopic composition of the paleoceans due to changes in global ice volume. According to Hambrey et al., (1991) and Zachos et al., (1994), prior to the Late Eocene the world was ice-free as illustrated by $\delta^{18}O_{sw}$ values of about -0.96‰ (SMOW). Zachos et al., (1994) suggested that, during most of Late Eocene time, ephemeral continental ice sheets existed that slightly affected the $\delta^{18}O_{SW}$. Therefore, the $\delta^{18}O_{SW}$ of the Late

Eocene and Early Oligocene was about -0.8 and -0.5‰, respectively. They also added that times of full continental glacial activity were the Earliest Oligocene and the Middle Oligocene. Correspondingly, for the Late Oligocene and the Early Miocene a $\delta^{18}O_{SW}$ values of -0.96‰ was used, for the Middle Miocene a $\delta^{18}O_{SW}$ values of -0.8‰ and for the Late Miocene a $\delta^{18}O_{SW}$ of -0.5‰, consistent with ice volume increases during these times. The $\delta^{18}O_{SW}$ values of the modern Southern Ocean (south of Australia) are close to zero (Rahimpour-Bonab et al. 1997a, b).

The $\delta^{18}O$ values of different meteoric cements in the study area have recorded the terrestrial paleotemperature and reflect its variations since the Eocene time (Fig. 8.2). The overall trend is toward lower temperatures, as is also exhibited by the paleotemperature variations versus paleolatitude (Fig. 8.3). Therefore, the terrestrial paleoclimate has been varying during the Cenozoic due to the northward drifting of Australia and global glacial events. The higher temperature of the early Late Eocene observed here is consistent with a higher marine temperature estimated from different fossils in the study area (next section). The Late Eocene/Early Oligocene marine cooling event is recorded by meteoric cements of the Late Eocene Gull Rock Member of the Blanche Point Formation. This meteoric cement probably precipitated during the marine regression of the Early Oligocene in the St.Vincent Basin, with the exposure of the marine carbonates to meteoric waters. The other terrestrial record of that cooling event is palynomorphs of cool-temperate Nothofagus-dominated rainforest that covered the southern part of South Australia (Benbow et al. 1995).

The Early Miocene global marine warming trend which is recorded by different foraminifera (Shackelton 1986) and studied macrofossils fossils, is also recorded by meteoric cements of the Mannum and Lower Morgan Limestones (Fig. 8.2). The terrestrial evidence of this climatic amelioration is the Early Miocene extensive rainforest in Australia (Brown 1985). The Middle Miocene to Late Miocene in

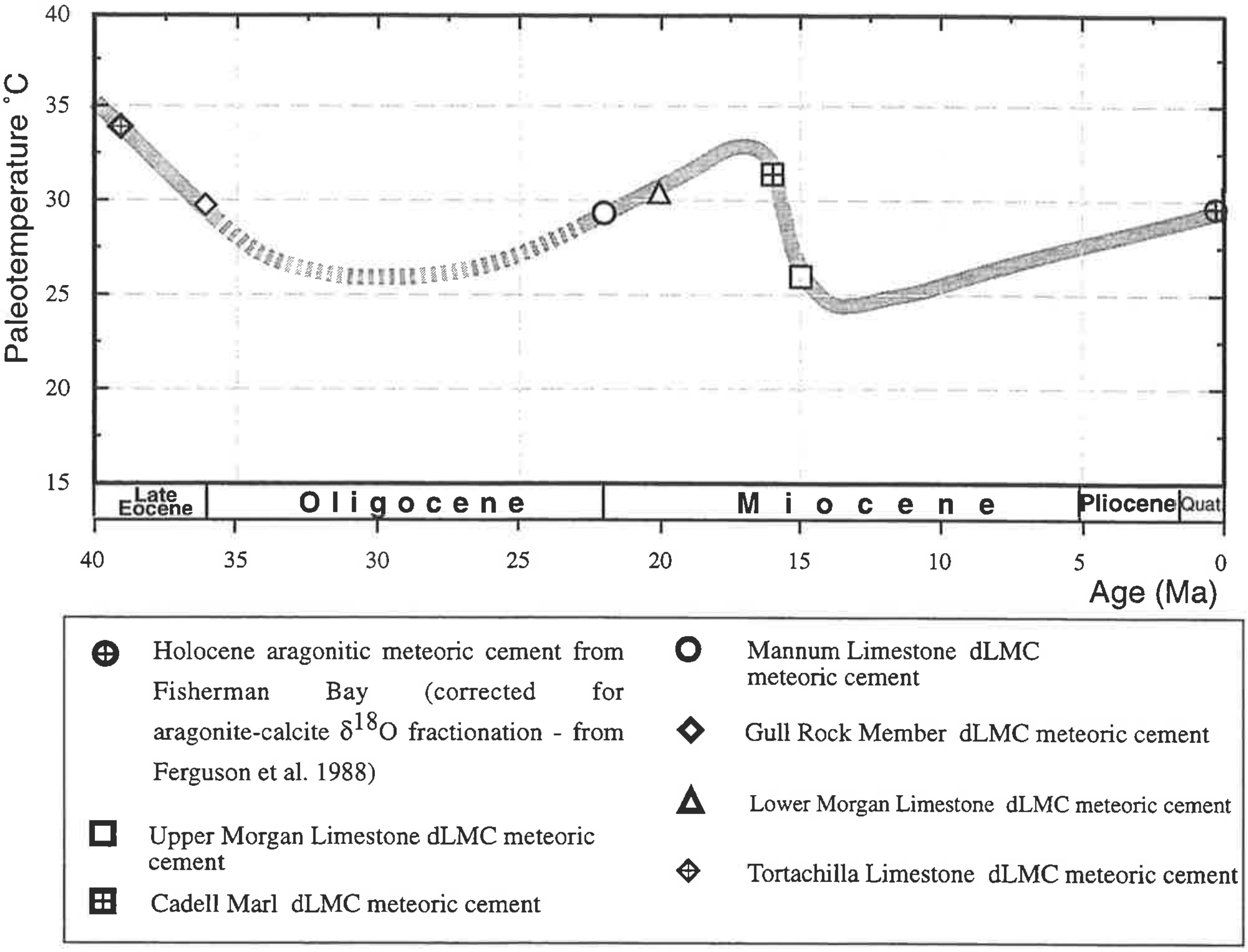


Fig. 8.2. Coastal paleotemperature variations during the Cenozoic as a consequence of the northward drifting of Australia, calculated from $\delta^{18}O$ composition of meteoric calcite cements. There is no isotopic data for the dashed parts of the curve, and it is deduced from sedimentological and paleoclimatological evidence.

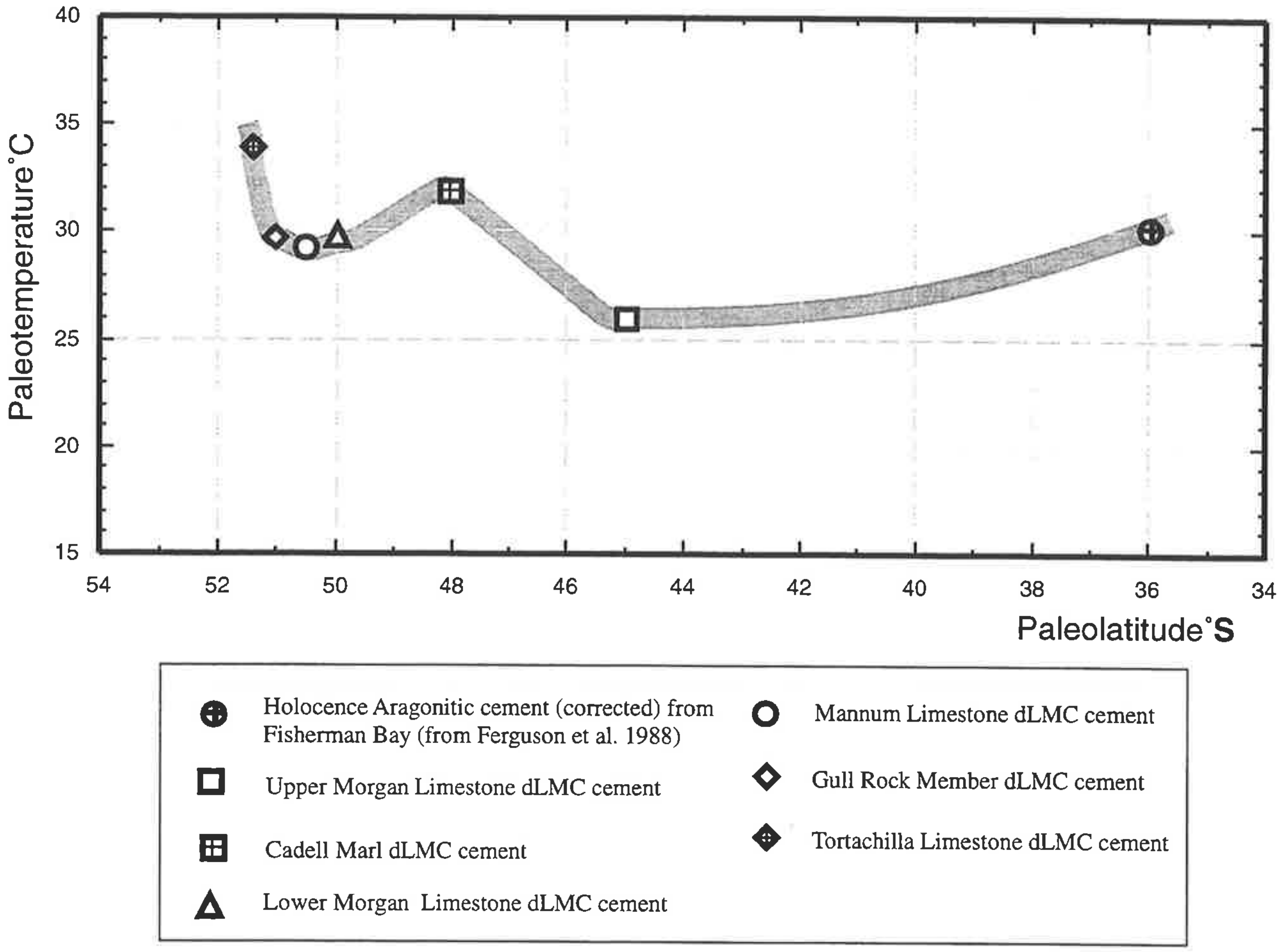


Fig. 8.3. The paleotemperature variations in the meteoric environment during the Cenozoic, a consequence of the combination of northward drifting of Australia and glacial events. All cements are meteoric in origin, and the meteoric aragonitic cement from Fisherman Bay is corrected for aragonite-calcite $\delta^{18}O$ fractionation (paleolatitude data from Smith et al. 1981).

Australia, similar to other parts of the world, was a time of climatic deterioration and the replacement of rainforest by drier sclerophyll forest and grasslands (Brown 1985). This terrestrial cooling is especially recorded by meteoric cements from the Upper Morgan Limestone, where a remarkable decline in temperature is indicated. Since the Middle to Late Miocene the terrestrial climate has warmed but has never reached the values of the Late Eocene. This trend is shown by the Holocene meteoric cements of Fisherman Bay (Figs 8.2, 8.3). The ambient temperature for the near-surface diagenetic environment has been calculated from the aragonitic meteoric cements of Fisherman Bay using equation (A), after the appropriate corrections for fractionation between calcite and aragonite ($\Delta\delta^{18}O_{\text{aragonite-calcite}} = 0.8‰$), at about 29°C. This is about 3°C higher than the maximum temperature prevailing in the area (26°C) today. This observation is consistent with MacKenzie's (1981) finding that in Sabkhas of the Persian Gulf the temperature in the near-surface sediments of the coastal area can reach values considerably above the ambient surface temperature.

Accordingly, it should be emphasised that these coastal paleotemperatures calculated from the oxygen isotope signatures of different meteoric cements from diverse ages, exhibit approximately their maximum near-surface ambient temperature because active meteoric cementation happens during the warmer seasons when evaporation is at its maximum rate. Evaporation in near-surface environments gives rise to CO_2 escape from meteoric water and pH increase, thus leading to higher precipitation of carbonate minerals (as cement). Therefore, temperatures obtained from meteoric cements show the highest ambient temperatures.

Today, the $\delta^{18}O$ content of Adelaide rainfall is about -4.6‰ (International Atomic Energy Agency 1979). On the other hand, the average $\delta^{18}O$ value of the Holocene cements from Fisherman Bay is about 0.86‰ (Ferguson et al. 1988) which indicates evaporation, which leads to $\delta^{18}O$ enrichment of meteoric water prior to infiltration through the carbonate sediments. This in turn, consequently, leads to cementation by $\delta^{18}O$ enriched meteoric waters.

8.4. Implications of Marine Fossils in Terrestrial Paleoclimatology:

Southern Australia was in relatively high latitudes (50-55°) when widespread sedimentary deposition in the St.Vincent Basin began in the late Middle Eocene (Benbow et al. 1995). Extensive rainforests, including dense fern and moss forests, existed over much of Australia during this time. Pollens of macroflora indicating high rainfalls, have been found from this period (Benbow et al. 1995). In agreement with this, isotopic paleotemperature data from the Tortachilla Limestone, indicate relatively higher temperatures for this time, as bottom water temperature was about 16.4°C (See Fig. 6.1). This is higher than the successive unit of the Gull Rock Member, which has an average temperature of 15°C (See Fig. 6.1). This high bottom water temperature reflects a higher surface temperature, thus indicating a warm climate and is consistent with higher temperatures calculated from meteoric cements of the Tortachilla Limestone for near-surface environments. The warm climate continued until the Eocene/Oligocene boundary major cooling event, which triggered a relatively arid phase in Australia. This cooling event is partially recorded in the Gull Rock Member fossils by a decline in the average isotopic temperature by about 1.4°C, and is concomitant with the cool-temperate *Nothofagus*-dominated rainforest that covered the southern part of South Australia during this time interval (Benbow et al. 1995). This cooling event, caused by an ice sheet build-up in Antarctica, was accompanied by a marine regression during the Early Oligocene in the St.Vincent Basin, leading to the deposition of shallow water clastic sediments.

The Late Oligocene marine transgression led to almost open marine conditions in the Murray Basin and to deposition of the marine limestone of the Mannum Formation. The average bottom water temperature of 16.5°C for the Mannum Limestone reflects warm conditions of Late Oligocene-Early Miocene time, which is consistent with the work of Dorman (1966, 1968), Shackelton and Kennett (1975a, b) and Shackelton et al., (1984a, b). The Early Miocene fossils of the Lower Morgan Limestone give a maximum bottom water temperature of 16.9°C which reconfirms the contention of other workers that this time was warmer than any other time in the Tertiary (McGowran 1979; Adams et al. 1990). This period of climatic amelioration in the Early Miocene (20 to 15 Ma) led to the development of extensive rainforests in Australia. Paleoclimatological evolution is reflected in the relatively light $\delta^{18}O$ values of different Early Miocene fossils of the Lower Morgan Limestone. Pecten fossils exhibit $\delta^{18}O$ average values of -0.8‰, brachiopoda -0.45‰, and Turritellidae 0.2‰, which, on the whole, are lighter than their younger counterparts from the Cadell Marl (See Fig. 6.4). These lighter $\delta^{18}O$ values reflect higher temperature and warmer climates on the surrounding Australian continent during this interval. The meteoric cement paleotemperature data also exhibit this warming trend toward the early Middle Miocene.

Since the latest Early Miocene, with the inception of ice build-up intensification in Antarctica, bottom water temperature began to decline as the average paleotemperature recorded by the Cadell Marl fossils is about 13.3°C, with a minimum of 10.4°C. This observation is in agreement with Matthews and Poore (1980) who showed a major increase in the $\delta^{18}O$ values of the South Tasman Rise area during this time and, as the cause, suggested an ice-cap build-up in Antarctica. Presumably, this ice-sheet greatly influenced the atmospheric and oceanic circulation patterns in the Australasian region resulting in patterns that were almost similar to those of today (Kemp 1978). The ice-build-up of the latest Early Miocene-earliest Middle Miocene led to a marine regression together with temperature decline. This period is the time of extensive marine limestone deposition (Upper Morgan Limestone), despite sea-level falling in the Murray and other basins (Abele et al. 1976, 1988). The sea-level fall of this time left its imprint on the isotopic composition of the Upper Morgan Limestone, especially by imposing restricted circulation and limited access to open oceans.

Similar to other continents, the Middle Miocene to Late Miocene in Australia was the time of climatic deterioration and replacement of rainforest by drier sclerophyll forests and grasslands, indicating progressive aridification of Australia (Kemp 1978; Tedford 1985; Stein and Robert 1986; Martin 1989). The increasing aridity was controlled, for the most part, by Antarctic cooling and ice sheet growth (Tedford 1985) and to a to lesser extent by the northward drift of the Indo-Australian plate. Desertification advanced southward, as Australia drifted northward into an intensifying mid-latitude high pressure belt. The aridification resulting in an oceanward biomass transfer which started in the northern parts of the continent and expanded southward during the Late Miocene (e.g., Stein and Robert 1986). Locker and Martini (1989) suggested that the first occurrence of phytoliths (small particles of opaline silica secreted by grasses in epidermal cells) in cores from the Tasman Sea in the mid-Miocene (14 Ma) indicate the initiation of grassland development.

In the Upper Morgan Formation, climate deterioration that led to a biomass transfer to the ocean and organic matter enrichment in the Murray Basin seawaters during the Middle to Late Miocene contributed significantly to lowering of the $\delta^{13}C$ values of DIC and also to the precipitation of carbonates. Accordingly, terrestrial biota underwent major changes, beginning in the early Middle Miocene and continuing to the end of Late Miocene, as a response to continental environmental changes. For example, fossil terrestrial floral assemblages from different continents also confirm an Early Miocene climatic optimum, that was followed by a rapid and abrupt climatic cooling in mid to high latitudes (Wolfe 1985). Martin (1989) in his study of different microflora of the eastern Murray Basin, suggested that the region was largely covered by rainforest prior to the Middle Miocene, but that in the early Middle Miocene to the Late Miocene, due to an extension of the drier climate, a change from rain forest to drier sclerophyll forest took place. This indicates the reduction of biomass on the continent because of climatic deterioration and the transfer of organic matter to the oceans, which produced the low $\delta^{13}C$ values in fossil carbonates observed in the Upper Morgan Limestone. This climatic deterioration is also recorded by the meteoric cements of the Upper Morgan Limestone, which exhibit the lowest paleotemperature in all of the studied Tertiary records. Since Middle/Late Miocene, paleotemperature data from marine fossils and terrestrial meteoric cements, reveal a climatic amelioration towards the present time.

8.5. Conclusion:

The $\delta^{18}O$ values of the meteoric cements from different stratigraphic intervals during the Cenozoic (and hence, diverse paleolatitudes) exhibit a negative correlation with paleolatitude which is consistent with theoretical findings. These observations indicate that the meteoric cements, despite some inconsistencies due, for example, to evaporation and seawater mixing with groundwaters, were precipitated in near equilibrium with their parent fluids. Consequently, these cements have approximately recorded variations in the temperature of their ambient environment. These reflect variations in the $\delta^{18}O$ value of their parent meteoric waters, which in turn are mainly due to the latitudinal changes of these Tertiary basins. The paleoclimate and paleotemperature results calculated from isotopic values of meteoric cements from the marine carbonate sediments are compatible with those derived from the different fossil samples from within these marine carbonates. These indicates the creditability of the data and a mutual interaction between the marine environment and the adjacent coastal area.

CHAPTER NINE

UPWELLING, TEMPERATURE VARIATIONS, FRESHWATER INFLUX AND ONTOGENETIC EFFECTS RECORDED IN STABLE ISOTOPIC PROFILES

9.1. Introduction:

The stable isotopic profiles from modern and fossil mollusc shells allow a quantitative evaluation of temperature ranges and other environmental conditions. The stable isotopes in well-preserved biogenic carbonates are one of the most reliable indicators of paleoenvironmental conditions. The isotopic composition of biogenic carbonate depends upon both the temperature during deposition and the isotopic composition of the water. Variations in the oxygen and carbon isotopes within carbonate shells of different organisms, especially molluscs have been utilised to:

1) evaluate annual marine temperature cycles and its variations (e.g., Jones et al. 1983, 1989),

2) assess seasonality changes (e.g., Williams et al. 1982),

3) detect upwelling events (e.g., Killingley and Berger 1979; Geary et al. 1992),

4) examine hydrographic patterns on continental shelves (e.g., Arthur et al. 1983; Krantz et al. 1989). Similar isotopic variations along growth lines of well-preserved fossils have been used by researchers (Abell 1985; Geary et al. 1989; Wefer and Berger 1991; Jones and Quitmyer 1996) to reconstruct marine and terrestrial short-

term paleotemperature and paleoclimatic fluctuations, thus giving the potential for high-resolution paleoenvironmental reconstructions.

The main factors that influence the $\delta^{18}O$ profiles of these organisms are the oxygen isotope composition of seawater, the temperature and salinity of the ambient water (e.g., Jones et al. 1978; Arthur et al. 1983; Romanek and Grossman 1989; Geary et al. 1992; Jones and Allmon 1995; Bemis and Geary 1996; Jones and Quitmyer 1996; Swart et al. 1996; Klein et al. 1996). The $\delta^{18}O$ cycles recorded in the molluscan isotopic profiles can be directly related to seasonal and annual environmental variations. The $\delta^{13}C$ records, in contrast, proved much more difficult to interpret, despite exhibiting significant cyclicity. The major factors that contribute to this situation are:

1) carbon isotopic composition of carbonate skeletons has received less attention than the oxygen isotopic ratios (Wefer and Killingley 1980; Allmon et al. 1992),

2) whereas temperature is usually the main cause of the oxygen isotopic variations, no single similar cause is identified for carbon isotope variations. The predominant influences on the $\delta^{13}C$ content of mollusc shells are:

1) variations in the DIC of ambient waters resulting from changes in upwelling, runoff, seasonal productivity and food supply,

2) $\delta^{13}C$ fractionation due to changes in the shell growth rate,

3) mixing of metabolic carbon derived from various food sources with dissolved inorganic carbon,

4) various kinds of vital effects of organisms,

5) reproductivity status,

6) salinity,

7) temperature of ambient waters (e.g., Emrich et al. 1970; Eisma et al. 1976; Killingley and Berger 1979; Arthur et al. 1983; Grossman and Ku 1986; Tanaka et al. 1986; Krantz et al. 1989; Geary et al. 1992; Bemis and Geary 1996; Rahimpour-Bonab et al. 1997 a, b). Because of the variety of environmental and biological factors that influence the $\delta^{13}C$ value of mollusc shells, and due to possible multiple concomitant influence of these factors, the interpretation of the carbon isotopic profile is more problematic than that of the oxygen one.

Generally, seasonal and annual trends are evident in all isotopic profiles of studied samples (where these profiles are not interrupted by environmental variations such as upwelling, freshwater influx and so on), with heavier $\delta^{13}C$ and $\delta^{18}O$ values in winter and lighter values in summer. Because the carbon isotopic fractionation with temperature is considerably less than that of oxygen (0.035‰ per ˚C versus 0.22‰ per °C respectively: Emrich et al. 1970), a maximum of 0.35‰ seasonal variations would be expected even assuming a high seasonal bottom temperature variation of up to 10°C. Therefore, only part of the $\delta^{13}C$ variations can be related to temperature changes. However, temperature has indirect effects on the $\delta^{13}C$ value of organisms by influencing growth rates. Accordingly, under lower temperatures and slower growth rates, the $\delta^{13}C$ content of carbonate secreted by organisms is closer to equilibrium values and exhibits less metabolic/kinetic effects (e.g., Rahimpour-Bonab et al. 1997a, b).

Examination of the integrated variations of $\delta^{13}C$ and $\delta^{18}O$ within each shell can help in interpretation of the environmental conditions and variations. For a better understanding of such variations and conditions, the study of $\delta^{13}C$ profiles variations should be accompanied by the $\delta^{18}O$ changes, which can produce information on the upwelling and freshwater runoff influx into the basin, (paleo)productivity and growth rate changes, and other environmental/biological factors.

The growth rate of carbonate secreting organisms is influenced by a variety of environmental and biological factors such as temperature, food supply and quality, oxygen supply and upwelling and metabolic processes. However, usually temperature variations have been recorded by oxygen isotopic profiles in sufficient detail that can be retrieved from shell carbonate. The other factors such as upwelling, food supply, freshwater influx are reflected in both carbon and oxygen profiles. Therefore stable isotope studies along growth lines of molluscs can provide a powerful tool for the interpretation of marine climatic variations of both modern and ancient carbonate environments.

