Globigerina bulloidies
Preservation State and Stable Isotope Variation.

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Abstract

A ‘preservation index’ has been developed that enables selective population sampling of the planktic foraminiferal species *Globigerina bulloides* for geochemical and isotopic analyses. Specimens from deep-sea core horizons were separated into 5 grades, based on the degree of transparency exhibited under the transmitted light microscope (grade 1 = thick-walled, non-transparent tests, to grade 5 = thin-walled, entirely transparent tests). ‘Preservation indices’ were then derived for a down-hole sequence of 23 samples from deep-sea core SO 136-005 (Eastern Tasman Sea, 958m). These indices indicate a general increase in dissolution downhole and significant variation in preservation between alternate sampled horizons. Fragmentation counts were made using the same samples and indicate increased fragmentation with depth. Analysis of $\delta^{18}O$ showed a significant difference in concentration of that isotope (0.2 to 1.2‰) between grade 1 and grade 5 specimens (where usually, a divergence of >0.3‰ is considered significant).

The fact that it is possible to derive contrasting $\delta^{18}O$ results from specimens of one foraminiferal species extracted from the same sample has far reaching implications for paleoceanography in general, and oxygen isotopic studies in particular. These results show that significant variation in $\delta^{18}O$ signal can be entirely owing to preservation level. Collection of samples exhibiting the same preservation state, or systematic selection of the same number of specimens from different grades for all horizons in a sediment pile, should lead to increased accuracy with respect to the resultant oxygen isotope data for paleoceanography studies. In many cases, foram tests used in this study also exhibited a secondary calcite layer on the external surface. The fact that the remains of nannofossils were occasionally found submerged in the same layer is interpreted as a potential source of contamination of the primary oxygen isotope signal. The ease with which this secondary layer of calcite, on the exterior surfaces of foram tests, could be removed through acid etching was also examined. Foram tests were exposed to acetic acid solutions of pH 5.5-6.5 for differing exposure times and the effects of the acid on tests examined under the Scanning Electron Microscope. An optimum exposure time of 2 days at pH 5.5 was derived for total
removal of the surface layer. A number of recommendations are made with regard to areas of future research resulting from the present study.
Chapter One

Introduction

Fig. 1 The FS Sonne cruising the southwest Pacific during the TASQWA mission in 1998.
1.1 Research Objectives

Oxygen isotope ratios from fossilized, calcareous remains of marine organisms have been used since the 1950's as a means of determining fluctuations in sea level, seawater temperature and global ice volume through geological time (Emiliani 1954; Douglas and Savin 1978; Moore et al. 1980; Fairbanks et al. 1982; Anderson et al. 1989; Dudley and Nelson 1989; Kudrass 1991; Nees et al. 1992; Nelson et al. 1993; Dudley and Nelson 1994; Bond et al. 1997; Houston et al. 1999). Downhole changes in the ratio of $^{16}$O (light oxygen) to $^{18}$O (heavy oxygen) in the tests of a few target species preserved in deep-sea sediment are today widely used to distinguish glacial stages from interglacials. As the threat of an anthropogenically driven greenhouse gas global warming has gathered momentum, the need for an equivalent effort to understand natural climate fluctuations over a much longer record has become apparent. The oceans play an important role in this climate system, because they regulate the amount of CO$_2$ in the atmosphere (Murray and Riley 1971; Emerson and bender 1981; Bearman 1989; Boyle 1988; Braatz and Corliss 1987; Broeker and Denton 1989; Chester 2000;). Huge volumes of atmospheric CO$_2$ have been sequestered to the deep-ocean sea floor via a continuous rain of metabolisable detritus and, the mineral content found in skeletal remains of planktic organisms. The proportion of constituent species, the rate at which the sediments accumulate, their preservation state, and their chemical make-up all represent proxies which provide detailed and often precise information about climate/ocean interactions through time. Analysis of stable oxygen isotopes is now one of the most routinely used tools for investigating how the interlinked climate and ocean systems have altered over a period that now encompasses almost the entire Cenozoic record.