The excellent preservation of fossil shells in the Tertiary sequences of the St.Vincent and Murray Basins of South Australia makes them particularly suitable for geochemical studies aimed at reconstructing paleoenvironmental conditions and variations.

In this chapter the isotopic profiles of gastropods and bivalves, both of which clearly display their original growth lines, have been studied in order of decipher the different paleoenvironmental factors and events.

9.2. Bivalves:

Bivalves were analysed in the first studies on the geochemical investigation of calcareous shells (e.g., Epstein et al. 1951; Epstein and Lowenstam 1953). A large number of investigations have been carried out on different bivalves from freshwater to marine environments (e.g., Gross 1964; Keith and Parker 1965; Fritz and Poplawski 1974; Killingley and Berger 1979; Williams et al. 1982; Jones et al. 1983; Bemis and Geary 1996; Rahimpour-Bonab et al. 1997b).

Most bivalves grow by addition of material at the outer rim of the valves, producing several layers called peristracum, the prismatic layer, and the nacreous layer (mother of pearl) (Rhoads and Lutz 1980). Growth lines are usually visible as macroscopic growth-increment patterns which form with annual periodicity. Over the past four decades, researchers have shown that this process of accretionary shell growth is strongly influenced by environmental factors, in both bivalves and gastropods (next section). Many bivalves live for several years and record seasonal and annual fluctuation of environmental parameters such as temperature, $\delta^{13}C_{DIC}$ variations due to upwelling or freshwater influx and so on. Therefore, as molluscs grow, their growth-lines become biogeochemical recorders of the environmental and climatic conditions experienced throughout their life time (e.g., Rhoads and Lutz 1980; Jones and Quitmyer 1996). The outer layer is commonly sampled to the appropriate depth (<0.5 mm) along the growth lines in radial shell cross-section, to produced the isotopic profiles of the organism. The isotopic analyses along the radial shell cross-sections typically reveal a much clearer view of variations in the environmental factors and parameters in consecutive years of the life of the organism. Therefore, year-to year environmental, ontogenetic and climatic information is recorded in growth-line isotopic profiles of molluscs. This marine equivalent of dendrochonology is referred to as sclerochronology (Jones 1983), which is based on geochemical study of the annual shell increments of different molluscs and some corals.

One of the most abundant and familiar bivalves is Pecten, which lived from the Mesozoic to the Recent as an epifaunal organism (and rarely infaunal) of the world oceans from subtropics to high latitudes. This bivalve is abundant in the study area both as well-preserved fossils in different Tertiary units and in the Holocene carbonate sediments of the southern shelves of Australia.

9.3. Gastropods:

Gastropods have also been the subject of geochemical investigations by several researchers in the past few years (e.g., Fritz and Poplawski 1974; Jones et al. 1983; Allmon 1988; Allmon et al. 1992; Wefer and Berger 1992; Rahimpour-Bonab et al. 1997 b). Most gastropods precipitate aragonite. Their major habitats are nearshore marine, planktonic, abyssal and freshwater. Patterns of isotopic profiles in gastropods are comparable with those of bivalves.

Turritellidae, which are the subject of this study, are diverse and abundant components of many ancient and modern marine benthic communities, and their assemblages are common in the geological record. Their life span is from the Mesozoic to recent and they live as semi-epifaunal to epifaunal organisms along the shores of the world oceans from the subtropics to high latitudes.

This family is also abundant in different Tertiary units of the study area but in many cases they are altered due to their metastable aragonitic mineralogy. They are also abundant in the Holocene carbonate sediments of the southern shelves of Australia.

In this study Pecten and Turritellidae samples have been selected for geochemical studies because:

1) They are easy to recognise and are abundant in both the Tertiary and Holocene sediments.

2) In the case of the Pecten samples, due to their low-Mg-calcite composition they are frequently well preserved in the Tertiary sediments. Turritellidae, despite their aragonitic mineralogy, have the highest potential for preservation among the aragonitic gastropods.

3) They show conspicuous growth increments which make them ideal for radial cross sectional growth-line sampling to produce isotopic profiles.

4) Geochemical study of the Holocene samples of these molluscs revealed that they precipitate their calcareous shell in isotopic equilibrium with their ambient environment (Rahimpour-Bonab et al. 1997b) and therefore, they can be utilised as a valuable tool for study of the (paleo)environmental factors and their variations.

The effects of diagenesis are investigated in all samples used in this study, using criteria discussed in Chapter Four and only pristine samples are selected for growth-line isotopic analyses. In the case of Pecten fossils from the Mannum Formation, to avoid contamination from soil-derived vadose cements, the sample was selected from a section distal to the soil zone and especial attention was paid to avoid contamination during microsampling.

9.4. Results and Discussion:

Oxygen and carbon isotopes have been measured across major (annual) growth increments in several fossils and modern samples of Pecten bivalves and Turritellidae gastropods.

9.4.1. Turritellidae:

Powdered samples obtained by consecutive sampling along the whorls of the Turritellidae samples from the Gull Rock Member, Cadell Marl and Lacepede Shelf were analysed for $\delta^{13}C$ and $\delta^{18}O$. The resulting isotopic records are plotted in Figs 9.1, 9.2 and 9.3, in the standard fashion with lighter (depleted) values toward the top and ontogenetically by whorl number from left to right. This graphical convention derives from paleotemperature interpretation of the isotopic variations ($\delta^{18}O$ in particular) in which warmer temperatures, and their correspondingly

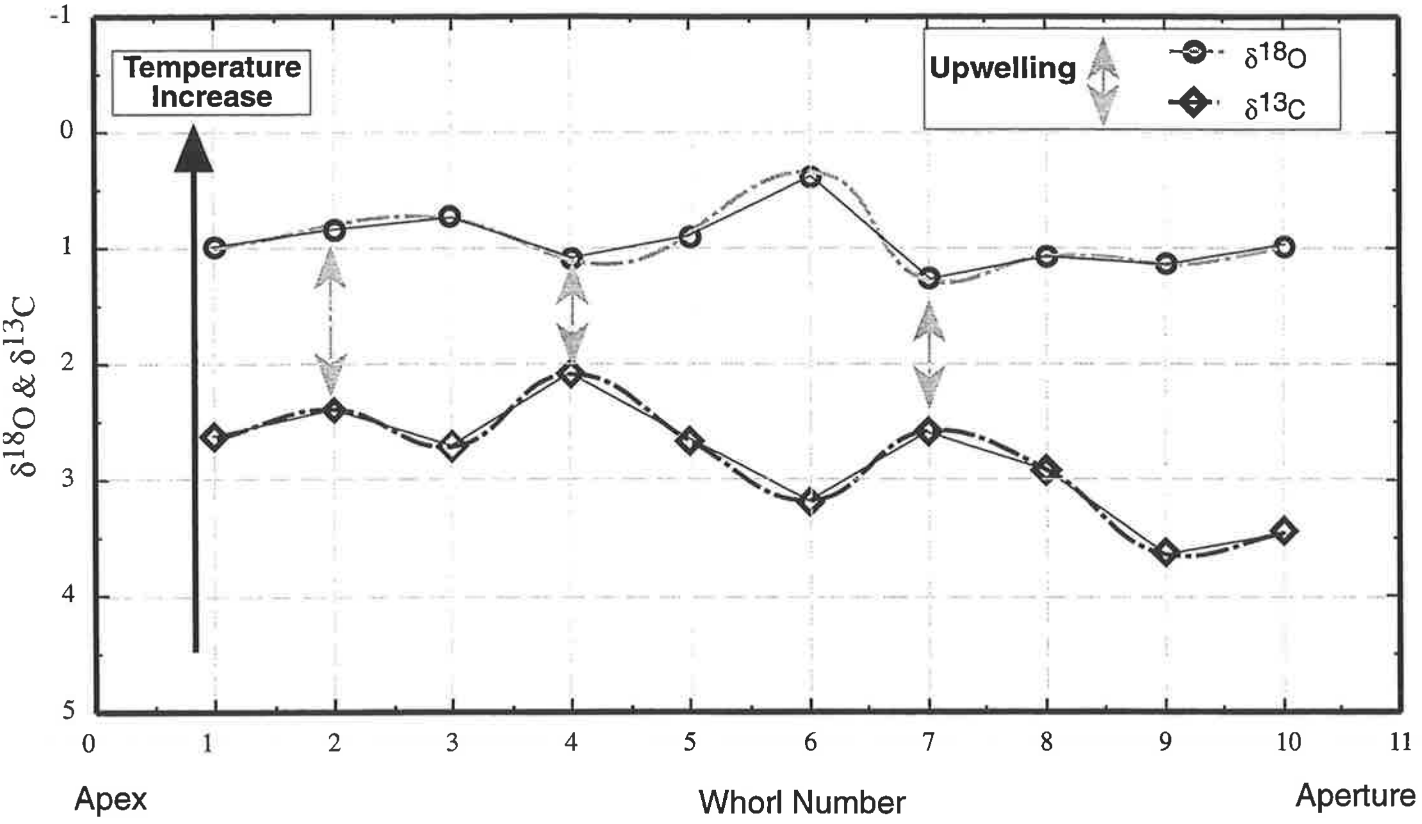


Fig. 9.1. Carbon and oxygen isotopic profiles for theTurritellidae sample from the Gull Rock Member, plotted in ontogenic sequence by whorl number from left (shell apex) to right (shell aperture).

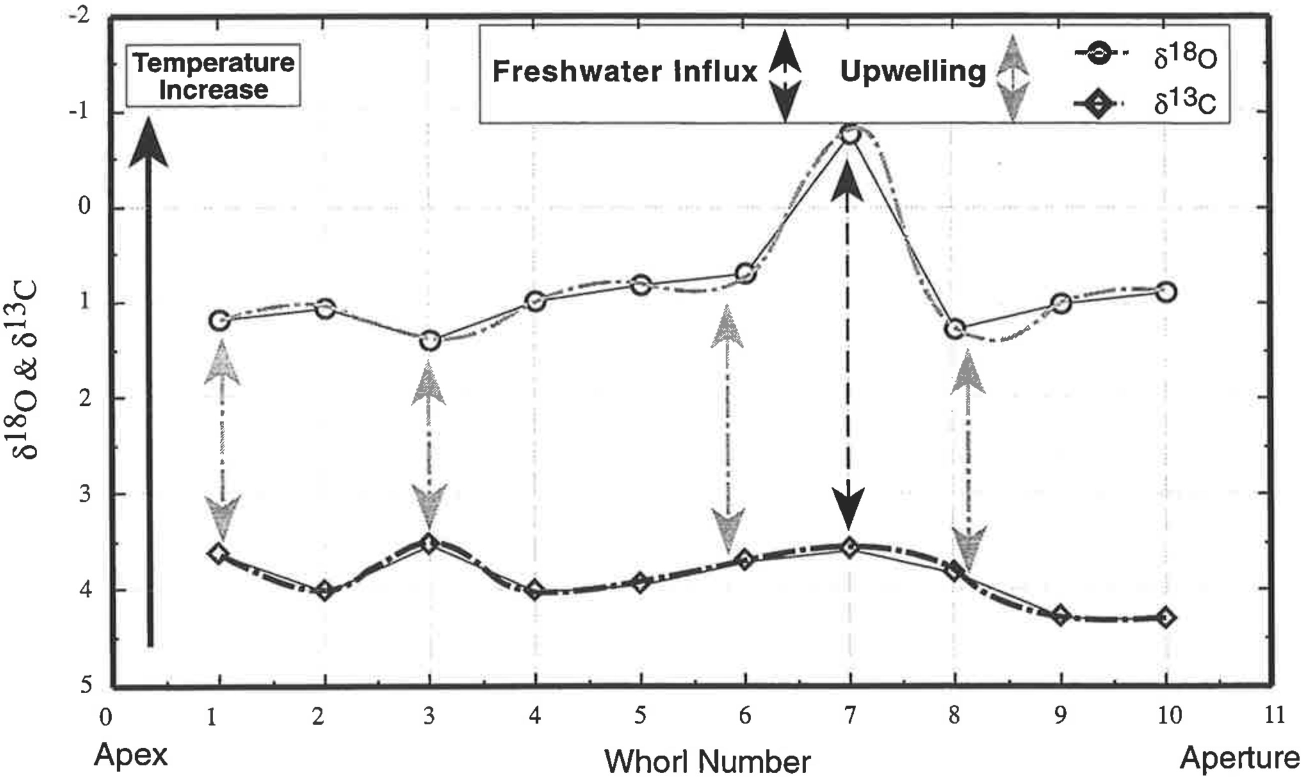


Fig. 9.2. Carbon and oxygen isotopic profiles for the Turritellidae sample from the Cadell Marl, plotted in ontogenic sequence by whorl number from left (shell apex) to right (shell aperture).

depleted isotopic values, are plotted toward the top and cooler temperatures and heavier (enriched) values toward the bottom. In all Figs, the records of isotopic changes are plotted from the shell apex (left) to the aperture (right).

The carbon isotopic profile in Turritellidae fossil from the Gull Rock Member exhibits varying semi-cyclical patterns (Fig. 9.1). An initial lighter $\delta^{13}C$ value of 2.7‰ is followed by gradually heavier values up to a final value of 3.5‰. The oxygen isotopic profile in this specimen also shows an approximately asymmetrical cyclical pattern. Comparison of the carbon and oxygen profiles reveals that they are partly concordant and follow the same pattern but in many parts they display opposite trends. In whorl one to three, both isotopes almost follow each other, but from whorl three and four depletion in the carbon isotope is concomitant with enrichment in the oxygen isotope. However, from whorl four to six, the pattern of both isotopes is shifting to the opposite direction again. Toward the last whorl (8 to 10) (ontogeny), the general isotopic pattern of both isotopes fluctuates in similar (opposite) trends. Overall, the isotopic profile of carbon fluctuates (range of 2.0 - 3.4‰) but shows enrichment through ontogeny, whereas the oxygen isotopic profile also fluctuates (range of 0.4 - 1.2‰) but is the same at whorl ten as whorl one.

The Turritellidae sample of the Cadell Marl shows the same cyclical pattern in the carbon isotopic profile, with a general positive excursion through ontogeny (Fig. 9.2). However, the magnitude of the carbon cycles is small and close to the mean $\delta^{13}C$ values. The $\delta^{18}O$ pattern in this specimen shows a cyclical pattern which, except in whorl seven, is almost symmetrical and does not display enrichment with ontogeny as carbon does. The comparison of carbon and oxygen isotopic profiles reveals that in some parts they follow each other, while in some whorls they show converse trends. In whorl three, an increase in the oxygen isotope values is synchronous with depletion in the carbon isotopic values and in whorls eight to ten enrichment in carbon is concomitant with depletion in oxygen.

The *Turritella* sp. sample from the Lacepede Shelf shows a strong cyclical pattern in both carbon and oxygen isotopic profiles and the magnitude of the fluctuations in both profiles is greater than in the other samples (Fig. 9.3). The comparison of these two profiles again displays that the carbon isotopic variation in most whorls is associated with converse variations in the oxygen isotopic profile, as, for example, in whorl one to two, the depletion in the carbon isotopic value is associated with enrichment in the oxygen isotopic value, and in whorl two to four the enrichment in the carbon isotope values is associated with depletion in the oxygen isotope value. Overall, the isotopic profile of carbon, again shows enrichment with ontogeny, while the general oxygen isotopic profile shows a slight depletion.

9.4.2. Pecten:

Powdered samples of Pecten fossils from the Tortachilla Limestone, Mannum Formation, Cadell Marl and Lacepede Shelf were analysed for their carbon and oxygen isotopes. The resulting isotopic profiles are plotted in Figs 9.4 to 9.7, in standard conventional fashion with lighter values toward the top. In all of the Figs the records of the isotopic change are plotted from the shell umbo (left) to the ventral margin (right).

The carbon isotopic profile of the Tortachilla Limestone sample shows very low magnitude asymmetrical cyclicity, and the magnitude of the fluctuations increases with ontogeny (Fig. 9.4). The oxygen isotopic profile of this specimen follows the carbon profile and its cyclicity, again, increases toward the margin. In both profiles the overall trend is depletion with ontogeny.

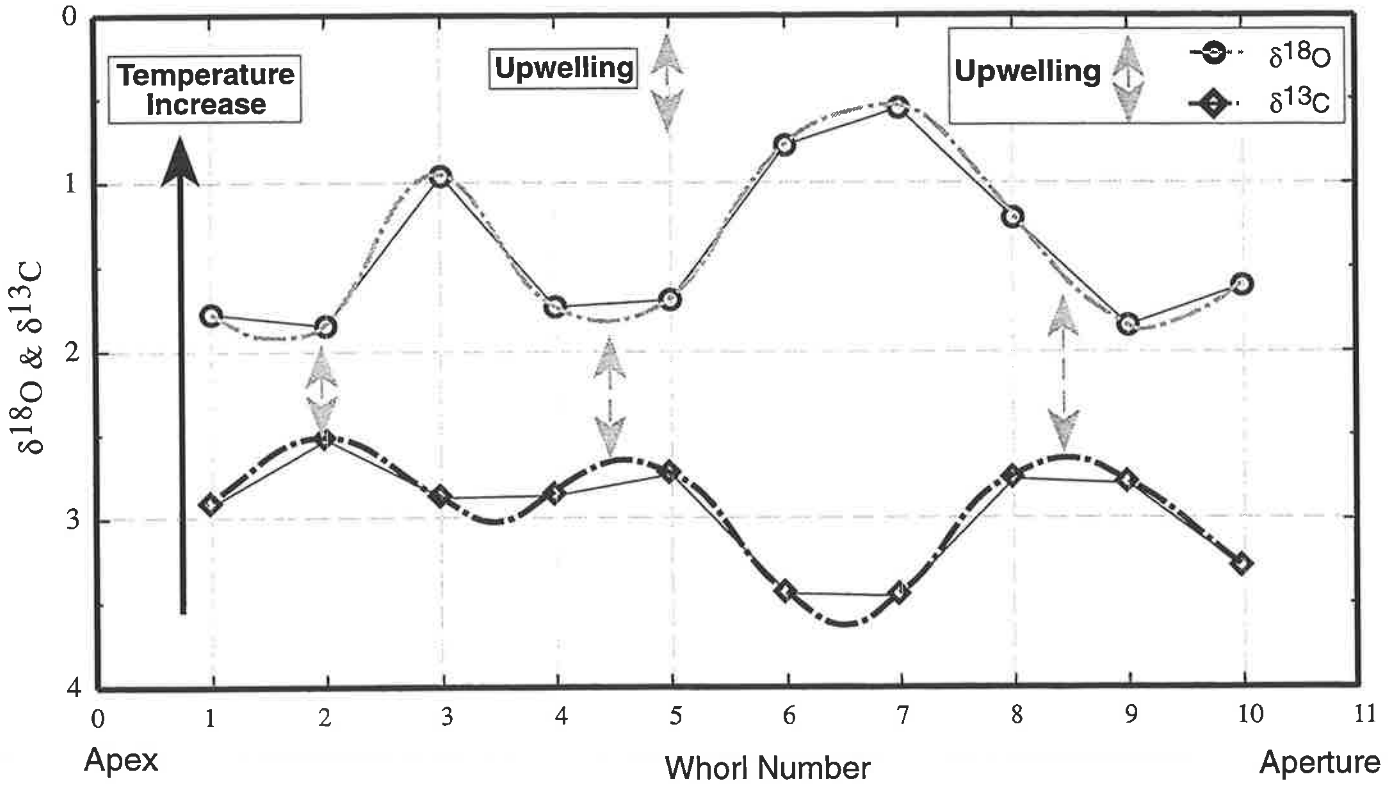


Fig. 9.3. Carbon and oxygen isotopic profiles for the *Turritella* sp. sample from the Lacepede Shelf, plotted in ontogenic sequence by whorl number from left (shell apex) to right (shell aperture).

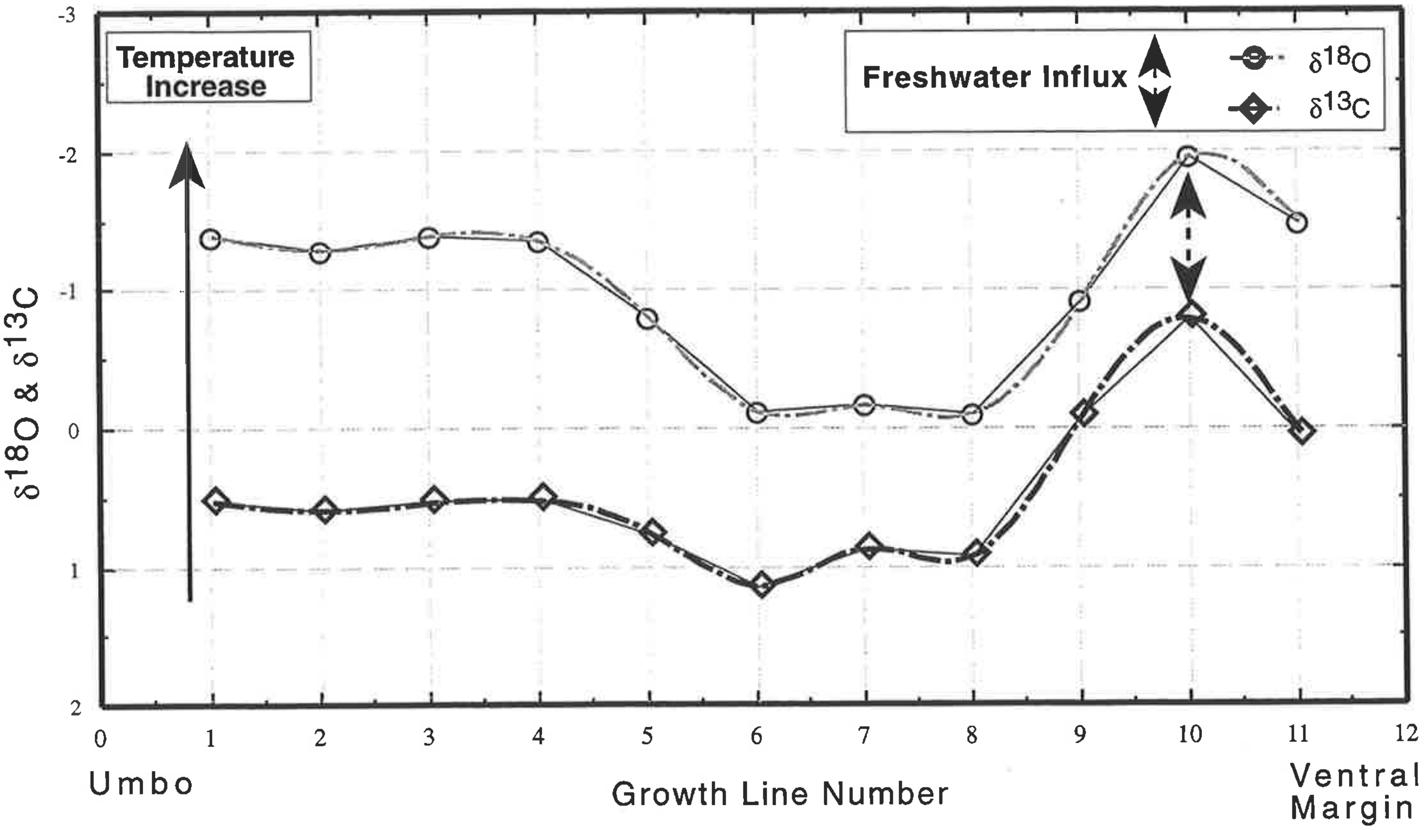


Fig. 9.4. Carbon and oxygen isotopic profiles for the Pecten sample from the Tortachilla Limestone plotted in ontogenic age of cross-sectional growth lines from left (umbo) to right (ventral margin).

The carbon isotopic profile of the Mannum Formation specimen displays an overall asymmetrical but cyclical pattern, with high magnitude fluctuations (Fig. 9.5). The oxygen isotopic profile shows a cyclical pattern which is approximately symmetrical, with high magnitude fluctuations. Comparison of the two profiles reveals that they have opposite trends in the younger part of the profile but from growth line number six their profiles follow each other and became parallel. The general trend in both profiles is toward heavier values with ontogeny.