The main aim of the research project described herein was to test the robustness of current practices employed to isolate foraminifers from marine sediment cores for oxygen isotope analysis. This was to be achieved by examining the variation in oxygen isotope values produced by various morphotypes (including diagenetic variants) of Globigerina bulloides. A series of intra-specific grades were established,
representing variations in the preservation state of tests as determined under the binocular microscope. The hypothesis being, that samples of the most poorly preserved grade from the same core sample would produce a signal, which differed significantly from that produced by a population of well preserved specimens. It was anticipated that by selecting all morphotypes (within a nominated size class) of a particular species for $\delta^{18}$O analysis the resultant values would be biased with respect to $\delta^{18}$O concentrations derived for a sample of one preservational morphotype alone. From previous studies and this project, it was concluded that growth rate, growth environment, growth style, syndiagenesis and diagenesis may be capable of inducing variations in $\delta^{18}$O values derived for morphotypes of a given species.

Representative samples of each group were examined using the Scanning Electron Microscope (SEM) to determine the character of the microfabric associated with each preservation grade and to ensure such variations were consistent with those observations made on the same specimens using a binocular microscope. Once consistency was established, each of the preservation grades could then be defined, such that classification of specimens on the basis of preservation could be achieved repeatedly and easily.

The main implication of finding significant offset in $\delta^{18}$O between morphotypes would be that most current sample selection processes routinely used by laboratories analysing oxygen isotopes would have to be modified in order to minimize the effect of morphtotypic variation induced by degradation on the relative proportions of $^{16}$O and $^{18}$O. This clearly also has implications for isotope data previously derived for foraminifers from ocean floor cores, especially at those sites where alkalinity fluctuations of the bottom waters have resulted in significant syndiagenetic alteration of the foraminiferal tests.

This thesis also describes and references a number of ways in which stable isotope chemistry may be affected by other biological and preservation factors.
1.2 Core Collection and Age

1.2.1 Collection

The core samples used in this study were collected from the Challenger Plateau in 1998 during the TASQWA SO 136 expedition. Between October 16 and November 12, 1998 the German vessel FS SONNE completed a cruise of the Tasman Sea and Southern Ocean, starting in Wellington, New Zealand and finishing in Hobart, Australia. During that time, sea-floor core and dredge samples and hydrologic data were collected from 37 different stations en route (Fig. 1.1).

Fig. 1.1 Cruise track taken by FS Sonne during the 1998 TASQWA Wellington-Hobart expedition. Numbers 1-37 = stations occupied. For a comprehensive list of data/samples collected at each site see GEOMAR Cruise Report 89 (1998).
The following is the cruise outline from GEOMAR 89 (1998).

"The aims of the project were approached by means of an interdisciplinary expedition with scientists from institutions in Germany, Australia, France and New Zealand involved. To understand the present and past physiochemical processes the major investigations included studies of Recent planktic and benthic organisms, of hydrographic properties and fossil remains of planktic and benthic organisms (foraminifers, ostracodes, diatoms, radiolarians, dinoflagellate cysts, molluscs, gastropods; transfer functions), as well as sedimentological studies”.

"The German FS SONNE visited the study area for a 28 day cruise during October and November 1998. Both long (approx. 12m) and short (approx. 0.5m) cores were taken to provide a sedimentary record from several sites in the Tasman Sea and Southern Ocean. Numerous scientific measurements and analyses in the water column and on the sediment surface provided a modern framework for calibration of the fossil data”.

"The project follows the guidelines set out in the National Programme of the German Federal Government, as well as those for other scientific programmes which focus on obtaining high-resolution data for global climatic change (e.g. PAGES-Past Global Changes, IMAGES- International Marine Global Change Study)”. 