The carbon isotopic profile of the specimen from the Cadell Marl displays symmetrical cyclicity with mostly low magnitude fluctuations (Fig. 9.6). The oxygen isotopic profile also shows the same cyclical symmetrical low magnitude pattern. Comparison of these profiles reveals that their trend is mostly in opposite directions with an increase in one isotope accompanied by a decease in the other. In both profiles the general pattern is toward a depletion with ontogeny.

The carbon isotopic profile of the specimen from the Lacepede Shelf shows relatively high magnitude asymmetric cyclical pattern with a general trend of depletion with ontogeny (Fig. 9.7). The oxygen isotopic profile displays a relatively lower magnitude symmetric cyclical pattern with a general trend toward heavier values with ontogeny. The comparison of these profiles reveals that they are mainly parallel and concordant, but with ontogeny they converge and show opposite isotopic trends.

9.4.3 Paleo-upwelling and Freshwater Influx:

In general, some basic environmental variations and differences are reflected in the isotopic profiles of a sample or samples from different areas and ages. Upwelling periods result in the highest fluctuations in isotopic profiles, compared with non-upwelling periods or non-upwelling areas (Figs 9.1 to 9.7), with the latter exhibiting the flattest profiles.

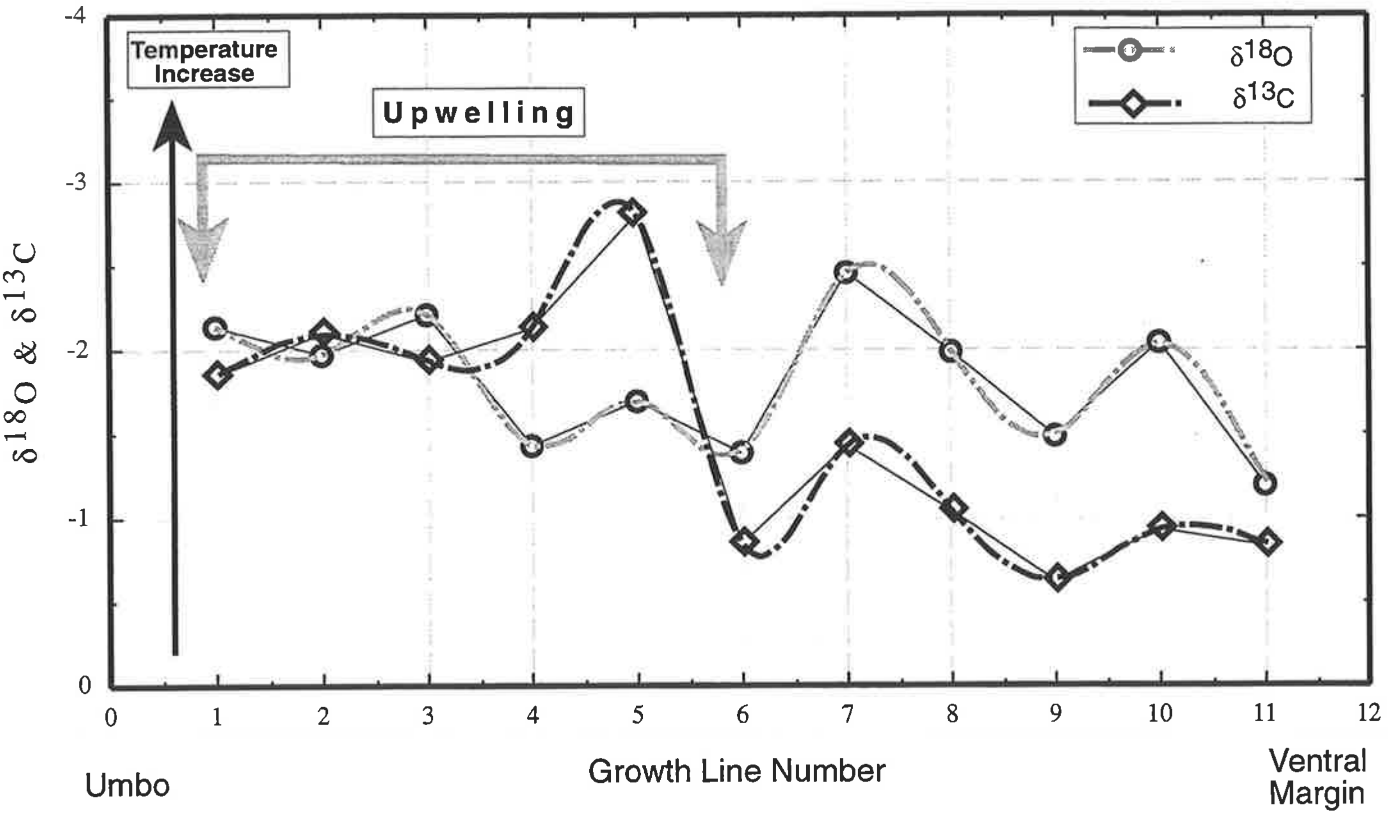


Fig. 9.5. Carbon and oxygen isotopic profiles for the Pecten sample from the Mannum Formation plotted in ontogenic age of cross-sectional growth lines from left (umbo) to right (ventral margin).

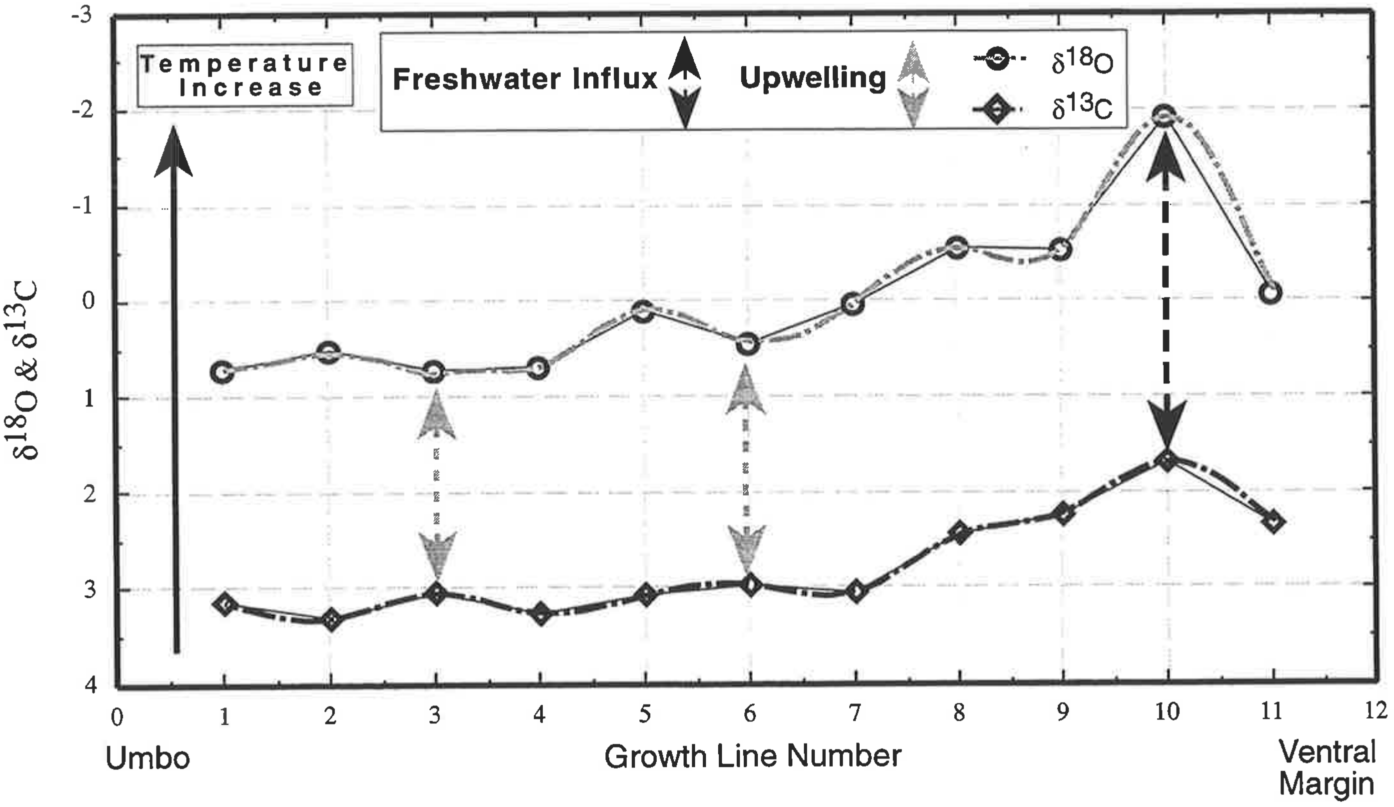


Fig. 9.6. Carbon and oxygen isotopic profiles for the Pecten sample from the Cadell Marl plotted in ontogenic age of cross-sectional growth lines from left (umbo) to right (ventral margin).

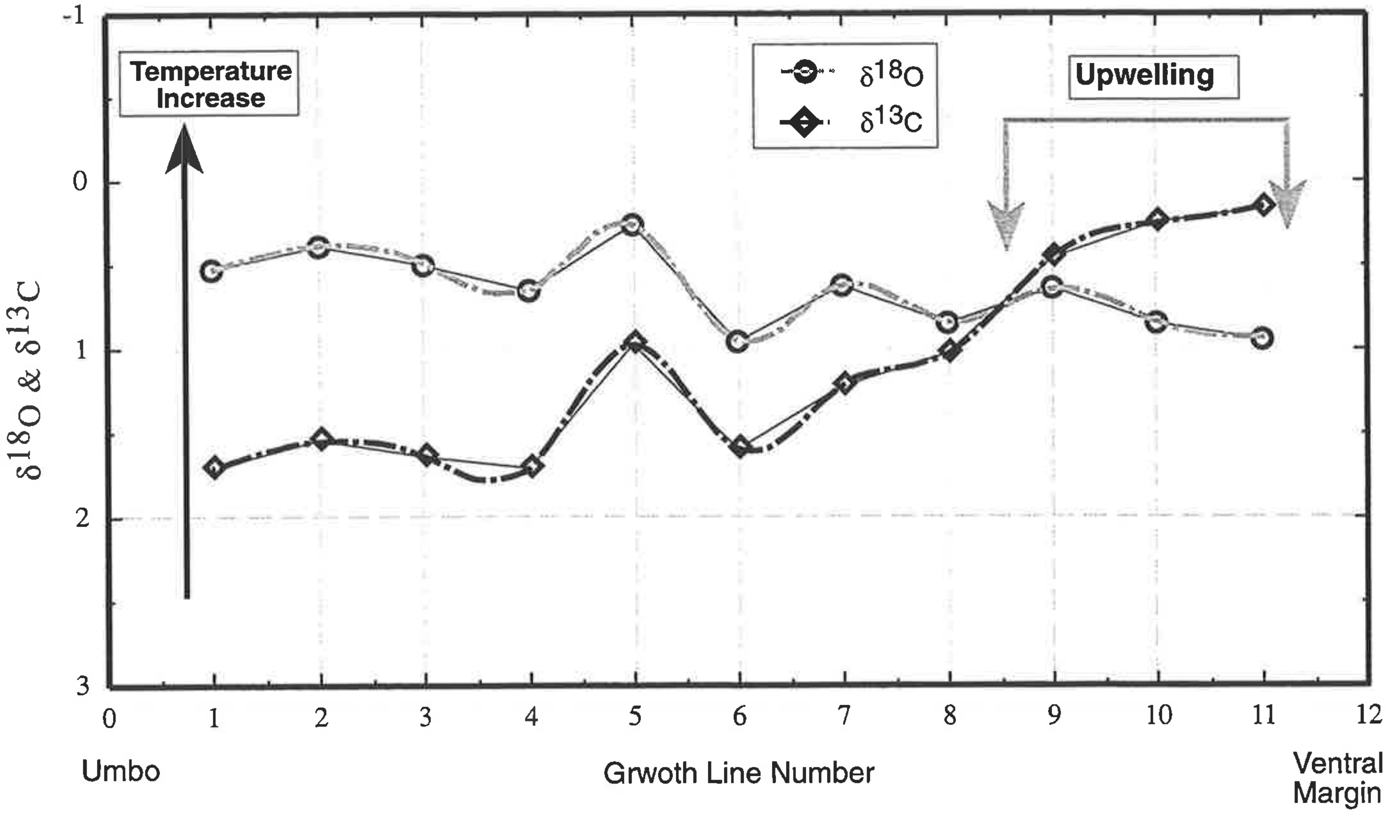


Fig. 9.7. Carbon and oxygen isotopic profiles for the *Pecten* sp. sample from the Lacepede Shelf plotted in ontogenic age and growth lines from left (umbo) to right (ventral margin).

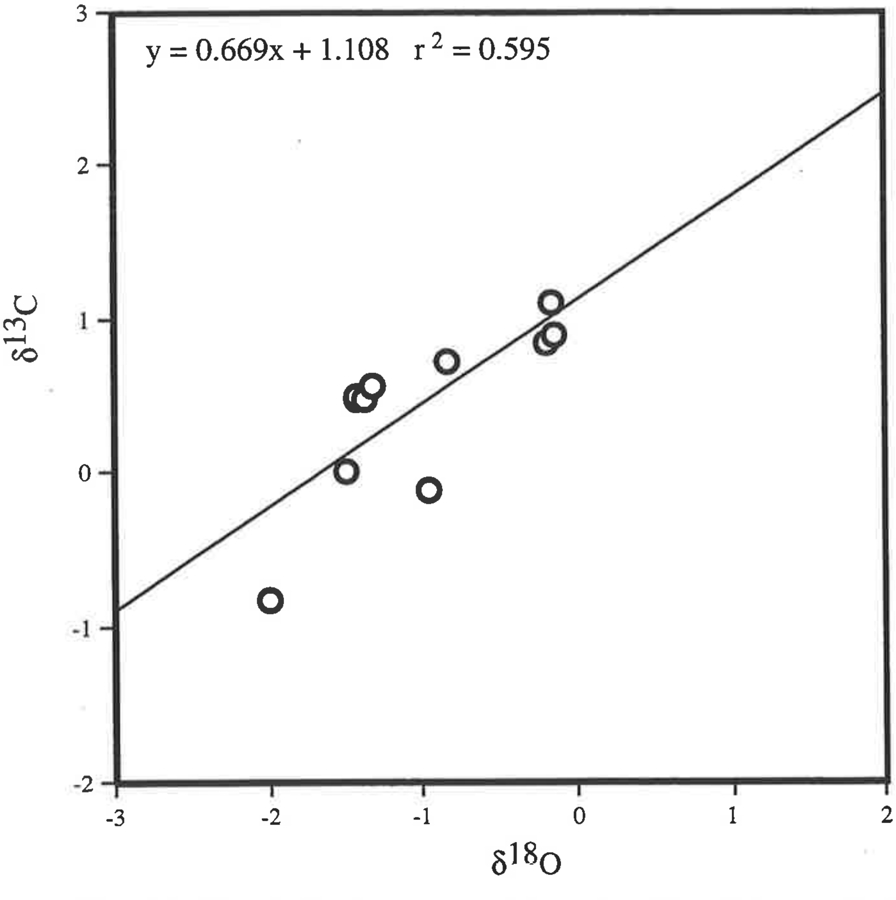


Fig. 9.8. Correlation between carbon and oxygen isotopes along the growth lines of Pecten from the Tortachilla Limestone.

The correlation between carbon and oxygen isotopic profiles within a shell can exhibit consistent differences among environments. Assuming that warmer temperatures result in the precipitation of more negative $\delta^{18}O$ and $\delta^{13}C$ in non-biogenic (Emrich et al. 1970; Turner 1982) and biogenic carbonates (Grossman and Ku 1986; Rahimpour-Bonab et al. 1997 a and b), and conversely cooler temperatures more positive $\delta^{18}O$ and $\delta^{13}C$, a positive relationship between $\delta^{18}O$ and $\delta^{13}C$ can be expected when temperature changes are the predominant control on the shell isotopic composition. However, in marine environments, other factors also influence the environmental conditions and consequently the isotopic signatures.

Upwelling is one of the most important environmental factors that interrupts the positive correlation between $\delta^{18}O$ and $\delta^{13}C$, due to its cooler water (heavy $\delta^{18}O$) and high organic matter content (light $\delta^{13}C_{DIC}$). Generally, areas of upwelling are regions of high primary productivity, as well (e.g., Murray 1995) (Primary Productivity is the rate of photosynthetic fixation of carbon by chlorophyll-containing organisms, Berger et al. 1989). These currents supply nutrients (nitrogen, phosphorous) to surface waters where they can be utilised by phytoplanktons and increase primary productivity.

Photosynthetic activities by phytoplanktons in surface seawaters selectively remove ^{12}C from the ambient dissolved inorganic carbon (DIC) reservoir and this leads to $\delta^{13}C_{DIC}$ enrichment in surface waters. Therefore, this photosynthetic activities remove organic carbon out of the surface waters and sequesters it at depth and within sediments (the idea of biological pumping or carbon pumping - Berger and Vincent 1986). Oxidation of this organic debris at depth releases relatively large amounts of nutrient materials (organic PO_4^{-3}) and isotopically light carbon (depleted $\delta^{13}C_{DIC}$) into these deep waters (Kroopnick 1980). So, during upwelling events, the cool water with an isotopically light $\delta^{13}C_{DIC}$ and but rich in nutrients, is brought to the shallower regions (Killingley and Berger 1979; Geary et al. 1992). Therefore, the isotopic signature of upwelling events is recorded in isotopic profiles of molluscs as a depleted $\delta^{13}C$ values associated with an enriched $\delta^{18}O$ signature .

The effects of upwelling are even conspicuous in benthic shelf organisms (not deep sea organisms) as the bottom water of continental shelves, below the upwelling areas, is also affected by these $\delta^{13}C$-depleted currents, as shown by Kroopnick (1985). The enriched $\delta^{18}O$ values are due to the lower temperature of these currents. During non-upwelling seasons, due to higher water temperatures and heavier $\delta^{13}C_{DIC}$, isotopic profiles exhibit the opposite trend to upwelling, namely, enriched $\delta^{13}C$ and depleted $\delta^{18}O$. It should be added that, during upwelling events, due to the replacement of normal stratified shelf seawaters with cool nutrient-rich upwelling waters (temporary elimination of water stratification and so greater homogenisation), the isotopic differences between planktonic fauna and benthic fauna (on the continental shelf) reduce dramatically (e.g., Arthur et al. 1983; Steens et al. 1992). Steens et al., (1992) showed that, at the peak of upwelling, the difference in the $\delta^{18}O$ content of two planktonic and benthic foraminifera, due to the obliterating effects of upwelling on the thermocline, was zero. The difference in the $\delta^{13}C$ values of these benthic foraminifera also declined drastically during upwelling seasons.

Changes in salinity usually results in a positive $\delta^{18}O$ and $\delta^{13}C$ correlation, similar to the effects of temperature variations (e.g., Bemis and Geary 1996). Moreover, freshwater influx brings more negative $\delta^{18}O$ and more negative $\delta^{13}C$. Therefore, the isotopic signal of the upwelling currents onto the shelf water, recorded by calcareous shells, could be confused with the effects of freshwater runoff from the surrounding continents. However, although freshwater runoff usually also has depleted $\delta^{13}C_{DIC}$ due to its organic material content, this is usually associated with depleted $\delta^{18}O$ (the signature of meteoric water), as well. Thus, the typical influence of an upwelling event on the isotopic profiles of marine organisms is shown by depleted $\delta^{13}C$ associated with enriched $\delta^{18}O$. Therefore, the upwelling events can be detected by isotopic profiles of mollusc shells as depleted $\delta^{13}C$ which is coincident with heavy $\delta^{18}O$ values (Killingley and Berger 1979), while, in the case of the freshwater influx the depleted $\delta^{13}C$ is accompanied by depleted $\delta^{18}O$ values. Freshwater runoff brings isotopically light carbon into the system. The $\delta^{13}C$ of this carbon may vary widely, depending on the type of soil, bedrock, and vegetation in the runoff area, and how far or how long the rainwater has travelled in the runoff area (Domenico and Schwartz 1990).

On the other hand, seawater dilution by rainwater or runoff has its maximum effects in restricted to semi-restricted shallow water basins, and tends to decrease the salinity and $\delta^{18}O$ value of seawater. However, because the $\delta^{18}O$ content of rainwater in coastal settings is close to that of marine waters (minimum effects of Rayleigh distillation), freshwater dilution in marginal basins, such as the St.Vincent and Murray Basins (and, obviously, the open marine deep basin of the Lacepede Shelf) has only a minor effect on the $\delta^{18}O$ value of carbonates. Contrary to the freshwater influx effects on the $\delta^{18}O$ content of seawater, evaporation can cause an increase in salinity and in the $\delta^{18}O$ value of seawater. However, as suggested by Romanek and Grossman (1989), the $\delta^{18}O$ enrichment in carbonate caused by evaporation may be moderated by increased water temperatures associated with evaporative conditions. Moreover, the St.Vincent and Murray Basins were mostly under open marine conditions throughout their history, as reflected in their lithology and marine fossil assemblage, thus minimising the effects of such terrestrial influences.

Turritellid-dominated and turritellid-rich communities in modern seas occur primarily in areas of cool (<18°C) and nutrient-rich waters and are often associated with upwelling (Allomon 1988). This family is usually associated with other molluscs such as bivalves. Similar environmental conditions in the Lacepede Shelf and the Great Australian Bight led to abundance of these organisms on these areas. Hence, the presence of this family as an abundant fossils in different stratigraphic units of the St.Vincent and Murray Basins, can be attributed to the dominance of cool-water conditions associated with upwelling during the Tertiary period.

Turritellidae fossils are abundant in the Tortachilla Limestone and the Gull Rock Member. However, only in the latter unit are samples well preserved and so suitable for geochemical studies. In different units of the Murray Basin this family is also present and preserved as body fossils or moulds and casts. In the Cadell Marl they are remarkably well preserved and are suitable for geochemical studies.

The upwelling of cool, nutrient-rich water occurs today on a seasonal basis in many places along the southern coast of the Australian continent, such as the Bonney and Lacepede Shelves and the Great Australian Bight. The upwelling events can be detected on the isotopic profiles of pristine carbonate secreting organisms, providing that they precipitate their calcareous shells in isotopic equilibrium with their ambient waters.

Even though the intensity and magnitude of upwelling events are generally impossible to determine without direct measurements, the size of such coincident peaks (depleted $\delta^{13}C$ and enriched $\delta^{18}O$) in mollusc isotopic profiles can provide a rough approximation (Jones and Allomon 1995). Killingley and Berger (1979) reported that upwelling accounts for at least part of the seasonal variations in $\delta^{13}C$ (up to -1.4‰) recorded in the shell of a recent Californian mussel. Geary et al., (1992) estimated that upwelling led to about a -1.5 to -2‰ depletion in the $\delta^{13}C$ content of molluscs from the Pacific, which is close to the difference of $\delta^{13}C$

values (about 2‰) between surface water and deepwater, reported for that area by Kroopnick (1974).

The Pecten sample isotopic profiles from the Tortachilla Limestone do not show any evidence of upwelling events, despite the abundance of Turritellidae (altered) in this unit. However, in growth line number ten of this specimen, the significant depletion of carbon is coincident with a significant depletion in the oxygen isotope content, which probably indicates a strong fresh water influx into the basin during a time of heavy rainfall (Fig. 9.4). The correlation of carbon and oxygen isotopic profiles in this specimen, cannot be simply attributed to seasonal temperature variations, because the temperature sensivity of $\delta^{13}C$ is small (e.g., Grossman and Ku 1986). However, the observed correlation can be ascribed to the integrated effects of temperature and metabolic activities on the isotopic compositions of biogenic carbonates. Accordingly, due to higher summer temperatures (lighter $\delta^{18}O$ content), the metabolic activities of organisms increase which lead to higher growth rates. Higher growth rates and consequently faster precipitation of biogenic carbonates give rise to more kinetic fractionation and result in a lighter $\delta^{13}C$ signature, as discussed in the comparison of cool-water mollusc of the Lacepede Shelf with their tropical counterparts (Rahimpour-Bonab et al. 1997b). Conversely, due to cooler winter waters (heavier $\delta^{18}O$), the metabolic activity of organisms reduces and so the rate of carbonate precipitation decreases and leads to minimum kinetic effects and so a heavier $\delta^{13}C$ signature. Consequently, the $\delta^{13}C$ values closest to equilibrium are their heaviest ones, as suggested by McConnaughey (1989).