During the 1998 TASQWA expedition (cruise SO 136) core number SO 136-005 and dredge sample SO136-002 were collected from the first cruise station (16-18 October). This station was located west of the South Island of New Zealand on the southern flank of the Challenger Plateau (Fig. 1.1). In 958m of water, the sediment surface was sampled by multicorer (MUC) and upper part of the sediment pile by gravity corer (GC). In both cases the recovered sediment consisted of hemipelagic calcareous sandy muds with no evidence of bioturbation.
Co-ordinates for core SO 136-005, and dredge sample SO 136-002 are as follows:

SO 136-002  Latt. 42:17.29; Long 170:00.11

SO 136-005  Latt. 42:18.12; Long 169:52.23

Core SO 136-005 was collected using a multicorer, a devise designed to extract relatively undisturbed cores of the active layer and the uppermost relatively unconsolidated part of the underlying sediment. The entire core length of 23cm was sub-divided onboard into 23, 1cm thick sub-samples, then stored in a cooler until required for the present study.

The total weight of the multicorer (Fig. 1.2) is 700kg; it uses in total 8 plexiglass tubes of 9cm in diameter and 50cm in length. By penetrating the sediment surface very slowly any disturbance of the seafloor is minimized such that in many cases the entire living biotic assemblage and the overlying sea water can be recovered. Prior to recovery from the seafloor, both ends of each plexiglass tube are automatically sealed such that reworking or contamination of core/water samples is prevented as the device is winched to the surface. The multicorer naturally is a more fragile instrument than the gravity corer and as such requires calm sea conditions whilst it is being deployed. Due to the adverse weather conditions, the multicorer was employed only a few times during the TASQWA cruise. At the first sites on the Challenger Plateau and the eastern Campbell plateau no problems were encountered with any of the gear employed.
Fig. 1.2. Photograph of multicorer on the deck of the FS Sonne (1998). The 8 plexiglass tubes used to collect surface sediment samples can be seen arranged in the centre of the device. Photograph courtesy of Kerry Swanson (2001).

1.2.2 Core age

The age of the sediment in multicore SO 136-005 can be inferred from data available from the gravity core SO 136-003, taken from the same location as SO 136-005. A radiometric carbon age was obtained from SO 136-003 at the 52-54 cm depth, which gave an approximate age of 19,000 years B.P. (appendix 4). When the isotope curve for SO 136-003 is compared to the SPECMAP isotope chronology (Bradley 1999), and peaks between the two curves correlated (appendix 4), it becomes apparent that an age of about 10,000 years B.P. is most likely for the base of SO 136-005. This would indicate a sedimentation rate of approximately 2-2.5cm per thousand years for both SO 136-005 and SO 136-003. It must be noted that core SO 136-003 is a gravity core and as such may have a portion of the top of the core missing. The gravity corer is dropped through the water column at speed to ensure maximum penetration of the sediments. As the corer heads towards the sea floor, a hydraulic front is established in
front of the core cutter creating a small pressure wave which forces most of the nepheloid layer and some of the unconsolidated sediment away before the core cutter penetrates the sediment. It is therefore likely that the multicore SO 136-005 contains a more intact sample of the top few centimetres of the sea floor sediment pile as this device is lowered slowly to the sea floor and disrupts the sediment much less than does the gravity corer.

Cores taken during the TASQWA expedition on the Challenger Plateau are described in appendix 3 and consist of: sandy silty, foraminiferal ooze with a colour change from brown to grey/green at about 30cm depth. Core SO 136-005 used herein was taken from the uppermost 23cm (assuming no loss from the top of the core) of pelagic sediment on the sea floor of the Challenger Plateau including the oxygen-rich AAIW water mass immediately above the sediment. The colour change at approximately 30 cm depth below sea floor in core SO136-003 from the same location as SO 136-005, is taken as the boundary between oxic and anoxic conditions in the sediments column. The colour changes from brown (oxidized) to grey-green (anoxic).

1.3 Oceanographic setting

The Challenger Plateau (fig.1.1) represents a submerged, westward extension of the New Zealand sub-continental landmass. For the most part, the Plateau is submerged by 1000m of water or more and is roughly triangular in shape, being widest in the north and narrowing as it links with the South Island. Much of the Plateau is draped with a thick (200- >1000m), relatively undisturbed sequence of calcareous, biogenic oozes, representing a continuous Miocene-Pleistocene depositional history at mid-upper bathyal depths (Packham and van der Lingen, 1973; Nelson, 1985; Martinez 1994b).