The major cycles in the $\delta^{18}O$ profile are best interpreted in terms of annual cycle temperature changes in each basin, as the influence of temperature upon the $\delta^{18}O$ value of molluscan shell carbonates is well constrained. According to relationships describing equilibrium oxygen isotopic fractionation between calcium carbonate and water at environmental temperatures (e.g., Wefer and Berger 1992), a 1.0 per mil change in carbonate $\delta^{18}O$ values corresponds to a temperature change of about 4°C. Hence, the measured range in $\delta^{18}O$ of 2‰ (Fig. 9.4) suggests an annual range in seawater temperature of approximately 8°C (depth 90 to 120m, See Fig. 2.1).

Shell growth rates of molluscs fluctuate due to variations in environmental factors, especially temperature changes. Molluscan growth may even cease due to the low temperatures of the ambient seawater during winter, and consequently, shell $\delta^{18}O$ profiles do not always record the entire range of ambient temperatures and should be regarded as a recorder of the minimum range of environmental variations (e.g., Krantz 1990). Since all fossil samples used in this study are from high latitude Tertiary basins, and the maximum seawater temperatures of those basins has never been higher than the maximum temperature tolerance of molluscs, the maximum ambient temperatures are represented in the shell profiles of these molluscs. However, the real minimum temperature of ambient seawater may not have been recorded by molluscs in some cases (due to growth cessation caused by very low ambient winter temperatures, indicating that the actual minimum ambient temperature was probably some degrees cooler than those recorded in the shells). Although local salinity changes can affect paleotemperature estimates, salinity effects seem to be insignificant, based on the lithology and fossil assemblages of the units included in this study, which indicate open marine conditions for the most of the Tertiary.

In the study areas, the first significant upwelling signal is recorded in the isotopic profiles of the Turritellidae specimen from the Gull Rock Member (Fig. 9.1). In this sample, several negative correlations events in the carbon and oxygen isotopic profiles are recorded. They display the variability of upwelling current influx during different years. The strongest negative excursion of carbon, which is associated with a positive excursion of oxygen, is about -0.8‰ in whorl four. In whorl six, the relatively significant positive excursion of carbon is coincident with a significant depletion in oxygen isotope composition, which probably indicates the termination of a strong upwelling event in summer. The major cycles in the $\delta^{18}O$ profile represent annual cyclic temperatures in that basin. The measured range of $\delta^{18}O$ is about 1.1‰ which suggests an annual range in seawater temperature of approximately 5°C.

The next important upwelling event was apparently recorded in the Pecten fossil of the Mannum Formation (Fig. 9.5). The magnitude of the $\delta^{13}C$ variations in the carbon isotopic profile is high and up to 2‰ which probably indicates a high upwelling influx into the basin and significant difference in the $\delta^{13}C_{DIC}$ of surface and deep waters during that time interval. The rest of the isotopic profiles of this specimen show significant correlation, which probably indicates the integrated linkage of temperature and metabolic activity. The annual cycles of temperature are clearly recorded in the $\delta^{18}O$ profile of this specimen. The measured range in $\delta^{18}O$ is about 1.3‰ that suggests an annual range in seawater temperature of approximately 5.5°C.

Another significant upwelling event is recorded in the isotopic profiles of the Turritellidae and Pecten fossil from the Cadell Marl (Figs 9.2 and 9.6). The highest magnitude of $\delta^{13}C$ negative excursions, where they are accompanied by $\delta^{18}O$ positive excursions, is about -0.6‰, which reconfirms the existence of upwelling currents in the Murray Basin during Middle Miocene time, in accordance with the global intensification of upwelling during that time. This is recorded as the Monterey Excursion in the northern Pacific area (Vincent and Berger 1985) and in the Cadell Marl in Australia. In whorl seven of this gastropod, the characteristic freshwater spike, which is a short-lived negative excursion of both $\delta^{18}O$ and $\delta^{13}C$, is an indicator of an influx of freshwater runoff into the basin (Fig. 9.2). A similar freshwater influx is recorded in the isotopic profile of the Pecten fossil from this unit (Fig. 9.6). The annual temperature cycle is recorded in the $\delta^{18}O$ profiles of both molluscs. The measured range in the $\delta^{18}O$ values of the bivalve is lower than that of the gastropod, about 1.6‰ and 2‰, respectively, which suggests an annual range in seawater temperature of up to 8°C. Generally, the $\delta^{18}O$ profile of Pecten sample follows the $\delta^{13}C$ profile, which demonstrates the direct effects of temperature on the isotopic composition of this organism (the warmer, more depleted $\delta^{18}O$ values and higher growth rates and so more depleted $\delta^{13}C$, and vice versa).

The records of the upwelling events in the Holocene samples of *Pecten* sp. from the Lacepede Shelf display relatively strong $\delta^{13}C$ depletion (up to -1‰) accompanied by $\delta^{18}O$ enrichments, in mature-age organisms (Fig. 9.7). However, in the younger parts of the isotopic profiles, the correlation is high, indicating the integrated effects of temperature and metabolic activities. The *Turritella* sp. specimen of the Lacepede Shelf also exhibits this $\delta^{13}C$ depletion event associated with $\delta^{18}O$ enrichment (Fig. 9.3). In the isotopic profiles of *Turritella* sp., there are some positive excursions of carbon which are coincident with depletion in oxygen isotope, indicating a decline in upwelling. There is no indication of freshwater influx on to the shelf, which is consistent with the interpretation of James and Bone (1992), who suggested the influx of the Murray River on to the shelf water has no significant effects. The annual cycle of temperature is recorded in the $\delta^{18}O$ profiles of both molluscs. However, the measured range in $\delta^{18}O$ values of the bivalve is lower than that of the gastropod, about 0.8‰ and 1.6‰, respectively. These $\delta^{18}O$ variations represent a temperature range of 3.5 to 6.5°C. The annual bottom water temperature difference between winter and summer measured in the study area at a depth of 100m meters (the depth of sample collection) is about 6°C (See Fig. 2.1), which is significantly close to the temperature records of the gastropod. This observation substantiates the precision of the annual paleotemperature cycles measured by the isotopic records of fossil molluscs from the Tertiary units of the study area.

9.4.4. Ontogenetic Trends in $\delta^{13}C$:

Several authors have noted a depletion in $\delta^{13}C$ through ontogeny, and ascribed this observation to changes in diet or metabolisms with age, or the onset of reproductive activity (Jones et al. 1983; Krantz et al. 1987; Romanek and Grossman 1989).

The Turritellidae specimen from the Gull Rock Member not only does not show such $\delta^{13}C$ depletion through ontogeny but displays some enrichment (Fig. 9.1). The Turritellidae specimen from the Cadell Marl also shows some enrichment with ontogeny (Fig. 9.2). Moreover, the Holocene sample of this organism from the Lacepede Shelf also exhibits such ontogenetic enrichment in $\delta^{13}C$ (Fig. 9.3). These observations, however, are compatible with the study of Geary et al., (1992) which showed that the Strombid gastropods from the Pacific and Florida regions exhibit no such ontogenetic depletion and, on the contrary, sometimes show some enrichment. Also, the study of a specimen of Strombid gastropods from Bermuda by Wefer and Killingley (1980) showed some $\delta^{13}C$ enrichment through ontogeny. They suggested that growth rate and $\delta^{13}C$ values are inversely related in this gastropod, and because the growth rate is known to slow through ontogeny in gastropods (Brownell 1977), ontogenetic $\delta^{13}C$ depletion would be nullified by decrease in growth rate. That growth rates decrease through ontogeny in the Turritellidae family is verified by Allomon et al., (1992) by their study on this gastropod from the Gulf of California. Accordingly, it can be concluded that the general effect of $\delta^{13}C$ depletion in gastropod samples through ontogeny is masked and overruled by a decrease in growth rate (through ontogeny) and consequent enrichment in $\delta^{13}C$.

The Pecten fossil from the Tortachilla Limestone (Fig. 9.4) shows no general depletion through ontogeny, and the depleted $\delta^{13}C$ values of the last growth lines are probably due to fresh water influx, because they are associated with depleted $\delta^{18}O$ values. On the other hand, the Pecten fossil from the Mannum Formation (Fig. 9.5) exhibits $\delta^{13}C$ enrichment in the mature parts of the carbon isotopic profile. However, this can not be ascribed to ontogeny because the $\delta^{13}C$ values of the younger parts of the profile are probably affected by the upwelling current and so the general trend of the carbon isotope profile through ontogeny can not be determined. The Pecten fossil from the Cadell Marl (Fig. 9.6) exhibits some depletion with ontogeny in its carbon isotope profile. Although the *Pecten* sp. from the Lacepede Shelf shows a general depletion in $\delta^{13}C$ with ontogeny, this depletion can not be confidently attributed to ontogeny (Fig. 9.7), because of the influence of upwelling.

9.4.5. $\delta^{13}C$ and $\delta^{18}O$ Correlation:

Correlations of $\delta^{18}O$ and $\delta^{13}C$ are common in isotopic composition of non-equilibrium biogenic carbonates. These correlations are attributed to vital (metabolic) and environmental effects (e.g., Swart 1983; Romanek and Grossman 1989). Metabolic effects usually cause simultaneous depletion in $\delta^{13}C$ and $\delta^{18}O$ and are prevalent in symbiont-bearing taxa (Swart 1983; McConnuaghey 1989 a). Wefer (1985) suggested that such correlations are due to preferential incorporation of ^{13}C-depleted carbon during periods of rapid growth in the warm season (and so depleted $\delta^{18}O$). Pätzold (1984) suggested that positive correlation between $\delta^{13}C$ and $\delta^{18}O$ in some hermatypic corals are due to high photosynthetic rates. Meanwhile, the concomitant depleted $\delta^{18}O$ values are ascribed to the combination of warmer seasons with high photosynthetic rates.

Other workers have explained $\delta^{13}C$-$\delta^{18}O$ correlation in molluscs in terms of environmental effects. Aharon and Chapell (1983) attributed a positive $\delta^{13}C$-$\delta^{18}O$

correlation in *Tridacna gigas* from New Guinea to dilution by ^{18}O-depleted water in summer and higher activity of photosynthetic organisms and uptake of ^{12}C in the water column in winter. Krantz et al., (1989) explained a $\delta^{13}C$-$\delta^{18}O$ correlation in *Spisula solidissima* as due to the oxidation of organic matter produced by phytoplanktons blooms following spring upwelling.

In the study area, the Pecten fossil from the Tortachilla Limestone shows moderate positive correlation in $\delta^{13}C$-$\delta^{18}O$ (Fig. 9.8). However, the Pecten fossil from the Mannum Formation doesn't exhibit any $\delta^{13}C$-$\delta^{18}O$ correlation (Fig. 9.9), and the Pecten fossil from the Cadell Marl shows strong positive $\delta^{13}C$-$\delta^{18}O$ correlation (Fig. 9.10). *Pecten* sp. from the Lacepede Shelf exhibits no $\delta^{13}C$-$\delta^{18}O$ correlation (Fig. 9.11).

Turritellidae fossils from the Gull Rock Member and the Cadell Marl do not exhibit $\delta^{13}C$-$\delta^{18}O$ correlations, and the only specimen from the Lacepede Shelf shows some $\delta^{13}C$-$\delta^{18}O$ correlation (Figs 9.12, 9.13 and 9.14).

The presence of some $\delta^{13}C$-$\delta^{18}O$ correlations in Pecten fossil from the Tortachilla Limestone can not be attributed to vital effects or the presence of symbiont algae. Firstly, as already established, this bivalve does not exhibit significant metabolic effects during its carbonate precipitation processes (Rahimpour-Bonab et al. 1997b). Secondly, this bivalve does not have symbiont algae and so is not affected by photosynthetic effects and also usually lives below the photic zone. The presence of moderate $\delta^{13}C$-$\delta^{18}O$ correlation in this specimen may demonstrate environmental effects on $\delta^{13}C$ and $\delta^{18}O$ values, such as increased phytoplanktons productivity in winter (Aharon and Chapell 1983) or increased dilution by ^{18}O and ^{13}C-depleted meteoric waters in summer (Romanek and Grossman 1989). The second explanation is more likely, as isotopic profiles of this organism show some freshwater spikes (Fig. 9.4.). The lack of $\delta^{13}C$-$\delta^{18}O$ correlation in Pecten fossil from the Mannum Formations reconfirms our earlier

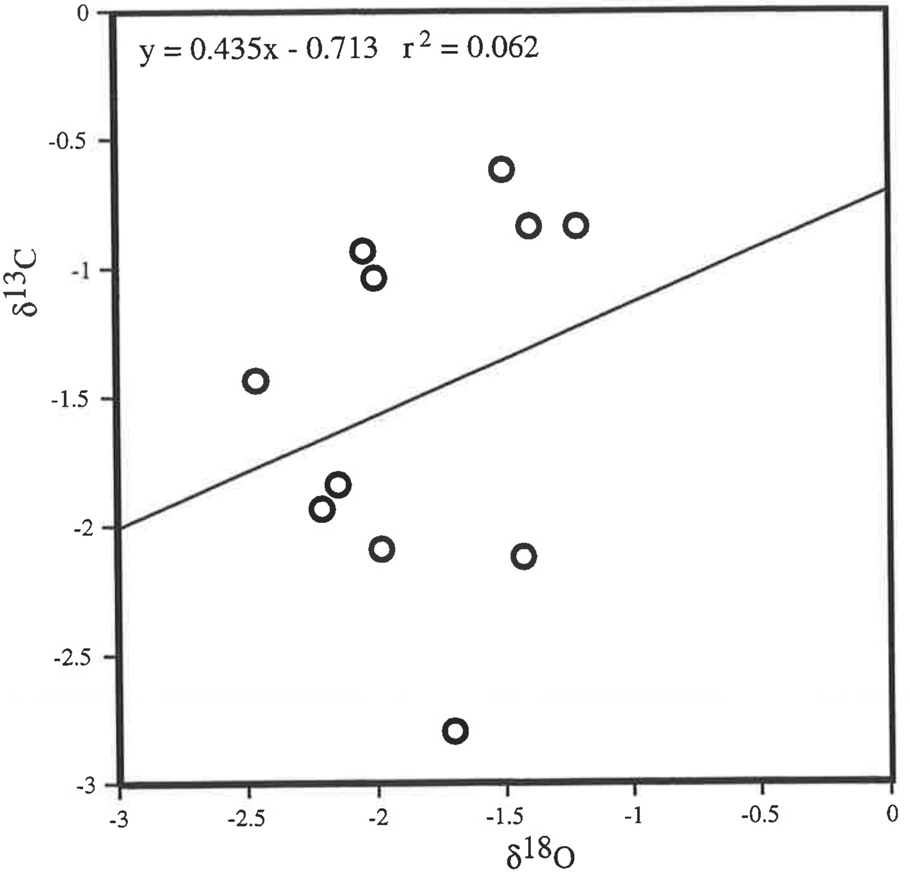


Fig. 9.9. Correlation between carbon and oxygen isotopes along the growth lines of Pecten from the Mannum Formation.

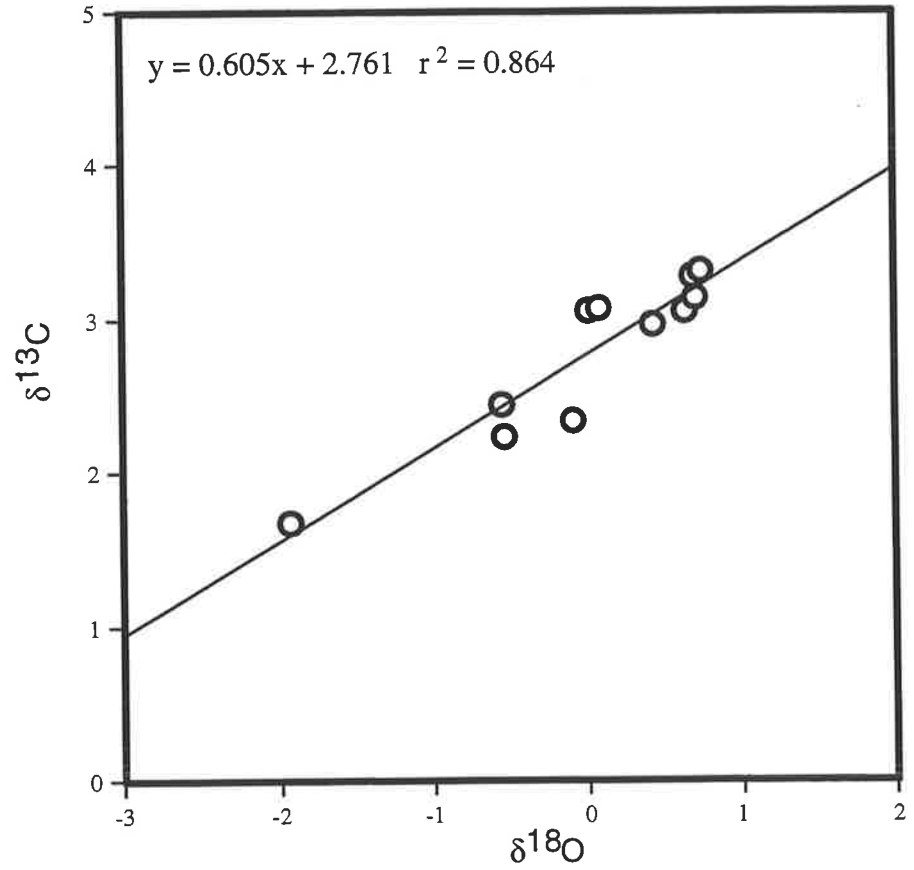


Fig. 9.10. Correlation between carbon and oxygen isotopic composition of Pecten from the Cadell Marl.

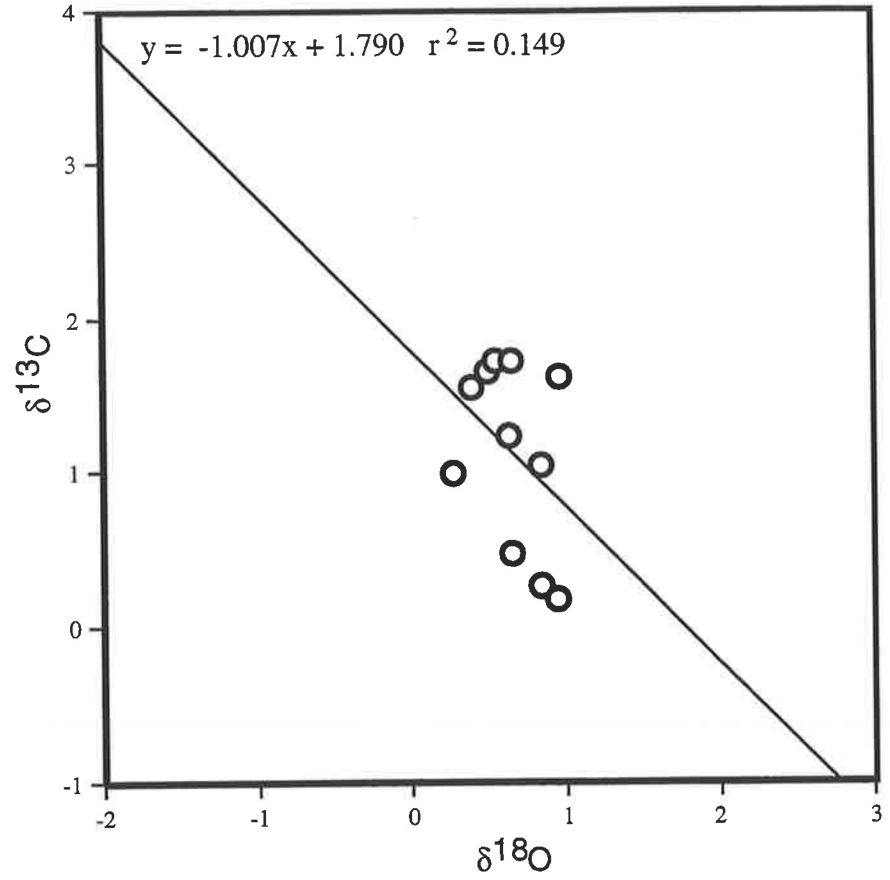


Fig. 9.11. Correlation between carbon and oxygen isotopes along growth lines of *Pecten* sp. from the Lacepede Shelf.

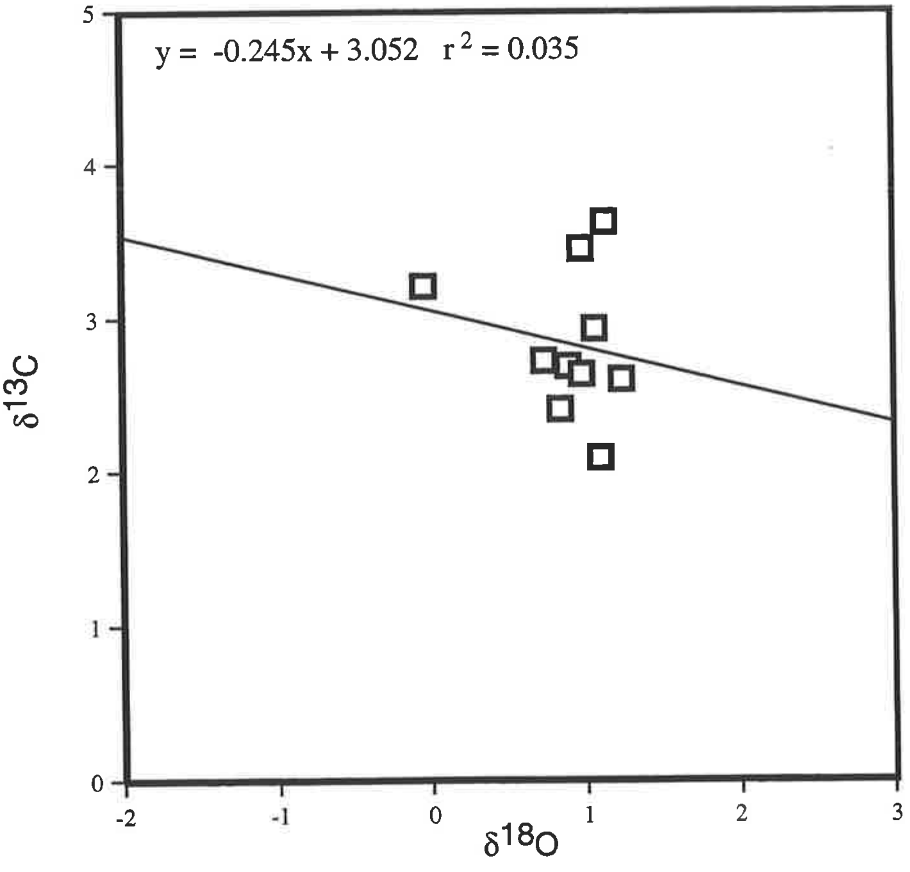


Fig. 9.12. Correlation between carbon and oxygen isotopes along different whorls of Turritellidae from the Gull Rock Member.

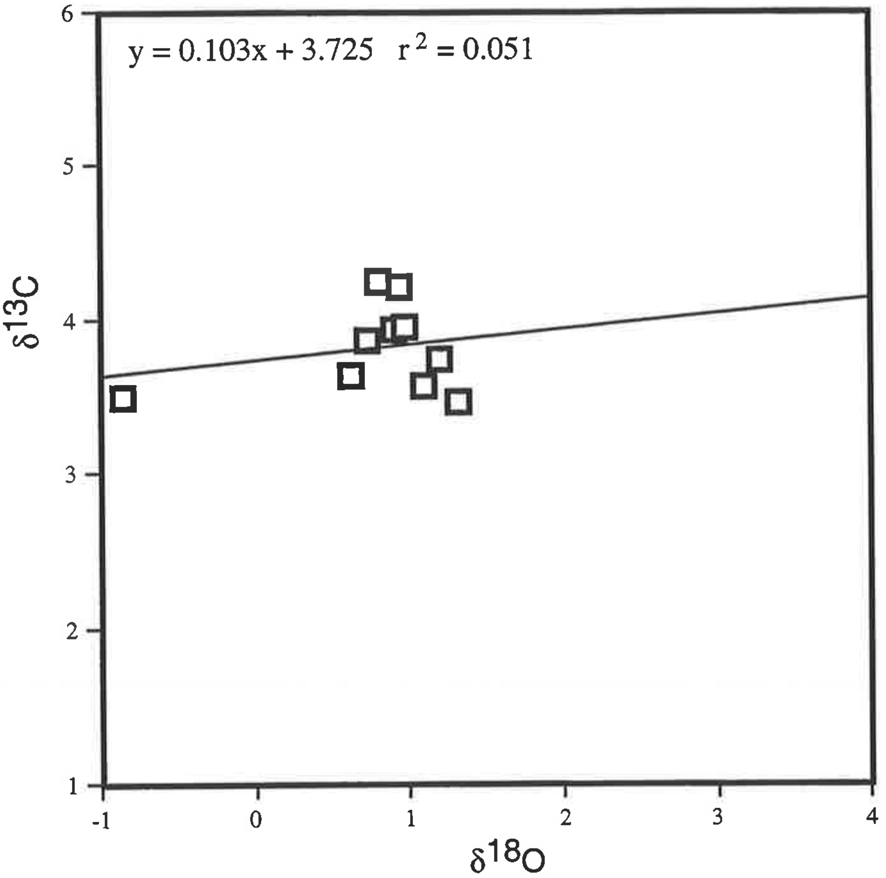


Fig. 9.13. Correlation between carbon and oxygen isotopes along different whorls of Turritellidae from the Cadell Marl.