1.3.1 Water Masses

The Challenger Plateau lies beneath the Tasman Sea, a body of water that is situated between New Zealand to the east and the continent of Australia to the west. This sea extends as far north as the Tropical Convergence (20°S) and as far south as the
Subtropical Convergence (45°S) (Fig. 1.4). The cross-sectional profile of the Tasman Sea in Fig. 1.3 illustrates the elevation of various water masses that impact on the Challenger Plateau. Surface water masses and ocean currents in the New Zealand region are illustrated in Fig. 1.4.

The Antarctic Intermediate Water (AAIW) is the most extensive and important water mass at intermediate depths in the world ocean. This cold, oxygenated water mass makes up a significant portion of the Tasman Sea water column. As it flows north from Antarctica as far as the Coral Sea it progressively deepens, although there is some evidence to suggest shoaling as it impacts against the topographic high of the Challenger Plateau. Because the core of AAIW is located at about 1000m water depth, station sites were positioned so that core and dredge samples targeted sediment deposited in that water mass (Fig.1.3).

Three major oceanic fronts are present between latitudes 10°S and 50°S in the Southwest Pacific Ocean (Kustanowich 1962; Martinez 1994; Braatz and Corliss 1987). These are, from south to north, the Subtropical Convergence (STC), the Tasman Front, and the southern Tropical Convergence (Hayward 1983; Martinez 1994a, 1994b; Weaver et al. 1998). The STC extends along 45°S (Tasmania to New Zealand) and is the boundary between the Subantarctic and the Tasman currents (Heath 1982; Martinez 1994b; Bradford and Roberts 1978). At about 30°S, the Tasman Front marks the line of contact between the subtropical East Australian Current (EAC) and the temperate Tasman Current (Fig. 1.4). Further north at about 20°S, the southern Tropical Convergence represents a zone where part of the deflected EAC meets the warm South Equatorial Current that flows to the southwest (Martinez 1994b; Foster and Battaerd 1985; Heath 1985).
Fig 1.3 Cross-sectional profile of Challenger Plateau. After Swanson (1993).

Fig. 1.4 Map of surface water masses in the Southern Ocean and currents around New Zealand. At the STC the EAC is deflected east as a result of hydrologic inputs whereas further north it is a true oceanographic/atmospheric dynamic.
Circulation in the Tasman Sea is dominated by the strong East Australian Current (Fig. 1.4), which forms in the Coral Sea and flows southwards along the edge of the Australian continental shelf (Stanton 1972; Weaver et al. 1998). The counter clockwise circulation of modified subtropical water in the Tasman Sea forms the Tasman Current along the southern boundary (Fig. 1.4). The predominantly eastward flowing Tasman Current is deflected northward as it impinges on the bathymetric platform created by the New Zealand landmass (Fig. 1.4). This becomes the Westland current a very weak, northward moving, near-surface flow on and near the continental shelf of the West Coast of the South Island, New Zealand (Heath 1982, 1985; Nees 1997). The remainder of the water flows south to form the Southland Current.

In general, ocean circulation patterns around the Challenger Plateau are poorly understood (Swanson 1993). Heath (1982 & 1985), on theoretical grounds, considered boundary forcing and local winds to be the most important contributing factors to current development. South of Cape Foulwind, sea surface slope and prevailing southwesterly winds produce a northward directed flow; north of Cape Foulwind the boundary forcing slope component is reversed, such that at or near the cape the two flows are in opposition. Under calm conditions, a southward drift is predicted by Heath’s model.