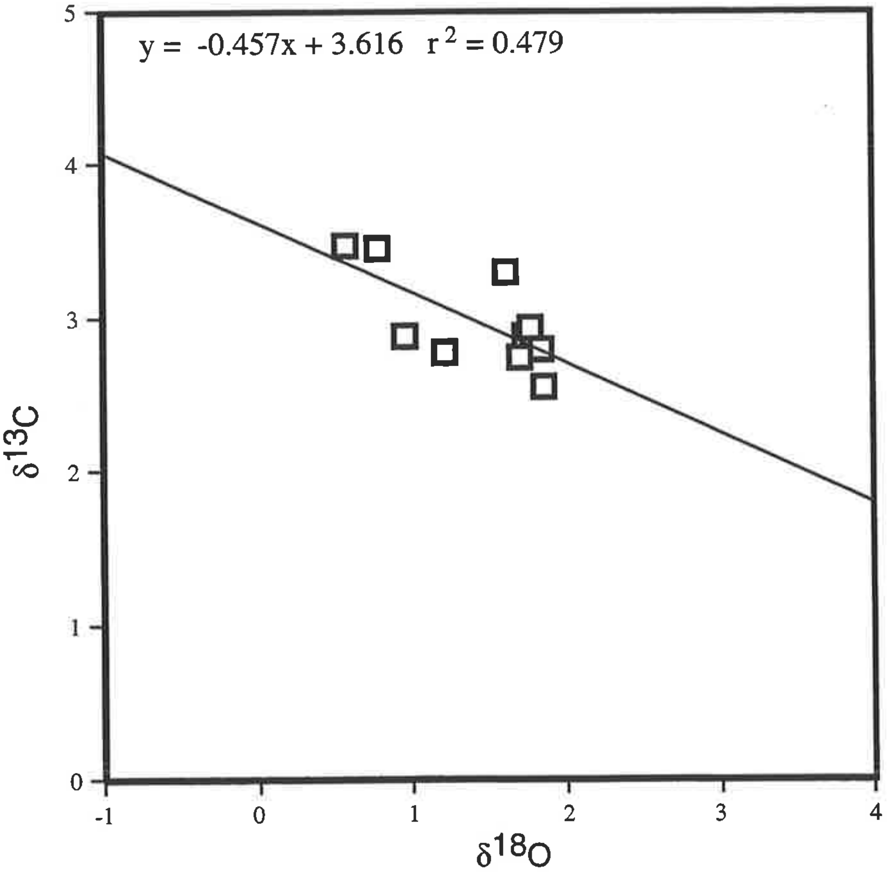


Fig. 9.14. Correlation between carbon and oxygen isotopes along different whorls of *Turritella* sp. from Lacepede Shelf.

contention about lack of metabolic effects in this bivalve. Moreover, there is no sign of major freshwater dilution in this unit, as seen in its isotopic profiles (Fig. 9.5). The strong positive $\delta^{13}C$-$\delta^{18}O$ correlation in Pecten fossil from the Cadell Marl, is apparently an environmental effect, and it probably indicates the negative relationship of temperature on both $\delta^{13}C$ and $\delta^{18}O$ content (depletion in $\delta^{18}O$ due to higher temperature and depletion in $\delta^{13}C$ due to higher growth rate caused by higher temperature, and vice versa), as seen in some foraminifera by Grossman and Ku (1986). The lack of $\delta^{13}C$-$\delta^{18}O$ correlation in *Pecten* sp. from the Lacepede Shelf, again demonstrates the lack of metabolic effects and the importance of upwelling events."

The Turritellidae fossil from the Gull Rock Member and the Cadell Marl both do not show any $\delta^{13}C$-$\delta^{18}O$ correlations, whereas the specimen from the Lacepede Shelf exhibits a relatively small negative $\delta^{13}C$-$\delta^{18}O$ correlation. The lack of $\delta^{13}C$-$\delta^{18}O$ correlation in the former represents the lack of metabolic effects and subsequent depletion in these gastropods. The ability of these gastropod to precipitate calcareous shells in isotopic equilibrium with their ambient waters, enabled them to record the environmental conditions and its variations with high resolutions (Figs 9.1 and 9.2). The presence of weak $\delta^{13}C$-$\delta^{18}O$ correlation in *Turritella* sp. from the Lacepede Shelf is not a metabolic effect, but is an environmental effect. As shown in Fig. 9.3, the relatively strong upwelling and productivity variations are recorded in the isotopic profiles of this organism, leading to the carbon and oxygen correlation.

9.5. Conclusion:

The stable isotopic records in the studied samples generally characterise their respective environments well. In particular, the overall $\delta^{18}O$ range and the presence or absence of a correlation between $\delta^{18}O$ and $\delta^{13}C$ exhibit the most consistent differences among environments. As expected, the $\delta^{18}O$ range is greater in upwelling periods, with its maximum degree shown in the Lacepede Shelf and its signature apparent in the Tertiary basins of St.Vincent and Murray.

Accordingly, the isotopic profiles of the Pecten samples from the different Tertiary units of the St.Vincent and Murray Basins, and the Holocene of the Lacepede Shelf, reveal variations in the isotopic signals. Presumably, since these samples are well preserved and precipitated their calcareous shells in isotopic equilibrium with their ambient waters, these variable isotopic signals are displaying the fluctuations in the environmental parameters.

The molluscs studied here (especially the gastropod) have recorded the annual temperature variations of ambient seawaters in their oxygen isotopic profiles, with high fidelity. The onset and termination of upwelling events are also recorded in the associated carbon isotopic signals. The $\delta^{13}C$ records also exhibit the variations in intensity of upwelling currents in these Tertiary and Holocene marginal basins. The systematic isotopic changes in these molluscan shells apparently reflect the annual seasonal changes in seawater temperature and chemistry.

CHAPTER TEN

CONCLUSIONS

10.1. Summary and Conclusions:

10.1.1. Holocene Cements:

The early marine cements from the Holocene cool-water/temperate carbonate environment of the Lacepede Shelf were precipitated in isotopic equilibrium with their ambient waters. The lower $CaCO_3$ saturation of seawater and the lower temperature lead to a lower precipitation rate and so diminished the influence of the kinetic effects on isotopic fractionation. Therefore, these inorganic carbonates represent the equilibrium isotopic values for the study area. These measured equilibrium values are compatible with the calculated equilibrium isotopic values for the study area.

10.1.2. Holocene Carbonate-Producers:

Coralline algae from the temperate environment of the study area show $\delta^{18}O$ values which are within, or close to, the equilibrium values and are heavier than their tropical counterparts. The $\delta^{13}C$ values of the studied coralline algae are similar to the $\delta^{13}C$ of their tropical counterparts.

The isotopic values of the studied ahermatypic corals are the heaviest isotopic compositions in this group that have been reported, confirming their lower calcification rates. However, even the studied coral samples that show the heaviest values of $\delta^{18}O$ and $\delta^{13}C$, are only partly in equilibrium with their ambient environments.

The studied bryozoan precipitated its calcareous skeleton in isotopic equilibrium with ambient waters and show higher $\delta^{18}O$ values in comparison with its tropical counterparts, probably due to the lower temperature of the study area. The $\delta^{13}C$ value of this bryozoan is within the range of the equilibrium values.

The $\delta^{13}C$ values of studied gastropods, contrary to their tropical counterparts, are in isotopic equilibrium with their ambient waters. The studied bivalves also show equilibrium $\delta^{13}C$ values. There are no significant metabolic effects on the $\delta^{18}O$ of the studied molluscs and it seems that $\delta^{18}O$ values in these molluscs are mainly controlled by ambient temperature.

Although $\delta^{18}O$ values of the studied brachiopods show some enrichment compared to equilibrium values, possibly because of the vital effect, the $\delta^{13}C$ values of these organisms are close to calculated equilibrium values.

Therefore, the slow precipitation of inorganic calcite and aragonite in lower temperatures produces an equilibrium isotope fractionation for carbon as well as oxygen, and diminishes the influence of kinetic effects. Consistently, biogenic carbonates produced by these cool-water organisms, generally reach equilibrium values due to lower temperatures and so slower precipitation rates, which in turn, diminishes the influence of kinetic/vital effects on the isotopic composition of these organisms. The rapid skeletal growth of different organisms under the higher temperatures of tropical carbonate environments is responsible for the general isotopic depletions (especially in the case of $\delta^{13}C$) observed.

For any $\delta^{18}O$ value, the photosynthetic coralline algae have heavier $\delta^{13}C$ values than non-photosynthetic ahermatypic coral, which suggests that photosynthesis elevates the skeletal $\delta^{13}C$ value, whereas respiration leads to depletion in $\delta^{13}C$ values.

10.1.3. Backtracking Technique:

This study also shows the importance of geochemical investigations on the Holocene carbonate environments for geochemical evaluation of their ancient counterparts. Accordingly, the isotopic composition of altered fossil samples can be retrieved in many cases by having a sound data base from their Holocene counterparts. The backtracking process can be employed to retrieve the original isotopic signature of the recrystallised, dissolved or contaminated fossil material. Although, paleoenvironmental interpretation can not be based solely on the backtracking data, a confident interpretation can be made by complementing this data with measured isotopic values from unaltered (pristine) fossil material.

10.1.4. Meteoric Diagenesis:

The carbonate sediments exposed in the meteoric systems undergo post-depositional alteration which eventually results in stabilisation of the metastable components of the carbonate sediments and precipitation of the diagenetic calcites as cement. The isotopic composition of these meteoric cements is influenced by the isotopic composition of both the original marine calcites and percolating meteoric fluids. Therefore, the isotopic composition of these cements are representative of the diagenetic fluids, the isotopic composition of which can be estimated from the isotopic composition of the cement. These estimates provide essential constraints for evaluating the nature of secular changes with time in the ocean and meteoric water chemistry. The diagenetic setting and processes involved in the formation of these cements are also recognisable from the isotopic composition of these cements.

The observed variations in $\delta^{18}O$ values of the studied calcite cements suggest formation from different $\delta^{18}O_{meteoric\text{-}water}$. The ultimate source of the meteoric water is seawater. The variations in $\delta^{18}O$ values reflect the northward drift of Australia during the Cenozoic.

10.1.5. Marine Sea-level Changes:

The isotopic study of different fossil samples revealed that the $\delta^{13}C$ variations mainly reflect secular variations in $\delta^{13}C_{DIC}$ of seawater during the Tertiary, and are neither facies-controlled nor influenced by diagenetic alterations. The global $\delta^{13}C$ cycles of Tertiary time are recorded in the isotopic signature of this fossil material. The $\delta^{18}O$ data of different fossils of the study area are successfully utilised for the reconstruction of sea-level fluctuations and estimations of paleotemperature.

The Monterey Excursion caused deposition of the Cadell Marl with an exceptionally heavy isotopic signature in the earliest Middle Miocene. The inception of ice-sheet growth in Antarctica in the Middle/Late Miocene, led to a global sea-level fall and climatic deterioration. This sea-level fall imposed some restrictions in the Murray Basin, which led to an increased influx of fresh-water runoff and organic material into the basin waters. This led to a light isotopic signature in the calcareous fossils in the Upper Morgan Limestone.

The general trend in $\delta^{18}O$ value of seawater, which shown an increase from the Early Eocene to the Holocene, is reflected in the isotopic composition of the different studied macrofossils.

10.1.6. Paleogeography:

The $\delta^{18}O$ values of the meteoric cements from different stratigraphic intervals during the Cenozoic (and hence, from diverse paleolatitudes) exhibit a negative correlation with paleolatitude, which is consistent with theoretical findings. These observations indicate that the meteoric cements, despite some inconsistencies due, for example, to evaporation and seawater mixing with groundwaters, were precipitated in a manner such that they give near equilibrium values for their parent fluids. Consequently, these cements have approximately recorded the variations in temperature of their ambient environment, reflecting variations in the $\delta^{18}O$ value of their parent meteoric waters, which in turn are mainly due to latitudinal changes of these Tertiary basins. The terrestrial paleoclimate and paleotemperature are reflected by the meteoric cements of the marine carbonate sediments, and are compatible with those derived from different fossil samples of these marine carbonates, which indicates the credibility of the data and a mutual interaction between the marine environment and the adjacent coastal area.

10.1.7. Paleoenvironment and Paleoclimatology:

The stable isotopic profiles of molluscs generally characterise their respective environments. In particular, the overall $\delta^{18}O$ range and the presence or absence of a correlation between $\delta^{18}O$ and $\delta^{13}C$ exhibits the most consistent differences among environments. As expected, the $\delta^{18}O$ range is greater in periods of upwelling, reflected most clearly on the Lacepede Shelf and can be traced in the Tertiary of the St.Vincent and Murray Basins.

The Pecten samples from the different Tertiary units of the St.Vincent and Murray Basins, and the Holocene of the Lacepede Shelf, reveal variations in the isotopic signals. Since these samples are well preserved and precipitated their calcareous shells in isotopic equilibrium with their ambient waters, these variable isotopic signals are displaying fluctuations in the environmental parameters.

Evidently, the molluscs studied here (especially gastropods) have recorded the annual temperature variations of the ambient seawaters in their oxygen isotopic profiles, with high fidelity. The onset and termination of annual upwelling events are also recorded in the associated carbon isotopic signals. The $\delta^{13}C$ records also exhibit the variations in intensity of upwelling currents in these Tertiary and Holocene marginal basins. These systematic isotopic changes in molluscan shells apparently reflect the annual seasonal changes in seawater temperature and chemistry.

10.1.8. Final Conclusion:

Finally, the contention of this study is that the Holocene marginal marine cool-water/temperate carbonate environments and their ancient counterparts deserve more attention with regard to different aspects of carbonate production and biomineralisation. Because organisms in temperate environments generally precipitate their calcareous shell/skeleton in isotopic equilibrium (or close to it) with their ambient environment, they are excellent recorders of their environmental conditions. Application of these findings to their Tertiary counterparts provide significant information about different aspects of paleoenvironment, paleoclimate and diagenesis in cool-water/temperate carbonate sediments.

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APPENDIX I: Publications related to this work:

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Stable isotope aspects of modern molluscs, brachiopods, and marine cements from cool-water carbonates, Lacepede Shelf, South Australia

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Abstract—The isotopic composition of some modern gastropods, bivalves, and brachiopods from the Lacepede Shelf of South Australia were investigated to determine the isotopic equilibrium and disequilibrium states of biogenic and non-biogenic (inorganic) carbonates and to understand the kinetic and metabolic isotopic effects on precipitating carbonates and the isotopic fractionation between these different carbonates and dissolved bicarbonate. Seawater and high Mg-calcite (HMC) marine cements from different depths were also analyzed to determine equilibrium isotopic composition.

This study shows that the shells of some cool-water gastropods and bivalves precipitate in isotopic equilibrium with their ambient waters while brachiopod shells show ^{18}O values heavier than equilibrium values and coralline algae, and ahermatypic corals exhibit significant metabolic and kinetic effects. The isotopic equilibrium precipitation seen in these biogenic carbonates results from lower precipitation rates that are, in turn, caused by the lower bottom temperatures in this area. *Copyright © 1997 Elsevier Science Ltd*

1. INTRODUCTION

Relative concentrations of the stable isotopes of carbon and oxygen in biogenic and inorganic carbonates give information about the different mechanisms of $CaCO_3$ precipitation. Most investigations, until recently, have focused on tropical skeletal and non-skeletal carbonates. There is a paucity of knowledge about cold/cool water skeletal and non-skeletal carbonate isotopic compositions, equilibrium states, and precipitation rates. Grossman (1984) stated that "our understanding of ^{13}C fractionation in biogenic carbonate suffers from a poor understanding of isotopic equilibrium at low temperatures due to the lack of inorganic precipitation data. Further studies should focus on this problem and also on determining accurate $\epsilon_{s\text{-}b}$ ($\delta^{13}C_{\text{calcium carbonate–DIC}}$ fractionation) values for other fauna (other than foraminifera) that are known to precipitate their shells in ^{18}O equilibrium with the water." As such, Romanek et al. (1992) stated that in spite of the fact that carbon isotopes are widely used in carbonates as paleoenvironmental and diagenetic tools, there are few comprehensive studies on the influences of mineralogy, temperature, and precipitation rates on the isotopic fractionation of carbonates. Our aims in this study were to document the skeletal and non-skeletal carbonates of the cool–water environments of the Lacepede Shelf, South Australia, their equilibrium or disequilibrium states in the case of the inorganic and organic (mollusc) precipitation, the relationship of the isotopic composition with precipitation rates, and comparisons with similar organisms from warm–water environments. Additionally, temperature and $^{18}O/^{16}O$ ratios have been studied over the available temperature ranges of this environment.

The isotopic composition of carbonate skeletons and cements varies in response to a wide range of environmental parameters (extrinsic factors) such as evaporation, condensation, precipitation rates, and temperature. In the case of biogenic carbonates, intrinsic factors such as metabolic fractionation and photosynthesis could also influence the isotopic compositions. The source of C and O also has a major influence on the isotopic composition of the precipitated carbonates. Mineralogy has some effects on the isotopic composition of precipitating carbonates, as aragonite co-precipitating with calcite in the same environment is enriched in heavier carbon and oxygen isotopes. The mineralogical enrichment itself is probably dependent on the precipitation rate that, in turn, could be influenced by the temperature of the ambient water, at least in biogenic aragonite (Grossman and Ku, 1986). Kinetic effects, the major cause of the simultaneous depletion of carbon and oxygen isotopes in high precipitation rates, are reduced by a decrease in the precipitation rates (e.g., Turner, 1982).

Salinity does not affect the isotopic composition of biogenic or inorganic carbonates, but its variation from the normal values for the open seas indicates the influences of different factors such as evaporation or influx of freshwater runoff. Freshwater dilution causes lighter isotopic values in the resulting precipitating carbonates. It seems that the small influx of River Murray waters onto the Lacepede Shelf (Fig. 1) has not had a major effect on the seawater salinity because the salinity in this area is in the normal range. In this area, evaporation is not important because of year-round low temperatures.

Disequilibrium in the isotopic composition of biogenic carbonates could be caused by either metabolic or kinetic effects. In the case of metabolic effects, respiration usually leads to ^{13}C depletion in biogenic carbonates whereas photosynthesis leads to ^{13}C enrichment. Therefore, if only the $\delta^{13}C$ is out of equilibrium, the disequilibrium could be ascribed to metabolic effects. Kinetic effects on carbonate precipitation, however, involve discrimination against both heavy isotopes, carbon and oxygen. Kinetic effects seem to be particularly effective during rapid carbonate precipitation in nonbiogenic (inorganic) (Turner, 1982) and biogenic carbonates (e.g.,

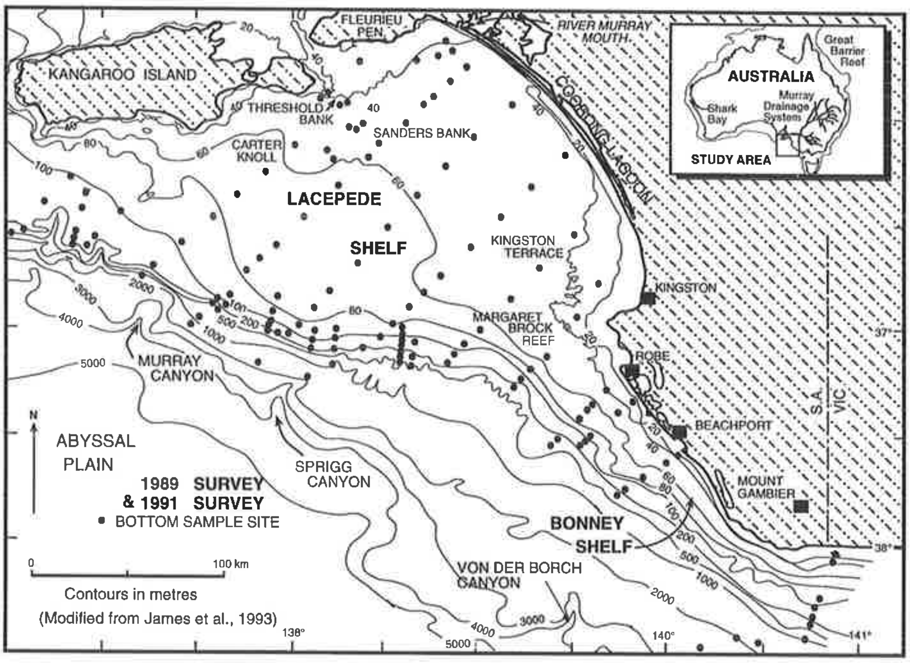


Fig. 1. Location map of the Lacepede Shelf, South Australia.

Weil et al., 1981; McConnaughey, 1989a,b). On the other hand, in cool/temperate carbonate environments, the growth rates of the different calcareous organisms are slow due to low temperatures. Moreover, at low temperatures, inorganic carbonate cement is not common and precipitates slowly.

In cool/temperate environments, usually because of lower temperatures, growth rates tend to be slow, and, similar to other oceanic environments, the $\delta^{18}O$ of seawater is constant and close to 0.0‰. Therefore, the $\delta^{18}O$ of calcareous molluscs is mainly dependent on the temperature of ambient waters and possible kinetic effects. On the other hand, factors that influence the $\delta^{13}C$ values of marine biogenic carbonates include (1) the isotopic composition of the inorganic carbon dissolved in seawater (DIC), (2) the equilibrium fractionation factors between the various forms of carbon, (3) dependency and variations of the $\delta^{13}C$ fractionation factors with temperature, (4) influx of $\delta^{13}C$-depleted upwelling currents, and (5) the possible influence of the metabolic and/or kinetic effects. Therefore, before utilising the $\delta^{18}O$ and $\delta^{13}C$ of biogenic carbonates for paleoenvironmental studies, it should be verified that they are precipitated in isotopic equilibrium with their ambient waters and that no significant metabolic or kinetic effects were exerted over their isotopic compositions. For this approach, two methods can be followed. First, the inorganic carbonates that usually precipitate as HMC or aragonite marine cements can be analyzed for mineralogy and isotopic composition. The isotopic composition of synsedimentary marine cements reflects the equilibrium isotopic values (Lohmann and Meyers, 1977; González and Lohmann, 1985). The second method is the calculation of the equilibrium inorganic carbonate (high Mg-calcite (HMC), low Mg-calcite (LMC), and aragonite) that could precipitate from this seawater under equilibrium conditions. These calculations require the assessment of the isotopic composition and temperature record of the seawater of the study area. The resultant equilibrium values obtained from these two different methods should be close, or ideally, identical. Thus, resultant data on the isotopic equilibrium values of inorganic carbonates (that obviously are not affected by metabolic effects) could be compared with the isotopic composition of the different biogenic carbonates of the diverse organisms from this area. These comparisons would exhibit either equilibrium or disequilibrium within the isotopic composition of the different biogenic carbonates.

Three major classes of molluscs, the bivalves, cephalopods and gastropods, are among the major carbonate producers in recent and ancient marine environments. They have been studied from diverse aspects such as mineralogy, microstructures, and geochemistry (Milliman, 1974; Bathurst, 1975; Grossman and Ku, 1986; Morrison and Brand, 1986; Wefer and Berger, 1991).