Upwelling along the Nelson-Westland coast is almost certainly induced by prolonged periods of northeast directed winds. For waters off western Nelson Stanton (1972) estimated that wind conditions favouring the formation of upwelling existed for at least one third of the year. The sporadic occurrence of modern, light-green glauconitic pellets in upper slope muds and brown, goethite-rich glauconitic pellets at mid-shelf depths of Westland suggest upwelling occurs along the shelf. However, Stoffers et al. (1984) concluded that the extremely high detrital sediment accumulation rate would mask any impact such upwelling might have on the sedimentary record.
1.3.2 Productivity

Variation in the relative abundances of planktonic foraminiferal species is controlled by a number of factors such as the position of the thermocline/mixed layer, variations in sea surface temperature (seasonal fluctuations) and the availability of nutrients, as well as other ecological factors (Foster and Battaerd 1985; Martinez 1994b). Zooplankton concentrations are consistently low over the entire Tasman Sea and biomass shows a similar pattern to productivity. Maximum biomass returns are recorded in a narrow strip west of the South Island at about 44°S and over and west of the Challenger Plateau. Overall the Tasman Sea is oligotrophic (Bradford and Roberts 1978; Foster and Battaerd 1985; Martinez 1994; Nees 1997). However, the intermittent upwelling of cold bottom water on the west coast of South Island has obvious implications for pelagic primary productivity in that region (Heath 1982, 1985; Foster and Battaerd 1985).

Examination of reactive phosphorous distribution in surface waters indicates a progressive increase in productivity to the south, with a sharp increase at the Subtropical Convergence (Bradford and Roberts 1978). This reflects the seasonal variation in surface water stratification. In sub-Antarctic waters during winter mixing is complete, resulting in nutrient replenishment of surface waters. In contrast, subtropical water is comparatively stable in winter. Scattered high values for reactive phosphorous over the Challenger Plateau indicate some nutrient enrichment does occur in that area (Bradford and Roberts 1978). *G. bulloides* is very much a nutrient chaser and is therefore found in greatest concentrations in areas of upwelling (Bradford and Roberts 1978; Sautter and Thunell 1991a; Kroon and Darling 1995; Little et al. 1997). Summer hydrological records for the Challenger Plateau suggest the presence of a low temperature, low salinity body of water, with a cyclonic motion of AAIW at about 800m on the northern flank of the plateau (Heath 1982). However the effects of this circulation on surface waters are not well understood (Swanson 1993). Off the west coast of the South Island, much of the warm, saline, low nutrient water has been emplaced by the general southward moving circulation. Occasionally some of this water may be displaced by colder, low salinity water upwelled from greater depths during persistent southwesterly winds. Just south of the Challenger Plateau is the Hokitika submarine canyon, an area in which upwelling events are
primarily responsible for the occurrence of a major Hoki fishery in that region. In general productivity in the Tasman Sea is greatest at points of upwelling, where nutrient rich, oxygenated water reaches the surface such as the upwelling plume northwest of South Island (Foster and Battaerd 1985).

1.3.3 Effects of Glaciations on the Tasman Sea

Increased foraminiferal abundance on the Lord Howe Rise (to the north and east of Challenger Plateau) indicates a slight northward shift of the Tasman Front during times of glaciation. Data from the East Tasman Plateau show a more complex situation. The northward migration of the Tasman Front may indicate a reduction in volume of the equatorial warm-pool and/or an increase in the strength of cool subtropical water-masses (Martinez 1994b). At interglacial stage 5.5, productivity evidence from deep-sea cores suggests that the Tasman Front was located further south compared to its modern position (Nelson et al. 1993; Nees 1997; Weaver et al. 1998). Nees (1997) deduced that changes in abundance of benthic foraminiferal species on the East Tasman Plateau and Lord Howe Rise could be related to glacial/interglacial stages.

Estimated sea-surface productivity for both the East Tasman Plateau and the Lord Howe Rise indicates an increased nutrient input during glacial stage 6 and decreased input during interglacial stage 5.5. Benthic foraminiferal abundances are interpreted to be related to high levels of sea-surface productivity often recorded as a feature at or near oceanographic fronts. Martinez (1994b) studied downhole changes in planktonic species assemblages in the Tasman Sea and concluded that these were directly related to oscillating oceanographic conditions (especially those associated with the N-S migration of fronts). Evidence for higher productivity in the form of benthic and planktic foraminiferal abundances have been used to plot shifts in the Tasman front, as high productivity levels are usually associated with oceanic boundaries (Nees 1997; Weaver et al. 1998).
Chapter Two

The Planktic Foraminiferal Assemblage: Taxonomy and Ecology

2.1 Introduction

Planktic foraminifera (protozoans) are individually small, yet collectively they are an important component of the open ocean planktonic biomass. This importance results from their immense productivity, worldwide distribution, and the ability to secrete calcite tests (Be et al. 1979; Hayward 1983; Hemleben et al. 1989). The tests of dead planktic foraminifera constantly rain down on the seabed as part of marine snow. This process of accumulation has continued for the last 130 million years, so that today nearly half of the total ocean floor is now covered by 'globigerina ooze', composed predominantly of planktic foraminiferal tests (Berger 1970; Emerson and Bender 1981; Hayward 1983; Deuser and Ross 1989; Bearman 1989; Hemleben et al. 1989; Hodell and Ciesielski 1991; Wu and Berger 1991).

The deep-sea core site SO 136-005 lies at the southern edge of the Lord Howe Rise on the Challenger Plateau (Fig. 2.1). In an ecological sense, the sea-floor in this area is covered by an oceanic zone described as transitional by Hayward (1983) (Fig. 2.1). According to that author, the area around site SO 136-005 should contain approximately half of the 26 planktic foraminiferal species living around New Zealand. The transitional zone lies between the subtropical province to the north of New Zealand and the subtropical convergence to the south of the South Island of New Zealand. Those planktonic foraminiferal species positively identified as present in samples analysed for this study are compared to the assemblage predicted to be present in the transition zone at 42°S by Hayward (1983) (Table 2.1). Approximately 6 more species were found but not identified in the dredge sample SO 136-002 in the present study. Each of these species was a minor constituent of the overall assemblage. It was anticipated that not all of the species indicated by Hayward (1983) as living in waters covering the Challenger Plateau would be present in the samples used in the present study. The reason for this is that different species occur
in varying abundance and as such not all species form part of the sedimentary pile everywhere within the transition zone.

Fig. 2.1 Ocean province map showing core SO 136-005 and dredge sample SO 136-002 collection site within the transition zone between the subtropical province and subtropical convergence (front). After Hayward (1983).
Planktic foraminiferal species on the Challenger Plateau.

<table>
<thead>
<tr>
<th>Present in dredge sample SO 136-002 and multicore</th>
<th>SO 136-005 (Hayward 1983)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Globigerina bulloides</td>
<td>Globigerina bulloides (abundant)</td>
</tr>
<tr>
<td>Globigerina falconensis</td>
<td>Globigerina falconensis (common)</td>
</tr>
<tr>
<td>Globigerina inflata</td>
<td>Globigerina inflata (abundant)</td>
</tr>
<tr>
<td>Globigerinella aequilateralis</td>
<td>Globigerinella aequilateralis (common)</td>
</tr>
<tr>
<td>Globorotalia hirsuta</td>
<td>Globorotalia hirsuta (abundant)</td>
</tr>
<tr>
<td>Globorotalia truncatulinoides</td>
<td>Globorotalia truncatulinoides (abundant)</td>
</tr>
<tr>
<td>Neogloboquadrina pachyderma</td>
<td>Neogloboquadrina pachyderma (abundant)</td>
</tr>
<tr>
<td>Orbulina universa</td>
<td>Orbulina universa (common)</td>
</tr>
<tr>
<td></td>
<td>Globigerina humilis (rare)</td>
</tr>
<tr>
<td></td>
<td>Globigerina quinqueloba (abundant)</td>
</tr>
<tr>
<td></td>
<td>Globigerinita glutinata (common)</td>
</tr>
<tr>
<td></td>
<td>Globigerinita iota (rare)</td>
</tr>
<tr>
<td></td>
<td>Globigerinoides rubber (rare)</td>
</tr>
<tr>
<td></td>
<td>Globorotalia crassula (rare)</td>
</tr>
<tr>
<td></td>
<td>Globorotalia scitula (common)</td>
</tr>
<tr>
<td></td>
<td>Gloigerinita bradyi (common)</td>
</tr>
<tr>
<td></td>
<td>Hastigerina pelagica (rare)</td>
</tr>
<tr>
<td></td>
<td>Neogloboquadrina dutertrei (common)</td>
</tr>
</tbody>
</table>