Bivalve molluscs live in different marine environments, from warm tropical seas to subfreezing Arctic and Antarctic waters. They are epifaunal or infaunal and live as vagile or sessile organisms, with some of them nektonic. Calcification rates in molluscs are dependent on environmental factors such as temperature, energy, substrate, and some biological factors. Bivalves are aragonitic or calcitic, and some of them have mixed layered shells. Their mineralogy and shell structure remain constant within any super-family. *Pecten* sp. (*Chlamys* sp., super Family Pectinidae), one of the subjects of our study, is mainly calcitic with some (up to 5%) aragonite, as shown by XRD analysis. This bivalve is widespread on the Lacepede Shelf. Gastropods are mainly aragonitic and, similar to bivalves, they secrete thinner shells in cooler and calmer waters and thicker shells in turbulent (agitated) waters. They inhabit diverse environments and most of them are epifaunal but a few are infaunal. *Turritella* sp. (*Ga-*

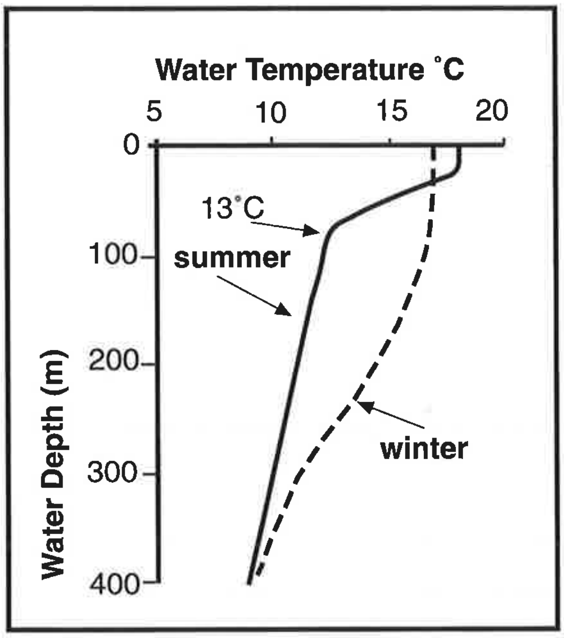


Fig. 2. The summer and winter temperature profiles for the Lacepede Shelf area. (modified from James et al., 1992)

zameda sp., Family Turritellidae), which has been studied in this research, is an aragonitic gastropod which lives in sands and silts, especially among the roots of sea grasses or algae.

2. GEOLOGICAL SETTING

The Lacepede Shelf is situated on the southern coast of South Australia. It is an open shelf with an area of 130 × 190 km (Fig. 1). This shelf is swell–dominated and is a typical temperate/cool–water carbonate environment. During summer, episodes of minor upwelling currents from the Bonney Shelf influence the seawater composition (Schahinger, 1987; Cai Wenju et al., 1991).

Shelf waters are low in nutrients throughout most of the year (Schahinger, 1987). James et al. (1992) provided temperature data for the Lacepede Shelf and neighbouring area. Their seawater temperature profiles (Fig. 2) show variations of bottom temperature with depth during summer and winter, and indicate summer temperature stratification. In summer, three temperature zones are indicated (1) a mixed surface layer (0–30 m) with an average of 18°C throughout; (2) from 30–80 m depth, the bottom temperature drops from about 18°C to an average of 13°C; and (3) below depths of 80 m, bottom temperature decreases about 1°C for every 100 m, to 600 m depths. During winter months, the shelf water temperature down to a depth of 100 m is about 17–18°C, with temperature decreasing 1°C per 50–100 m below 100 m. River Murray waters do not influence the shelf waters (James et al., 1992). Sponges, molluscs, bryozoans, and foraminifers are the most abundant benthic organisms on the shelf, with less significant groups being echinoids, brachiopods, ahermatypic corals, and serpulids. Crustaceans, coralline algae, hydroids, gorgonians, and ostracods are present in most sediments, but usually form less than 5% of bulk sediments.

3. METHODS

Isotopic composition of thirty-one samples of the gastropod *Turritella* (*Gazameda* sp.) and the bivalve *Pecten* (*Chlamys* sp.), ten brachiopods, nine HMC marine cements, and eleven water samples have been measured. The samples were collected during the cruises FR3/89 and FR2/91 of CSIRO R.V. *Franklin,* during March 1989 and January 1991, respectively. Samples were dredged using a simple Bleys Dredge, with a volume of approximately 20 L. Therefore, sediment samples are a mixture of surface and subsurface materials to depths of 5–10 cm. Bathymetry was determined by precise depth recording. Surface temperature was recorded every 10 min, and vertical temperature profiles for nineteen selected positions were determined by expendable bathythermography (XBT) (Bone and James, 1993). Samples were analyzed for their oxygen and carbon isotopes using a Micromass Model 602E stable isotope mass spectrometer. Mineralogy was determined by X–Ray diffraction (XRD) in all samples, using standard techniques (e.g., Tucker, 1988). For $MgCO_3$ measurements, the chart introduced by Goldsmith et al. (1961) was used, and precision is 0.5 mol%. All samples were washed in commercial bleach to remove the organic materials, then rinsed by deionised water and dried as recommended by Love and Woronow (1991) and Gaffey and Bronnimann (1993). They were cleaned several times, by brush, for removal of the adherent sediments. Samples were then powdered by dental drill or with pestle and mortar. The calculations of the isotopic equilibrium for seawater in this area require the measurement of stable carbon and oxygen isotopes in seawater and dissolved inorganic carbon. For this purpose, ten seawater samples collected from the study area and nearby surrounds had been examined. The dissolved inorganic carbon (DIC) in seawater samples was analyzed for $\delta^{13}C$ content, using methods similar to those of Kroopnick (1974a,b). The $\delta^{18}O$ content of water samples was determined by the CO_2-H_2O equilibration at 25°C, followed by mass spectrometer analysis of CO_2 as proposed by Epstein and Mayeda (1953). Carbon and oxygen isotopes of carbonates are displayed in the standard form of permil PDB and for $\delta^{18}O$ of seawater permil SMOW, with δ notation. The average precision of samples is ±0.2‰ for oxygen and ±0.1‰ for carbon. All measurements of seawater samples were duplicated.

To calculate the equilibrium LMC marine cements, the following equation (Shackelton and Kennett 1975a,b; Wefer and Berger, 1991) has been used:

$$T(^{\circ}C) = 16.9 - 4.38(\delta c - \delta w) + 0.10(\delta c - \delta w)^2 \quad (1)$$

To calculate the equilibrium potential aragonite marine cement that could precipitate in the study area the following equation, which was established by Tucker and Wright (1990, p. 310) combining results of Grossman and Ku (1986), is used:

$$t(^{\circ}C) = 20.6 - 4.34(\delta^{18}O_{arg} - \delta w) \quad (2)$$

The following equation for calculation of $\delta^{13}C$ values of equilibrium inorganic aragonite (Grossman and Ku, 1986) has been used:

$$\delta^{13}C - \delta^{13}C_{DIC} = 2.66 - 0.131t(^{\circ}C) \quad (3)$$

4. RESULTS AND DISCUSSION

The seawater samples have average $\delta^{18}O$ values of 0.0‰ (SMOW) (Table 1). The $\delta^{13}C$ values of dissolved bicarbonates in seawater of this area are between 0.0 to +0.5‰ (PDB) (Table 1). The differences between the duplicate samples were 0.05‰ and 0.08‰ for $\delta^{13}C$ (PDB) and $\delta^{18}O$ (SMOW), respectively. Mineralogy and $MgCO_3$ content and isotopic composition of the marine cement found inside some samples from different depths have been measured. All marine cements are HMC with $\delta^{18}O$ values between 1.75 to 1.0‰ and $\delta^{13}C$ values of 1.62 to 2.86‰ (Table 2). The

Table 1. Isotopic composition and temperature of seawater from Lacepede Shelf and Great Australian Bight at different depths, January 1995 and October 1995.

Depth (m)	Temp. (°C) Summer	Temp. (°C) Winter	δ^{18}O	δ^{13}O
0*	18	17	0.05	0.7
0*	18	17	0.0	0.6
0*	18	17	0.04	0.6
0*	18	17	0.03	0.2
0*	18	17	0.05	0.7
20	18	17	0.05	0.6
40	16	17	0.0	0.2
60	14	16.5	0.03	0.4
100	12.5	16	0.04	0.1
200	11	15	0.06	0.2

* Lacepede Shelf.

isotopic compositions of *Pecten* sp., *Turritella* sp. and brachiopods of the Lacepede Shelf area are shown in Tables 3 and 4.

4.1. Seawater Composition

In the study area, the $\delta^{13}C_{DIC}$ of the seawater samples showed values between +0.05 to +0.7‰ (Table 1), which are somewhat lighter than typical values of seawater which are between −1 to +2‰ (Deuser and Degens, 1967; Deuser and Hunt, 1969; Vogel et al., 1970; Weber and Woodhead, 1971; Kroopnic, 1974a,b, 1985; Land, 1989). These relatively light $\delta^{13}C_{DIC}$ possibly are a reflection of the influx of the ^{13}C-depleted upwelling current in the neighbouring areas. Thus, in the temperate environment of the Lacepede Shelf and the Great Australian Bight, the $\delta^{13}C_{DIC}$ value of seawater shows relatively lower values in comparison with average values.

4.2. Inorganic Carbonates

For the investigation of the isotopic equilibrium and disequilibrium, kinetic and metabolic effects in different taxa and inorganic carbonates (marine cements), mineralogy and isotopic composition of these carbonates, as well as temperature and isotopic composition of the ambient seawater, have been measured. These studies showed that the Lacapede Shelf HMC cements have precipitated in isotopic equilibrium with their ambient waters (Table 2). Therefore, they can be used as a standard for distinguishing equilibrium vs. disequilibrium in the isotopic composition of different biogenic carbonates. The values are within the range of the isotopic composition of inorganic equilibrium calcites from other areas (Morrison and Brand, 1986; Land, 1989) (Fig. 3). The values for the study area are confirmed by calculating the isotopic equilibrium values by measuring the seawater isotopic composition and the temperature ranges of this area. For calculation of the equilibrium isotopic fractionations in inorganic equilibrium marine calcite from this area, mean annual temperature recorded in each sampling site has been used.

Table 2. Isotopic compositions and calculated isotopic temperatures of the HMC marine cements (corrected values for $MgCO_3$ content) found at different depths, compared with measured temperatures in the study area.

Depth (m)	Measured temp. (°C) Summer	Measured temp. (°C) Winter	δ^{18}O	δ^{13}C	Calculated temp. (°C)
65	14.2	16.8	1.00	2.39	15.7
70	13.5	16.8	1.20	2.42	14.8
80	13.0	16.8	1.35	2.40	14.0
90	12.3	16.8	1.40	2.35	13.9
100	12.0	16.4	1.75	2.86	12.4
100	12.0	16.4	1.30	2.30	13.8
120	11.8	15.3	1.40	2.34	14.0
180	11.0	15.0	1.60	1.80	12.8
300	10.0	11.2	1.68	1.62	10.8

Table 3. Isotopic composition of *Pecten* sp., *Turritella* sp., and brachiopods from the Lacepede Shelf, South Australia.

Sample name	Depth (m)	Measured temp. (°C) Summer	Measured temp. (°C) Winter	Isotopic δ^{18}O	Composition δ^{13}C
Pecten	45	16.2	16.9	0.95	2.6
Turritella	50	15.8	16.9	1.95	2.68
Pecten	55	15	16.9	0.54	1.31
Pecten	55	15	16.9	0.46	1.12
Turritella	55	15	16.9	1.25	3.26
Turritella	65	14.2	16.8	1.74	3.34
Turritella	65	14.2	16.8	1.32	3.4
Turritella	70	13.5	16.8	1.2	2.75
Pecten	70	13.5	16.8	0.76	1.43
Pecten	80	13	16.8	0.69	1.8
Turritella	80	13	16.8	1.21	2.54
Turritella	85	12.8	16.6	1.35	3.26
Pecten	85	12.8	16.6	0.83	2.2
brachiopod	85	12.8	16.6	0.75	2.29
Pecten	90	12.3	16.5	0.57	1.5
Turritella	90	12.3	16.5	1.23	3.13
brachiopod	90	12.3	16.5	1.23	1.52
Turritella	100	12	16.4	1.49	2.77
Turritella	100	12	16.4	1.36	3.34
Pecten	100	12	16.4	0.56	1.95
Pecten	100	12	16.4	0.69	2.71
Pecten	100	12	16.4	0.92	2.38
brachiopod	100	12	16.4	1.86	2.53
Turritella	140	11.3	15.9	1.39	3.22
Pecten	170	11.3	15.2	0.65	1.75
brachiopod	170	11.3	15.2	2.15	2.08
Pecten	180	11	15	0.92	2.42
Pecten	180	11	15	0.85	2.2
Turritella	180	11	15	1.5	3.2
brachiopod	180	11	15	2.06	2.45
brachiopod	180	11	15	2.03	2.98
Turritella	190	10.9	14.8	1.8	3.22
Pecten	220	10.8	14	0.67	1.8
brachiopod	220	10.8	14	1.9	2.08
Pecten	250	10.5	13	0.75	1.95
brachiopod	250	10.5	13	1.8	2.12
Pecten	300	10	11.2	0.98	2.42
Turritella	300	10	11.2	1.59	3.34
brachiopod	300	10	11.2	1.8	2.63
Pecten	350	9.5	10.2	0.67	1.75
brachiopod	350	9.5	10.2	2.31	1.96

Table 4. Isotopic temperature calculated from aragonitic and calcitic molluscs of the Lacepede Shelf area from the same sampling sites, and comparisons with the recorded summer and winter temperatures.

Depth (m)	Measured temp. °C Summer	Measured temp. °C Winter	Calcitic $\delta^{18}O$	Mollusc $\delta^{13}C$	*Pecten* temp. calc. (°C)	Aragonitic $\delta^{18}O$	Mollusc $\delta^{13}C$	*Turritella* temp. calc. (°C)
55	15.1	16.9	0.46	1.21	14.9	1.25	3.26	14.6
70	13.5	16.8	0.76	1.43	13.6	1.20	2.75	14.8
80	13	16.8	0.57	1.50	14.4	1.20	2.54	14.8
90	12.3	16.8	0.69	1.80	13.8	1.23	3.13	14.7
100	12	16.4	0.56	1.98	14.4	1.49	2.77	13.6
180	11	15	0.85	2.20	13.1	1.50	3.20	13.5
300	10	11.2	0.98	2.42	12.6	1.59	3.34	13.1

Turner (1982) suggested that the $\delta^{13}C$ isotopic fractionation factor in $HCO_3^- - CaCO_3$ is dependent on the rate of precipitation and mineralogy: the $\delta^{13}C$ value in carbonates decreases with increasing precipitation rates, and a very slow precipitation rate could produce $\delta^{13}C$ enrichment in the solid carbonate phase. At low rates, this fractionation is up to 3.37 ± 0.36‰, but with an increase in precipitation rates, this decreases to 0.35 ± 0.23‰ at 25°C. At slow precipitation rates (no significant kinetic effects) the fractionation factor of $\delta^{13}C_{bicarbonate-aragonite}$ is up to 3.8 ± 0.35‰, $\delta^{13}C_{bicarbonate-calcite}$ is up to 2.26 ± 0.31‰, and $\delta^{13}C_{calcite-aragonite}$ may reach 1.6 ± 0.35‰. However, Romanek et al. (1992) concluded from experimental work on inorganic carbonates that the precipitation rates have no significant effect on $\delta^{13}C_{calcite-HCO_3^-}$ fractionation. They suggest that temperature does not affect the $\delta^{13}C$ of inorganic aragonite, and that temperature dependence of $\epsilon\delta^{13}C_{aragonite-HCO_3^-}$ in biogenic aragonite may reflect an increase in the influence of metabolic effect with temperature. They concluded that discrepancies between measured $\delta^{13}C$ values and experimental values do not reflect temperature or precipitation rates, but, rather, reflect (1) the difficulty in determining experimentally the real isotopic

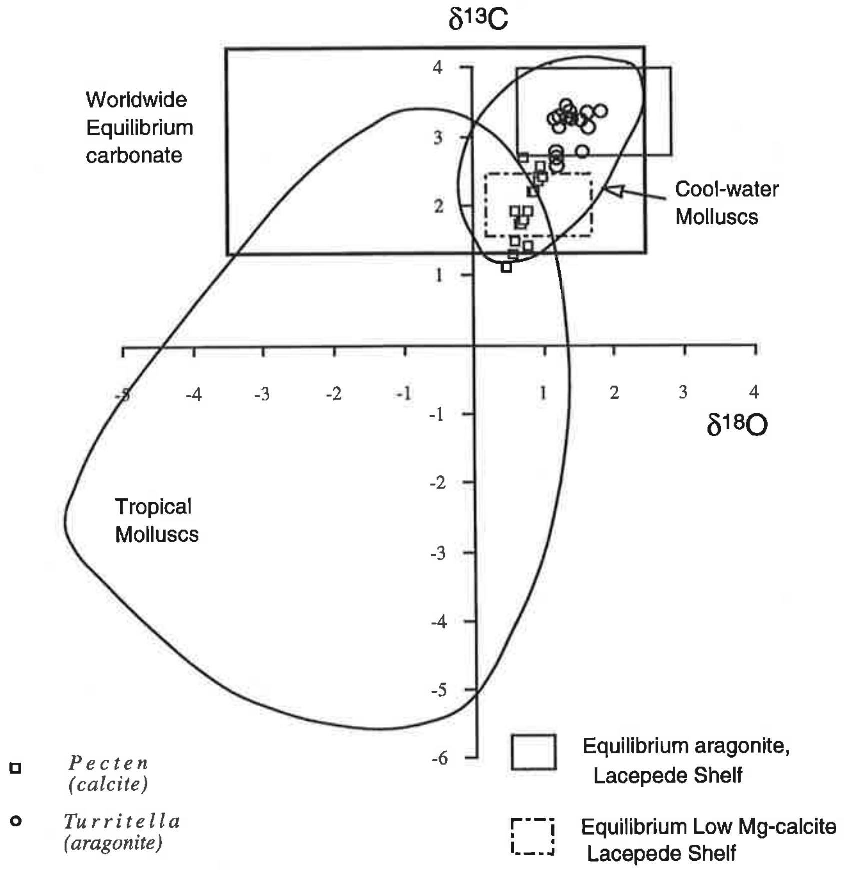


Fig. 3. Comparison between isotopic composition of various molluscs from cool-water carbonate environments with their tropical counterparts. Tropical data from Land (1989, and references therein) and world-wide equilibrium values form Morrison and Brand (1986), Land (1989), and McConnaughey (1989).

composition of the precipitating fluid (probably because of microenvironments), and (2) the metabolic effects and physiological microenvironments. However, in biogenic carbonates, the results similar to the experiments of Turner (1982) on precipitation rates and heavy carbon and oxygen isotope contents have been found. Accordingly, Land et al. (1975) showed that faster growing parts of photosynthetic corals are depleted in $\delta^{18}O$ and $\delta^{13}C$ compared to slower growing parts. These phenomena have been demonstrated by many workers for diverse biogenic carbonates (Vinot-Bertouille and Duplessy, 1973; Erez, 1977, 1978; Weil et al., 1981; McConnaughey, 1989a,b). On the other hand, the fractionation factor and precipitation rate, at least in most biogenic carbonates, are dependent on the temperature of the ambient waters and, as shown in cool–water carbonate environments, the latter decreases with the decline in the temperature of the ambient water. Grossman and Ku (1986) found similar results in the study of biogenic aragonite. Again, the experimental works of Romanek et al. (1992) have not demonstrated any clear temperature dependency of $\delta^{13}C$ fractionation in synthetic aragonite and calcite.

4.3. The $\delta^{18}O$ Equilibrium Calculations

To evaluate deviations from equilibrium values in the biogenic carbonate, we calculated potential equilibrium marine cements that could precipitate from seawater in this area. These results were compared with the actual values of HMC marine cements (Rahimpour-Bonab et al., 1997). The $\delta^{18}O$ of the equilibrium potential LMC marine cement (that theoretically could precipitate from seawater in this area) has been estimated by applying the seawater isotopic values and temperature records of the study area (Tables 1, 2) to Eqn. 1. It gives 0.25 to 1.8‰ for $\delta^{18}O$ values of potential equilibrium inorganic LMC. The $\delta^{18}O$ of potential equilibrium inorganic HMC (11 mol% $MgCO_3$), by applying corrections for $MgCO_3$ content (Tarutani et al., 1969), is 0.94 to 2.46‰. These results are close to $\delta^{18}O$ values of HMC marine cements (1.0 to 1.75‰) found in this area (Table 2). Therefore, isotopic values of HMC marine cement reconfirm the calculated equilibrium values for this area and agree with similar findings by (Aharon, 1991) that marine cement could precipitate in equilibrium with its environment. Due to the temperature prevailing in this area, however, aragonite has not precipitated as an inorganic marine cement in the area. Therefore, $\delta^{18}O$ of potential equilibrium aragonite has been calculated by Eqn 2 and gives values of 0.6 to 2.7‰. Moreover, to compare and substantiate these figures, the $\delta^{18}O$ values measured in cements have been corrected by applying appropriate corrections for fractionation between calcite and aragonite (Tarutani et al., 1969), giving $\delta^{18}O$ values of 1.6 to 2.35‰, which are close to calculated values.

4.4. The $\delta^{13}C$ Equilibrium Calculations

It has been shown by many workers (e.g., Nelson, 1988, and references therein) in temperate environments that because of low temperature, precipitation rates are slow. Therefore, kinetic effects have minimal influence on the fractionation factor of the $\delta^{13}C_{HCO_3^{-}-Calcite}$. Thus, the $\delta^{13}C$ values of carbonates could reach maximum values in such cool water environments, i.e., about 2.3‰ (Bottinga, 1968) or 2.26 ± 0.32‰ (Turner, 1982) heavier than $\delta^{13}C_{DIC}$. The $\delta^{13}C$ values of inorganic HMC cement from this area are between +1.62 to +2.86‰ (Table 2). Considering the fractionation factor for HCO_3^- − Calcite of about 2.26‰ and seawater DIC values between 0.0 to +0.50‰ in this area, HMC equilibrium cement would have $\delta^{13}C$ values between 1.51 to 2.46‰. These figures are close to the $\delta^{13}C$ values of the HMC marine cements (+1.62 to +2.86‰) found in the area. Using Eqn. 3 gives $\delta^{13}C$ values between 0.57 to 1.15‰ for equilibrium aragonite, but using the correction introduced by González and Lohmann (1985) (average $\epsilon^{13}C_{aragonite-calcite} = 1.2‰$), values of 2.8 to 4.05‰ for $\delta^{13}C$ of equilibrium aragonite have resulted.

4.5. Biogenic Carbonates

Apparently, the slow precipitation of inorganic calcite and aragonite from dissolved bicarbonates in seawater produces an equilibrium isotope fractionation for carbon, as well as oxygen, and diminishes the influence of kinetic effects. Accordingly, biogenic carbonates produced by some of these organisms that do not exert significant metabolic effects over their isotopic values could reach equilibrium values if their precipitation rates are slow. This has been demonstrated in some cool–water carbonate organisms of the Lacepede Shelf, e.g., bryozoans (Rahimpour-Bonab et al., 1997) and molluscs (this study). The aragonitic gastropod *Turritella* sp. shows some enrichment in its ^{13}C and ^{18}O compared to the calcitic bivalve *Pecten* sp. (Fig. 4). This isotopic enrichment in aragonite over calcite is about 1.5‰ in $\delta^{13}C$ and 0.8‰ in $\delta^{18}O$ and is in the range or close to the $\delta^{18}O_{calcite-aragonite}$ and $\delta^{13}C_{calcite-aragonite}$ enrichment values that are suggested by the many workers mentioned earlier.

The $\delta^{13}C$ composition of the biogenic aragonite could be influenced by other factors besides temperature. Metabolic effects, as seen in corals and coralline algae and some other taxa, can lead to either positive or negative deviations of the $\delta^{13}C$ from equilibrium values. In *Turritella* sp., however, as our results show, there is no significant biogenic fractionation and the isotopic composition is within the values for equilibrium inorganic aragonite (Fig. 4). Therefore, it could be concluded that variations in the $\delta^{13}C$ values of *Turritella* sp. are possibly caused by the temperature effect on the aragonite–sea water DIC fractionation ($\delta^{13}C_{biogenic\ aragonite-DIC}$) and DIC isotopic variations with depth. *Turritella* has an average $\delta^{13}C$ enrichment factor of 2.75‰ relative to $\delta^{13}C_{DIC}$, which is close to estimated equilibrium values introduced by Rubinson and Clayton (1969) and Grossman (1984).

Unlike the calcitic foraminifera examined by Grossman (1984), our calcitic bivalve *Pecten* sp. is not depleted in $\delta^{13}C$, but is actually enriched in $\delta^{13}C$ relative to the $\delta^{13}C_{DIC}$ (Fig. 4). This $\delta^{13}C$ enrichment is possibly because of the low precipitation rates of carbonates in this cool–water environment, enabling maximum fractionation between dissolved bicarbonates and aragonite/calcite systems. *Pecten* sp. has an average $\delta^{13}C$ enrichment factor of 1.5‰ relative to $\delta^{13}C_{DIC}$. This contradicts the opinion of Morse and Mackenzie (1990) that the $\delta^{13}C$ values of calcitic shells usually

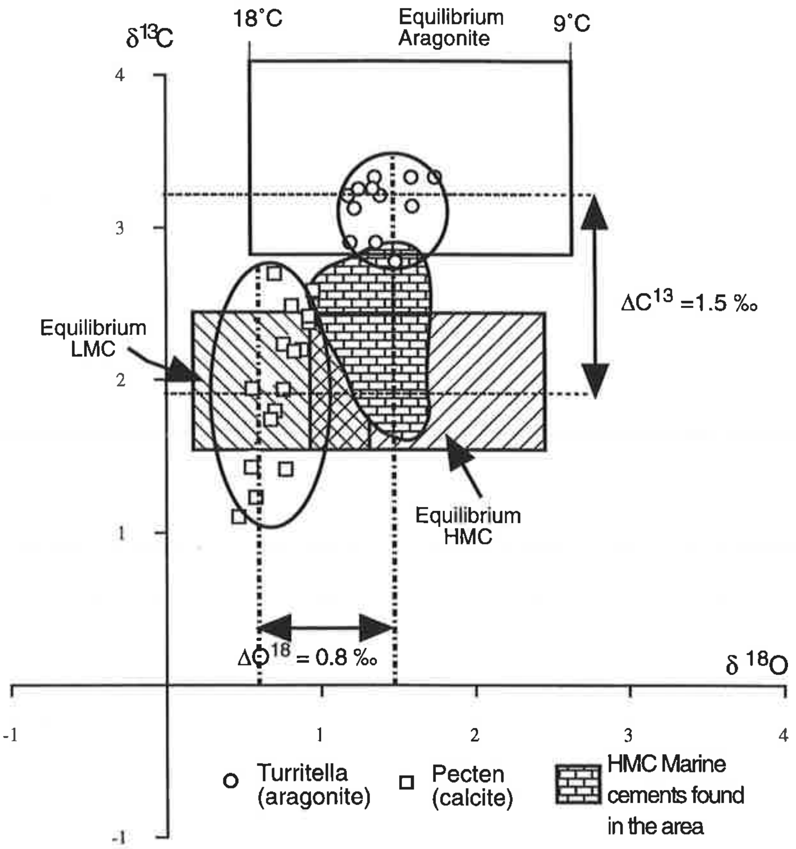


Fig. 4. The comparison between the isotopic compositions of the aragonitic gastropod (*Turritella*) and calcitic bivalve (*Pecten*) of the Lacepede Shelf. The Δ shows differences in $\delta^{18}O$ and $\delta^{13}C$ between biogenic aragonite and calcite. As shown, it is in the range of values for fractionation in these minerals in inorganic precipitates, as suggested by Rubinson and Clayton (1969), Turner (1982), Gonzalez and Lohmann (1985), and Romanek et al. (1992).

do not even show the 0.5‰ enrichment relative to bicarbonate. Our results show that the temperate calcitic and aragonitic molluscs of the Lacepede Shelf have an average $\delta^{13}C_{calcite-DIC}$ and $\delta^{13}C_{aragonite-DIC}$ of about 1.5‰ and 2.75‰, respectively. The $\epsilon\delta^{13}C_{aragonite-calcite}$ in these biogenic carbonates is, therefore, about 1.5 ± 0.3‰, which is comparable with inorganic values of 1.8 ± 0.2‰ (Rubinson and Clayton, 1969), 1.6 ± 0.35‰ (Turner, 1982), and 1.7 ± 0.4‰ (Romanek et al., 1992). This indicates that the $\delta^{13}C$ of the molluscs of this environment is precipitated in equilibrium with ambient seawater and testifies that because of lower temperatures, and thus slower precipitation rates, biogenic carbonates could reach equilibrium values.

These observations show that there is no major metabolic (vital) effect in our molluscs and the differences in the carbon isotope values are due to the different mineralogy and, consequently, different fractionation rates, and thus, are not due to metabolic effects. The mineralogy of *Pecten* sp. shows an average 0.5 mol% $MgCO_3$ and the aragonite content is up to 5%. Differences in $\delta^{18}O$ of *Pecten* sp. (mainly calcite) and *Turritella* sp. (aragonite) is about 0.8‰, which is in the range of the difference in fractionation values of inorganic calcite and aragonite (Fig. 4). Accordingly, it reconfirms that *Pecten* sp. and *Turritella* sp. from this cool–water carbonate environment are precipitating their carbonate shells in isotopic equilibrium with their ambient seawater. Thus, they do not exert significant metabolic effects over the isotopic composition of their calcareous shells and so could be used for paleoenvironmental studies with great precision. Table 4 shows measured temperatures, both summer and winter, and calculated temperatures from calcitic and aragonitic molluscs. The calcitic and aragonitic mollusc temperatures are similar and fall within the range of measured temperatures. Thus, the molluscs are probably precipitating their calcareous shells in both summer and winter, since the temperature of formation (the average temperature of carbonate secretion) is similar to the average temperature experienced throughout the year.

Land (1989), using data from, e.g., Clayton and Degens (1959), Eichler and Ristedt (1966), Eisma et al. (1976), Gross (1964), Keith and Parker (1965), Mook (1971), Teys and Naydin (1975), Zhirmunskiy et al. (1967), and Wefer and Killingley (1980), stated that the Oxygen isotopic values of molluscs are almost in equilibrium with ambient seawater, but that carbon values are considerably out of equilibrium (Fig. 3). They also observed that lower $\delta^{13}C$ values were associated with rapid growth rates in aragonitic gastropods *Strombus gigas* and *S. costatus.* Our results from the Lacepede Shelf, however, have shown that both oxygen and carbon isotopes in *Pecten* sp. and *Turritella* sp. are in equilibrium with their environment (Figs. 3, 4). Land (1989), based on the works of Lloyd (1964), Bandal and Hoefs (1975), and Wefer and Killingly (1980), stated that greater vital effects have been observed in gastropods than in bivalves and concluded that they are less reliable for paleoenvironmental interpretation. In addition, Wefer and Berger (1991), considering isotopic information on gastropods from different sources (e.g., Deuser and Degens, 1967; Hoefs and Sarthein, 1971; Bernal, 1980; Winter et al., 1983; Price et al., 1985; Grossman et al., 1986; Meinecke and Wefer, 1990), suggested that in the gastropods $\delta^{18}O$ is precipitated in equilibrium, whereas $\delta^{13}C$ is depleted, relative to equilibrium values. However, our results reveal that both bivalves and gastropods show no significant metabolic (vital) effects and so both are equally useful for paleoenvironmental studies. These differing results may arise from the fact that most previous isotopic data for molluscs are from tropical environments that are geochemically different from temperate ones.

Oxygen isotopic composition of *Pecten* sp. shows almost unimodal distribution, whereas $\delta^{13}C$ values are more scattered (Fig. 4). In equilibrium biogenic carbonates, such as molluscs that do not exert significant metabolic effects, $\delta^{18}O$ is controlled by temperature which varies within a narrow range in this environment, whereas the $\delta^{13}C$ composition is probably a function of several factors, such as food sources, temperature effects on $\delta^{13}C_{\text{carbonate-bicarbonate}}$ fractionation, DIC variations, and so on. However, these effects on the $\delta^{13}C$ of *Pecten* sp. are not significant, so that $\delta^{13}C$ values are still close to the equilibrium values. In *Turritella* sp., both $\delta^{13}C$ and $\delta^{18}O$ present a unimodal distribution that is in complete equilibrium with ambient waters.

Linear positive correlation between $\delta^{13}C$ and $\delta^{18}O$ of some organisms from the Lacepede Shelf, such as coralline algae and ahermatypic corals (Rahimpour-Bonab et al., 1997) and *Pecten* sp. (this study) (Figs. 4, 5), may indicate that the isotopic values of ambient waters have narrow ranges. However, other processes, such as fresh water mixing with seawater (Mook, 1971) or organism migration (except for sessile and encrusting organisms such as ahermatypic corals and coralline algae) between environments that have different isotopic composition (Mulcahy et al., 1979), could produce linear positive correlation. Mixing of freshwater input on the Lacepede Shelf had no significant influence (James and Bone, 1992). If freshwater mixing did give such correlation, it would be more conspicuous in the samples that are close to the mouth of the River Murray, which is not the case. McConnaughey, (1989a,b) pointed out that in non-photosynthetic corals, linear correlations between skeletal $\delta^{13}C$ and $\delta^{18}O$ is a result of a partial equilibration process. The range of isotopic correlation is apparently dependent on the

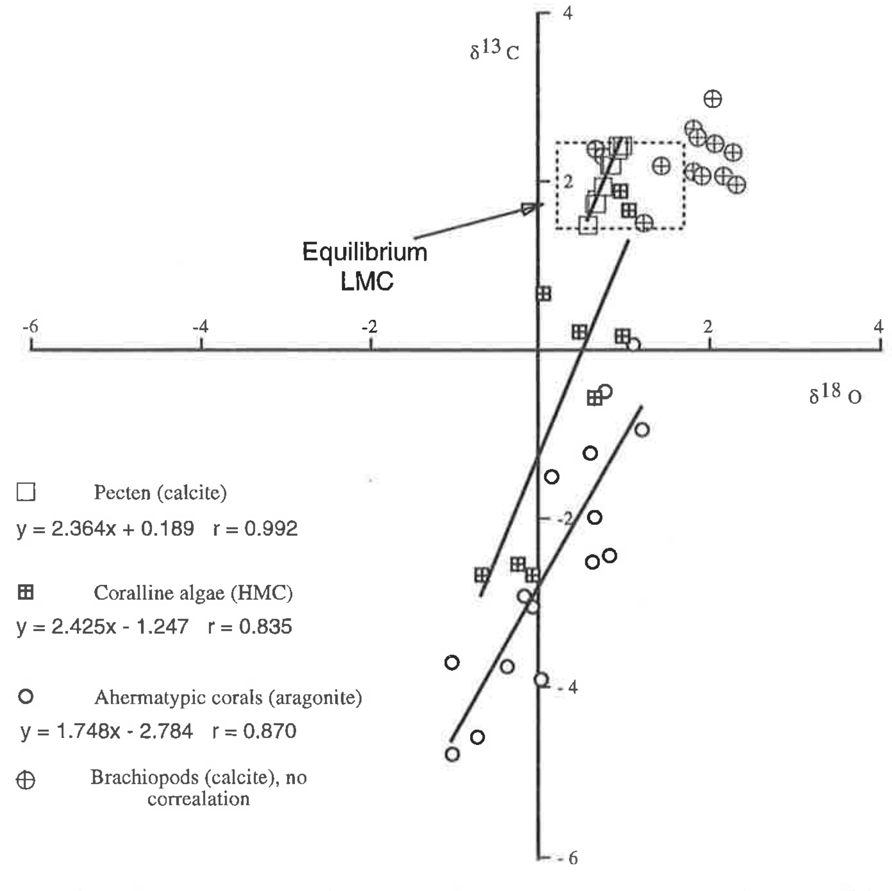


Fig. 5. Comparisons of the isotopic correlation of different organisms from cool-water environments of the Lacepede Shelf, South Australia.

extent of the partial equilibrium. Whereas ahermatypic corals and coralline algae exhibit a large range for their δ^{13}C and δ^{18}O linear correlations, bivalves have limited δ^{13}C and δ^{18}O correlation range (Figs. 4, 5), demonstrating the greater influence of kinetic effects on the isotopic compositions of corals and coralline algae. Brachiopods do not show correlations between δ^{13}C and δ^{18}O, and their δ^{18}O values are mostly heavier than equilibrium values, which is consistent with Heibert et al. (1988) and Carpenter and Lohmann (1995) observations. They attributed the observed isotopic deviations from equilibrium values in brachiopods to metabolic effects (Fig. 5).

The comparisons between isotopic composition of *Pecten* sp. (LMC) and their co–occurring brachiopods (LMC) from the Lacepede Shelf indicate that the δ^{18}O of the former is closer to the equilibrium values (Fig. 5, Table 3), and brachiopods exhibit about 1‰ enrichment in their δ^{18}O average values. Thus, *Pecten* sp. would be more reliable for paleotemperature studies than the traditionally used brachiopods. The lack of covariations in the δ^{18}O of these two co-occurring organisms from the same depths could be explained by the influence of vital effects on the δ^{18}O fractionation in brachiopods. This observation is in agreement with Heibert et al. (1988), who, with experiments on living samples, showed some δ^{18}O variations in brachiopods. Carpenter and Lohmann (1995) also have found various disequilibrium values in different parts of modern brachiopods from diverse areas. On the other hand, comparisons of the δ^{18}O of Lacepede Shelf brachiopods (δ^{18}O between 0.75 to 2.31‰) with other modern samples from mostly warm water areas (δ^{18}O values between −4.6 to 1.5‰, Lowenstam, 1961; Lepzelter et al., 1983; Carpenter and Lohmann, 1995) exhibit higher δ^{18}O values in Lacepede Shelf samples that are close to δ^{18}O values from Ross Island, Antarctica (Carpenter and Lohmann, 1995).

Previous studies on the δ^{13}C of different biogenic carbonates have revealed a correlation between the δ^{13}C of some foraminifera and $\delta^{13}C_{DIC}$ (e.g., Williams et al., 1977; Graham et al., 1981; Grossman, 1984). Mook and Vogel (1968), Fritz and Poplawski (1974), and Grossman and Ku (1986) found a similar relationship for molluscs from different environments. The δ^{13}C of co-occurring *Pecten* sp. and brachiopods shows strong covariations close to the 1:1 correspondence line (Fig. 6). The main reason for such covariations in these organisms is that, despite differences in the δ^{18}O values, the δ^{13}C values of both organisms are almost in equilibrium with their ambient waters, and so, these organisms are able to record the approximate $\delta^{13}C_{DIC}$ variations of their environments. This result contradicts Heibert et al. (1988), who suggested both δ^{18}O and δ^{13}C in brachiopods show variations of ±1 and should not be used as precise indicators of seawater isotopic signature. This observation also is not in agreement with Carpenter and Lohmann (1995), who stated that both δ^{18}O and δ^{13}C of modern brachiopods exhibit biological fractionation in their primary and secondary layer calcite. Therefore, although δ^{18}O values of our brachiopods show about +1‰ enrichment, possibly because of the vital effect, the δ^{13}C values of these organisms are close to calculated equilibrium values, indicating their potential use for paleoenvironmental studies.

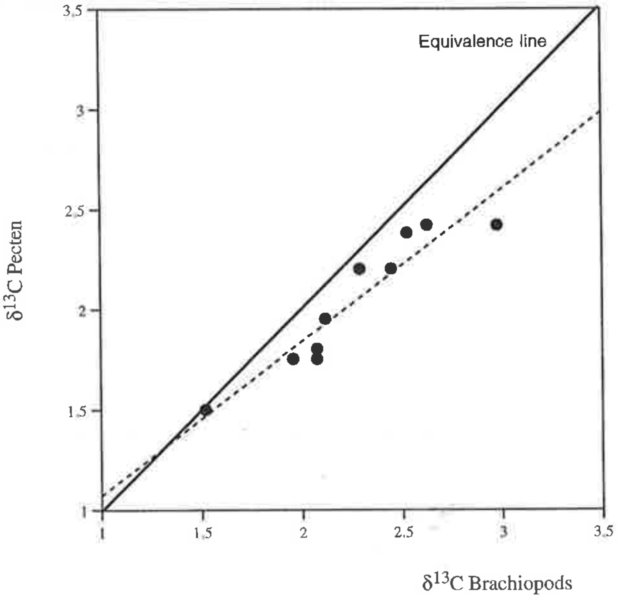


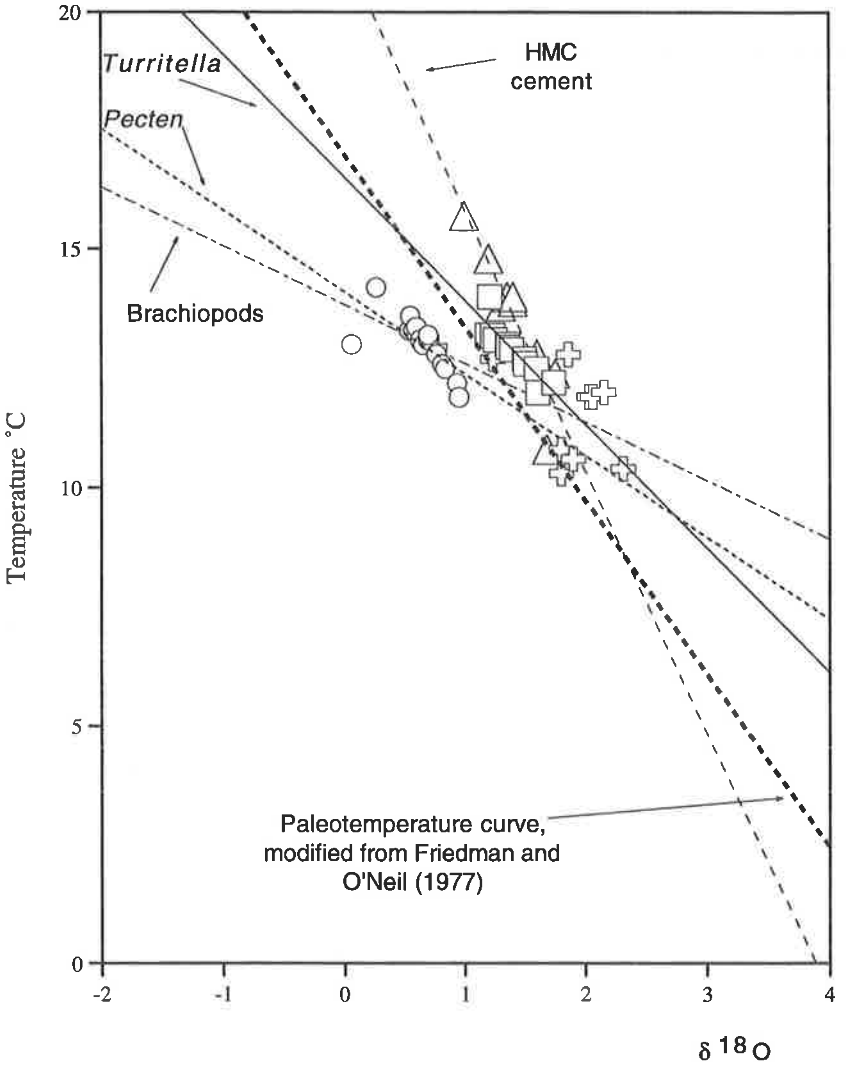
Fig. 6. Relationship between the δ^{13}C of co-occuring *Pecten* and brachiopods from the same depths (the same sampling sites), the Lacepede Shelf. The solid lines represent 1:1 correspondence (equivalence) and the dashed line is the regression curve.

The δ^{18}O values of the mollusc, brachiopods, and HMC marine cements from Lacepede Shelf exhibit clear variations with the temperature of the ambient waters (Fig. 7). The temperature-δ^{18}O curve of aragonitic sample is distinct from the calcitic ones and is closer to HMC and paleotemperature curves of Friedman and O'Neil (1977). Based on these curves, it could be concluded that the δ^{18}O and water temperature are closely correlated over the temperature spectrum in which these organisms live, and inorganic components (cements) also display these variations. Displacement of the HMC equilibrium curve relative to the paleotemperature curve of Friedman and O'Neil (1977) could be explained by the lower temperature and hence higher δ^{18}O values in the cool-water samples. These observations add to the potential credibility of molluscs of cool-water environments for paleoenvironmental and paleotemperature studies.

5. SUMMARY

Isotopic enrichments have been investigated in recent calcitic and aragonitic molluscs and in inorganic carbonates in order to determine possible kinetic and/or metabolic effects on the isotopic compositions of the calcareous organisms from the Lacepede Shelf and allow comparisons with their tropical counterparts. Additionally, comparisons have been made between isotopic composition of the biogenic and inorganic carbonates from this area to determine any possible disequilibrium state during carbonate precipitation.

Molluscs from this area precipitate their shell carbonate in isotopic equilibrium with their environment. The oxygen and carbon isotope values of these molluscs are close to the measured (marine cements) and calculated equilibrium values in this area. The values vary with depth (temperature)



□ *Turritella*, aragonite $y = -2.602x + 16.528$ $r^2 = 0.783$

○ *Pecten*, calcite $y = -1.719x + 14.105$ $r^2 = 0.507$

✚ Brachiopods, calcite $y = -1.232x + 13.839$ $r^2 = 0.308$

△ HMC marine cements $y = -5.483x + 21.303$ $r^2 = 0.839$

Fig. 7. Relationship between the $\delta^{18}O$ values (PDB) for different molluscs of the Lacepede Shelf (*Turritella* and *Pecten*), brachiopods, HMC marine cements, and temperature in the Lacepede Shelf. Paleotemperature curve of Friedman and O'Neil (1977) is shown for comparison.

and with the isotopic composition of seawater. Average temperatures which are derived from these molluscs are similar to recorded temperatures. Two quite different organisms give similar calculated temperatures.

Calcitic bivalves *Pecten* sp. of this area are not depleted in the $\delta^{13}C$, but are mainly enriched. Unlike $\delta^{18}O$, the $\delta^{13}C$ of the *Pecten* sp. and brachiopods from the study area exhibit strong covariations. Moreover, the $\delta^{18}O$ values of molluscs and HMC cements represent clear variations with the temperature of the ambient waters.

Our study has shown that on the Lacepede Shelf, because of lower temperatures and consequently slower precipitation rates (organic and inorganic carbonates), kinetic effects have a minimum influence on the isotopic compositions of different carbonates (molluscs and brachiopods), and that many of the biogenic carbonates (such as molluscs and bryozoans) and inorganic marine cements exhibit equilibrium isotopic values. However, the calcareous algae and ahermatypic corals of the study area still exhibit large deviations from equilibrium values, induced by metabolic and kinetic effects. Therefore, some calcareous organisms living in cool–water are able to record more accurate variations in seawater temperatures and chemistry than do their tropical counterparts in their environment. Thus, these temperate–inhabiting organisms are useful in paleoenvironmental, paleoclimatological, and diagenetic studies.

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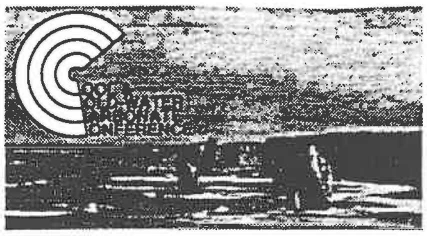


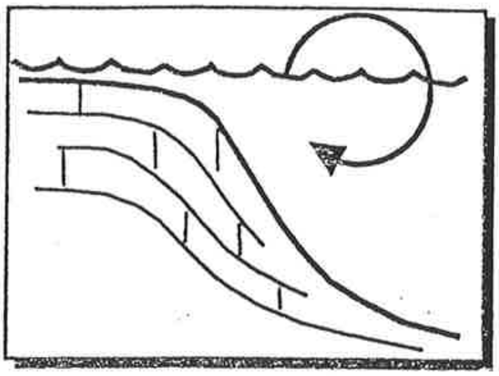
COOL & COLD-WATER CARBONATE CONFERENCE, GEELONG, VICTORIA, AUSTRALIA 14TH - 19 TH JANUARY 1995

Abstracts

Sedimentology Studies Group
Geological Society of Australia

Rahimpour-Bonab, H., Bone, Y., Moussavi-Harami, R. and Turnbull, K. (1995). Comparison of the geochemistry of cool-water corals, Coralline Algae and Bryozoans from the Lacepede Shelf, South Australia with their warm water counterparts. In J.A. Webb, S.Nicolaides and J. Kelly (Eds.) *Cool-water carbonates of the northeastern Otway Basin, southeastern Australia: excursion guide for Cool and Cold-Water Carbonate Conference, Geelong, Victoria, 14-19 January, 1995.* Sydney, Australia: Geological Society of Australia.

SEPM/IAS Research Conference



CARBONATES AND GLOBAL CHANGE: AN INTERDISCLIPINARY APPROACH

June 22-27, 1996, Wildhaus, Switzerland

ABSTRACT BOOK

CONVENORS

MARIA MUTTI, ETH, Zürich, Switzerland
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HELMUT WEISSERT, ETH, Zürich, Switzerland
PAUL BAKER, Duke University, Durham, USA

Bone, Y., James, N.P., Rahimpour-Bonab, H. and Moussavi-Harami, R. (1996). Stable isotope biogeochemistry of modern cool-water carbonate skeletons in southern Australia, and the implications for the rock record. In M. Mutti, T. Simo, H. Weissert and P. Baker (Convenors) *SEPM/IAS Research Conference, Carbonates and Global Change: an interdisciplinary approach, June 22-27, 1996, Wildhaus, Switzerland: abstract book,* Wildhaus, Switzerland: Society for Sedimentary Geology.

APPENDIX II: Tables of Geochemical Data:

Table .1. The isotopic data of Coralline Algae from Lacepede Shelf, South Australia.

Sample sites	$\delta^{18}O$	$\delta^{13}C$	Depth m	Recorded Temperature ˚C Summer	Winter	Mg ppm	Sr ppm	Fe ppm	Mn ppm
151	1.04	1.65	25	18	16.9	28164	1980	190	412
152	-0.25	-2.52	40	16.2	16.9	34678	2100	1200	45
19	0.03	0.67	40	16.2	16.9	29870	2300	105	10
89	0.95	1.88	40	16.2	16.9	34120	1990	1312	8
165	0.7	1.6	40	16.2	16.9	23876	2546	89	132
152	0.21	-0.35	40	16.2	16.9	31890	3700	2300	345
41	1.0	0.79	45	16.1	16.9	21453	3200	210	167
22	-0.1	0.67	55	15	16.9	24154	3145	321	541
23	-0.68	-2.66	55	15	16.9	50900	2310	456	190
77	0.65	-0.56	60	14.5	16.9	45132	2431	367	13
5	0.47	0.22	60	14.4	16.9	24560	2671	231	25
62	-0.09	-1.8	60	14.5	16.9	43123	2569	451	238
24	0.97	0.16	65	14.3	16.9	21320	3100	2450	194

Table .2. The isotopic composition, depth and temperature of different ahermatypic corals from Lacepede Shelf, South Australia.

Sample name	Sample sites	$\delta^{18}O$	$\delta^{13}C$	Depth m	Recorded Temp. ˚C		Mg ppm	Sr ppm	Fe ppm	Mn ppm
					summer	winter				
Cullicia tenella	45	0.58	-1.21	60	14.5	16.9	2056	7100	119	2
Cullicia tenella	136	0.77	-0.50	75	13.25	16.8	2450	7890	120	4
Cullicia tenella	135	0.92	-0.2	90	12.3	16.8	1609	8900	78	7
Cullicia tenella	57	0.95	-0.09	95	12.2	16.5	3400	7650	140	11
Flabellum pavonium	155	0.61	-2.50	150	11.5	15.8	4500	7896	163	21
Flabellum pavonium	155	0.81	-2.44	150	11.5	15.8	5089	8765	245	25
Cullicia tenella	168	1.15	0.50	180	11	15	2460	8745	506	12
Caryophyllia cultrifera	168	-0.09	-3.04	180	11	15	1789	8954	540	34
Cullicia tenella	59	1.43	1.1	220	10.8	14	1987	7698	341	23
Flabellum pavonium	58	0.02	-3.90	220	10.8	14	1765	7656	90	11
Flabellum pavonium	164	-1.05	-4.76	250	10.8	14	1786	7600	178	14
Flabellum pavonium	164	-1.05	-3.70	250	10.8	14	2670	6700	210	8
Flabellum pavonium	160	-0.40	-3.75	250	10.8	14	1802	6090	301	14
Caryophyllia cultrifera	164	1.21	-0.94	250	10.8	14	2451	7601	158	20
Caryophyllia cultrifera	160	0.64	-1.96	250	10.8	14	1767	6671	121	16
Caryophyllia cultrifera	160	-0.17	-2.91	250	10.8	14	1780	8100	190	7
Cullicia tenella	64	1.9	0.80	350	9.5	10.2	2090	7681	247	3

Table .3. Isotopic data of Bryozoan *Adeona* sp. from the Lacepede Shelf.

Sample sites	$\delta^{18}O$	$\delta^{13}C$	Depth m	Recorded	Temperature ˚C	Mg ppm	Sr ppm	Fe ppm	Mn ppm
				Summer	Winter				
33	1.35	2.32	75	13.25	16.8	1650	7650	44	12
32	1.26	2.68	75	13.25	16.8	2500	8345	106	3
136	0.84	2.01	75	13.25	16.8	1856	8900	294	9
32	0.90	1.95	75	13.25	16.8	3500	7600	35	5
47	1.35	2.32	80	13	16.8	4500	5610	67	5
57	1.35	2.57	80	13	16.8	3400	4950	43	6
47	1.25	2.80	80	13	16.8	2567	4500	543	14
30	1.20	2.92	90	12.3	16.7	2345	8965	234	5
130	1.22	2.22	90	12.3	16.7	4323	1025	36	6
67	1.23	2.3	90	12.3	16.7	1345	1054	98	9
120	1.38	3.12	95	12.2	16.5	1290	9845	167	2
50	1.24	2.55	95	12.2	16.5	2367	8796	245	4
153	1.19	1.87	95	12.2	16.5	2389	5698	567	29
120	1.23	2.45	95	12.2	16.5	2567	7698	680	3
167	1.42	2.79	100	12	16.4	4802	6785	234	44
73	1.36	2.85	100	12	16.4	2356	9823	78	10
70	1.12	2.42	100	12	16.4	5600	8795	78	12
142	1.12	2.42	100	12	16.4	4590	9012	56	12
143	1.35	2.72	100	12	16.4	5390	1090	650	11
154	1.4	2.85	100	12	16.4	6090	1189	345	10
65	1.22	2.23	300	10	11.2	5900	1076	231	9

Table .4. Isotopic composition of *Pecten* sp., *Turritella* sp. and Terebratellidae brachiopods from the Lacepede Shelf, South Australia.

Sample	Sample	Depth	Measured Tem. °C		$\delta^{18}O$	$\delta^{13}C$
Sites	Name	m	summer	winter		
157	*Pecten*	45	16.2	16.9	0.95	2.6
39	*Turritella*	50	15.8	16.9	1.95	2.68
56	*Pecten*	55	15	16.9	0.54	1.31
9	*Pecten*	55	15	16.9	0.46	1.12
56	*Turritella*	55	15	16.9	1.25	3.26
62	*Turritella*	65	14.2	16.8	1.74	3.34
24	*Turritella*	65	14.2	16.8	1.32	3.4
34	*Turritella*	70	13.5	16.8	1.2	2.75
6	*Pecten*	70	13.5	16.8	0.76	1.43
47	*Pecten*	80	13	16.8	0.69	1.8
47	*Turritella*	80	13	16.8	1.21	2.54
31	*Turritella*	85	12.8	16.6	1.35	3.26
31	*Pecten*	85	12.8	16.6	0.83	2.2
31	brachiopods	85	12.8	16.6	0.75	2.29
130	*Pecten*	90	12.3	16.5	0.57	1.5
135	*Turritella*	90	12.3	16.5	1.23	3.13
130	brachiopods	90	12.3	16.5	1.23	1.52
111	*Turritella*	100	12	16.4	1.49	2.77
140	*Turritella*	100	12	16.4	1.36	3.34
111	*Pecten*	100	12	16.4	0.56	1.95
140	*Pecten*	100	12	16.4	0.69	2.71
112	*Pecten*	100	12	16.4	0.92	2.38
112	brachiopod	100	12	16.4	0.86	2.53
30	*Turritella*	140	11.3	15.9	1.39	3.22
159	*Pecten*	170	11.3	15.2	0.65	1.75
159	brachiopod	170	11.3	15.2	2.45	2.08
155	*Pecten*	180	11	15	0.92	2.42
155	*Pecten*	180	11	15	0.85	2.2
155	*Turritella*	180	11	15	1.5	3.2
155	brachiopod	180	11	15	2.16	2.45
155	brachiopod	180	11	15	2.23	2.98
29	*Turritella*	190	10.9	14.8	1.8	3.22
65	*Pecten*	220	10.8	14	0.67	1.8
65	brachiopod	220	10.8	14	1.9	2.08
108	*Pecten*	250	10.5	13	0.75	1.95
108	brachiopod	250	10.5	13	1.3	2.12
103	*Pecten*	300	10	11.2	0.98	2.42
103	*Turritella*	300	10	11.2	1.59	3.34
103	brachiopod	300	10	11.2	1.1	2.63
64	*Pecten*	350	9.5	10.2	0.67	1.75
64	brachiopod	350	9.5	10.2	2.31	1.96

Table .5. Isotopic composition of fossil Turritellidae gastropods from the study area.

Sampled Units	$\delta^{13}C$	$\delta^{18}O$	Sampled Units	$\delta^{13}C$	$\delta^{18}O$
Backtracked			Backtracked		
Upper Morgan	2.89	2.21	Mannum Formation	3.80	-0.40
Upper Morgan	3.15	1.85	Mannum Formation	3.84	-0.25
Upper Morgan	3.23	1.80	Mannum Formation	3.66	-0.30
Upper Morgan	3.12	1.89	Mannum Formation	3.40	-0.60
Upper Morgan	3.13	2.16	Mannum Formation	3.60	-0.65
Upper Morgan	2.50	2.06	Mannum Formation	3.51	-0.60
Upper Morgan	2.62	1.51	Mannum Formation	3.79	-0.91
Upper Morgan	2.86	1.70	Gull Rock Member	3.05	0.98
Upper Morgan	2.93	1.61	Gull Rock Member	3.10	0.87
Upper Morgan	2.74	2.0	Gull Rock Member	2.93	0.65
Upper Morgan	3.2	2.06	Gull Rock Member	3.1	0.91
Upper Morgan	3.05	1.91	Gull Rock Member	2.91	0.40
Cadell Marl	3.89	1.25	Gull Rock Member	2.87	0.70
Cadell Marl	4.15	0.89	Gull Rock Member	3.15	0.69
Cadell Marl	4.23	0.80	Gull Rock Member	3.25	0.35
Cadell Marl	4.19	0.93	Gull Rock Member	2.94	0.25
Cadell Marl	4.13	1.20	Gull Rock Member	3.20	0.45
Cadell Marl	3.49	1.10	Tortachilla Limestone	-4.43	-2.18
Cadell Marl	3.62	0.55	Tortachilla Limestone	-5.73	-3.46
Cadell Marl	3.86	0.73	Tortachilla Limestone	-5.67	-3.53
Cadell Marl	3.93	0.89	Tortachilla Limestone	-3.85	-2.58
Cadell Marl	3.74	1.02	Tortachilla Limestone	-5.38	-3.41
Cadell Marl	4.21	1.11	Tortachilla Limestone	-6.72	-3.86
Cadell Marl	4.05	0.95	Tortachilla Limestone	-7.23	-4.32
Cadell Marl	4.10	0.90	Tortachilla Limestone	-7.80	-4.85
Cadell Marl	3.90	0.1.20	Backtracked		
Cadell Marl	3.85	1.10	Tortachilla Limestone	2.18	0.17
Cadell Marl	3.70	1.90	Tortachilla Limestone	1.95	0.52
Backtracked			Tortachilla Limestone	2.10	-0.05
Lower Morgan	3.65	0.32	Tortachilla Limestone	2.45	0.25
Lower Morgan	3.10	0.38	Tortachilla Limestone	2.1	-0.25
Lower Morgan	3.05	0.05	Tortachilla Limestone	2.25	0.57
Lower Morgan	3.20	0.04	Tortachilla Limestone	1.95	0.20
Lower Morgan	3.75	0.15	Tortachilla Limestone	2.19	-0.15
Lower Morgan	2.85	0			
Lower Morgan	3.30	0.25			
Lower Morgan	3.65	0.35			

Table .6. Isotopic composition of fossil Terebratellidae brachiopods samples from the study area.

Sampled Units	$\delta^{13}C$	$\delta^{18}O$	Sampled Units	$\delta^{13}C$	$\delta^{18}O$	Sampled Units	$\delta^{13}C$	$\delta^{18}O$
Upper Morgan	-0.39	-0.32	Lower Morgan	2.09	-0.90	Tortachilla Limestone	1.60	-0.50
Upper Morgan	-1.32	-1.89	Lower Morgan	2.42	-0.68	Tortachilla Limestone	0.50	-0.91
Upper Morgan	-0.43	-0.46	Lower Morgan	2.73	-0.29	Tortachilla Limestone	1.11	-1.21
Upper Morgan	-1.74	-1.84	Lower Morgan	2.22	-0.71	Tortachilla Limestone	1.62	-0.72
Upper Morgan	-0.63	-1.64	Lower Morgan	2.47	-0.15	Tortachilla Limestone	0.50	-1.13
Upper Morgan	0.24	-0.57	Lower Morgan	2.12	-0.02	Tortachilla Limestone	0.40	-0.72
Upper Morgan	-0.07	-1.09	Lower Morgan	2.41	-0.16	Tortachilla Limestone	0.73	-0.62
Upper Morgan	0.40	-0.05	Lower Morgan	2.03	-0.20	Tortachilla Limestone	0.11	-0.53
Upper Morgan	0.57	0.07	Lower Morgan	2.02	-0.03	Tortachilla Limestone	2.14	-0.11
Upper Morgan	0.26	-0.46	Lower Morgan	2.45	-0.52	Tortachilla Limestone	1.22	-0.55
Upper Morgan	0.84	-0.48	Lower Morgan	2.77	-0.41	Tortachilla Limestone	0.83	-0.63
Upper Morgan	0.34	-0.72	Lower Morgan	3.05	-0.35	Tortachilla Limestone	1.34	-0.91
Backtracked			Mannum Formation	2.08	-0.97			
Upper Morgan	1.16	0.88	Mannum Formation	2.04	-0.42			
Upper Morgan	1.52	0.84	Mannum Formation	1.87	-0.24			
Upper Morgan	1.37	0.94	Mannum Formation	1.60	-0.74			
Upper Morgan	1.54	1.0	Mannum Formation	1.84	-0.74			
Upper Morgan	1.03	0.96	Mannum Formation	1.72	-0.81			
Upper Morgan	1.02	0.88	Mannum Formation	1.99	-0.89			
Upper Morgan	1.23	0.91	Gull Rock	3.30	-0.50			
Cadell Marl	2.16	-0.08	Gull Rock	3.31	-0.30			
Cadell Marl	2.52	-0.12	Gull Rock	1.70	0.10			
Cadell Marl	2.37	-0.03	Gull Rock	2.70	-0.20			
Cadell Marl	2.54	0.04	Gull Rock	1.80	-0.41			
Cadell Marl	2.04	0	Gull Rock	2.10	-0.12			
Cadell Marl	2.02	-0.07	Gull Rock	2.91	-0.11			
Cadell Marl	2.23	-0.05	Gull Rock	2.10	0.33			
Cadell Marl	2.20	0	Gull Rock	2.31	0.11			
Cadell Marl	2.15	-0.09	Gull Rock	1.50	-0.64			
Cadell Marl	2.41	-0.15	Gull Rock	2.20	0			
Cadell Marl	2.09	-0.10	Gull Rock	2.20	0			
			Gull Rock	1.80	-0.10			

Table .7. Isotopic composition of fossil Pecten samples from the study area.

Sampled Units	$\delta^{13}C$	$\delta^{18}O$
Upper Morgan	0.15	-1.16
Upper Morgan	-0.54	-1.73
Upper Morgan	-0.92	-1.84
Upper Morgan	-0.47	-2.27
Upper Morgan	0.31	-1.07
Upper Morgan	-0.52	-2.10
Upper Morgan	-0.20	-1.89
Upper Morgan	-0.12	-1.50
Upper Morgan	-0.43	-1.11
Upper Morgan	-1.43	-1.71
Upper Morgan	-1.41	-2.60
Backtracked		
Upper Morgan	1.30	0.88
Upper Morgan	1.62	1.06
Upper Morgan	1.22	0.48
Upper Morgan	1.43	0.46
Upper Morgan	2.0	0.98
Upper Morgan	1.95	1.41
Upper Morgan	2.06	1.05
Upper Morgan	2.26	1.65
Cadell Marl	2.33	-0.08
Cadell Marl	2.68	0.11
Cadell Marl	2.20	-0.53
Cadell Marl	2.44	-0.55
Cadell Marl	3.04	0.02
Cadell Marl	2.96	0.43
Cadell Marl	3.0	0.09
Cadell Marl	3.26	0.68
Cadell Marl	2.45	-0.45
Cadell Marl	2.55	-0.60
Cadell Marl	2.80	0.15
Lower Morgan	2.15	-0.47
Lower Morgan	1.62	-0.75
Lower Morgan	1.53	-0.77
Lower Morgan	1.70	-0.72
Lower Morgan	2.20	-0.66
Lower Morgan	1.34	-1.08
Lower Morgan	1.81	-0.73
Lower Morgan	2.16	-0.20
Mannum Formation	-3.84	-1.20
Mannum Formation	-3.84	-1.04
Mannum Formation	-2.63	-1.10
Mannum Formation	-2.95	-1.41
Mannum Formation	-2.4	-1.46
Mannum Formation	-0.85	-1.39
Mannum Formation	-2.81	-1.70
Mannum Formation	-2.13	-1.43
Mannum Formation	-1.24	-1.21
Mannum Formation	-2.89	-1.35
Backtracked		
Mannum Formation	1.78	-1.60
Mannum Formation	1.74	-1.22
Mannum Formation	1.57	-1.04
Mannum Formation	1.31	-1.55
Mannum Formation	1.54	-1.54
Mannum Formation	1.42	-1.61
Mannum Formation	1.69	-1.69
Backtracked		
Gull Rock	1.92	0.18
Gull Rock	2.13	0.59
Gull Rock	1.43	0.27
Gull Rock	1.13	0.22
Gull Rock	1.42	0.31
Gull Rock	1.10	0.13
Tortachilla Limestone	0.68	-0.62
Tortachilla Limestone	0.46	-0.27
Tortachilla Limestone	0.58	-0.85
Tortachilla Limestone	0.94	-0.55
Tortachilla Limestone	0.5	-1.05
Tortachilla Limestone	0.74	-0.23
Tortachilla Limestone	0.46	-0.67
Tortachilla Limestone	0.69	-0.95

Table .8. The stable isotope composition of Turritellidae gastropods, sampled along the whorls.

Unit Name	$\delta^{13}C$	$\delta^{18}O$	Whorl Number	Unit Name	$\delta^{13}C$	$\delta^{18}O$	Whorl Number
Gull Rock Member	3.45	0.98	10	Lacepede Shelf	3.29	1.62	10
Gull Rock Member	3.63	1.14	9	Lacepede Shelf	2.79	1.85	9
Gull Rock Member	2.90	1.07	8	Lacepede Shelf	2.76	1.21	8
Gull Rock Member	2.60	1.25	7	Lacepede Shelf	3.47	0.57	7
Gull Rock Member	3.20	0.55	6	Lacepede Shelf	3.44	0.80	6
Gull Rock Member	2.68	0.90	5	Lacepede Shelf	2.79	1.70	5
Gull Rock Member	2.10	1.10	4	Lacepede Shelf	2.86	1.74	4
Gull Rock Member	2.72	0.74	3	Lacepede Shelf	2.88	0.96	3
Gull Rock Member	2.40	0.84	2	Lacepede Shelf	2.64	1.89	2
Gull Rock Member	2.63	0.98	1	Lacepede Shelf	2.92	1.78	1
Cadell Marl	4.23	0.90	10				
Cadell Marl	4.20	0.99	9				
Cadell Marl	3.84	1.21	8				
Cadell Marl	3.60	-0.85	7				
Cadell Marl	3.70	0.72	6				
Cadell Marl	3.95	0.83	5				
Cadell Marl	4.01	0.95	4				
Cadell Marl	3.55	1.32	3				
Cadell Marl	3.95	1.05	2				
Cadell Marl	3.66	1.15	1				

Table . 9. The stable isotope composition of Pecten bivalves, sampled along the growth lines.

Unit Name	$\delta^{13}C$	$\delta^{18}O$	Growth Lines	Unit Name	$\delta^{13}C$	$\delta^{18}O$	Growth Lines
Tortachilla Limestone	0.01	-1.50	11	Cadell Marl	2.33	-0.08	11
Tortachilla Limestone	-0.83	-1.99	10	Cadell Marl	1.68	-1.95	10
Tortachilla Limestone	-0.11	-0.95	9	Cadell Marl	2.23	-0.53	9
Tortachilla Limestone	0.88	-0.13	8	Cadell Marl	2.44	-0.55	8
Tortachilla Limestone	0.83	-0.20	7	Cadell Marl	3.04	0.02	7
Tortachilla Limestone	1.10	-0.15	6	Cadell Marl	2.99	0.43	6
Tortachilla Limestone	0.72	-0.83	5	Cadell Marl	3.07	0.09	5
Tortachilla Limestone	0.47	-1.38	4	Cadell Marl	3.26	0.68	4
Tortachilla Limestone	0.49	-1.42	3	Cadell Marl	3.05	0.71	3
Tortachilla Limestone	0.56	-1.32	2	Cadell Marl	3.31	0.59	2
Tortachilla Limestone	0.48	-1.43	1	Cadell Marl	3.14	0.69	1
Mannum Formation	-0.85	-1.21	11	Lacepede Shelf	0.17	0.95	11
Mannum Formation	-0.94	-2.04	10	Lacepede Shelf	0.26	0.85	10
Mannum Formation	-0.63	-1.49	9	Lacepede Shelf	0.46	0.65	9
Mannum Formation	-1.05	-2.0	8	Lacepede Shelf	1.04	0.85	8
Mannum Formation	-1.34	-2.46	7	Lacepede Shelf	1.22	0.63	7
Mannum Formation	-0.85	-1.40	6	Lacepede Shelf	1.61	0.97	6
Mannum Formation	-2.81	-1.70	5	Lacepede Shelf	0.98	0.27	5
Mannum Formation	-2.13	-1.43	4	Lacepede Shelf	1.71	0.66	4
Mannum Formation	-1.94	-2.21	3	Lacepede Shelf	1.65	0.50	3
Mannum Formation	-2.10	-1.98	2	Lacepede Shelf	1.55	0.39	2
Mannum Formation	-1.85	-2.15	1	Lacepede Shelf	1.72	0.54	1

Table .10. Stable isotope composition of dLMC meteoric cements from different stratigraphic units of the study area.

Sampled Units	$\delta^{13}C$	$\delta^{18}O$	Sampled Units	$\delta^{13}C$	$\delta^{18}O$
Upper Morgan	-3.56	-3.23	Mannum Limestone	-0.58	-0.21
Upper Morgan	1.13	-0.40	Mannum Limestone	-1.05	-1.18
Upper Morgan	-3.4	-1.8	Mannum Limestone	-0.92	-0.75
Upper Morgan	1.9	-2.4	Mannum Limestone	-1.2	-0.55
Upper Morgan	0.75	-1.2	Mannum Limestone	-0.75	-1
Upper Morgan	-2.25	-1.6	Mannum Limestone	-0.68	-0.8
Upper Morgan	-2.1	-0.65	Gull Rock Member	1.10	-0.27
Cadell Marl	-0.35	-1.1	Gull Rock Member	1.12	-0.10
Cadell Marl	-0.64	-1.40	Gull Rock Member	1.28	0.02
Cadell Marl	-0.52	-1.45	Gull Rock Member	0.89	-0.21
Cadell Marl	-0.17	-2.2	Gull Rock Member	1.10	-0.28
Cadell Marl	-2.38	-2.80	Gull Rock Member	0.95	-0.15
Cadell Marl	-2.76	-1.94	Tortachilla Limestone	-4.43	-2.17
Lower Morgan	0.20	-1.6	Tortachilla Limestone	-5.73	-3.45
Lower Morgan	0.54	-1.25	Tortachilla Limestone	-5.67	-3.52
Lower Morgan	0.19	-1.87	Tortachilla Limestone	-3.85	-2.58
Lower Morgan	0.24	-1.72	Tortachilla Limestone	-5.38	-3.40
Lower Morgan	0.55	-0.95	Tortachilla Limestone	-6.72	-3.86
Lower Morgan	0.43	-1.85	Tortachilla Limestone	-7.23	-4.32
Lower Morgan	0.35	-1.45	Tortachilla Limestone	-7.8	-4.85
Lower Morgan	0.46	-1.68			