Table 2.1 Comparison of foraminiferal species identified in the present study with those identified as present within the Transition zone of Hayward (1983).
2.2 Description of Globigerina bulloides d'Orbigny

The taxonomy of planktic foraminifera rests almost entirely on the morphology of the multi-chambered calcite test (Hayward 1983) (Figs. 2.1-2.5). *G. bulloides* was first described by d'Orbigny (1826) and his description included morphotypes which were later described by Parker (1962) as two new species, *G. calida* and *G. falconensis*. Parker (1962) provided sketches of all the morphotypes incorporated into the new definition of *G. bulloides* (Fig. 2.2) and it is this publication which largely influences the taxonomic character of *G. bulloides* today. Hayward (1983) further defined the description of *G. bulloides* as large, with 4 spherical chambers per whorl, and a large aperture with a high arch.

Specimens used in the present study were identified using Hayward's (1983) definition and previously identified specimens held in the University of Canterbury foraminifera collections of the Dept. of Geological Sciences and Scanning Electron Microscope images from other studies (Spero and Lea 1996). Some specimens (especially smaller than 200µm) are extremely difficult to place with respect to the two very-closely related taxa, *Globigerina bulloides* and *Globigerina falconensis*. This problem is exaggerated when tests of *G. falconensis* have had their bullae broken off (usually obvious under SEM). As a result, specimens smaller than 250µm were not used for this study.

The most obvious differences between tests of mature *Globigerina bulloides* and *Globigerina falconensis*, are the shape of the aperture and the surface texture. The aperture of *G. falconensis* is usually obscured by the bulla, and the test surface is more rugged and less porous looking than those of *G. bulloides*. 
Spero and Lea (1996) published images of two *G. bulloides* morphotypes, which bear a strong resemblance to the Challenger Plateau specimens used in this study (Figs. 2.3 and 2.5). One morphotype was previously classified as a separate species (*G. bermudezi*), but has since been established as a phenotypic variant of *G. bulloides* by cultured growth experiments (Kennett and Srinivasan 1983; Spero and Lea 1996). This morphotype, which possesses a very broad aperture, is clearly very-closely related to another group of Challenger plateau specimens (Fig. 2.5). Little et al. (1997) describe another *G. bulloides* morphotype (the Benguela species), which has a large, offset bulla; this morphotype was noticed during sample selection herein (Fig. 2.2 (2b)), but no specimens with bullae were selected because they could also be confused with *G. falconensis*.

Darling et al. (2000) found four extant morphospecies of *G. bulloides* throughout both northern and southern hemisphere polar regions. Their classificatory scheme was based primarily on DNA evidence (see chapter 5). The occurrence of different morphospecies living in the same region clearly illustrates that isolation of specimens
representing the same taxon is extremely difficult at the local level; regional and global comparisons being even more so (Reynolds and Thunell 1986).

It is therefore apparent that there is a considerable ambiguity with respect to both the specific definition and the morphologic beacons used by various authors to isolate specimens of _G. bulloides_. On this basis alone, there is increasing recognition that criteria used to isolate various morphotypes should always be presented when the results of associated research are published (Houston et al. 1999; Darling et al. 2000). There are 4 morphotypes that are selected as _G. bulloides_ in the present study (Figs 2.3-2.6). Characteristics looked for were 1) a large aperture with a reasonable arch to the upper lip 2) no sign of broken off bullae and 3) surface texture. Morphotype 1 (Fig. 2.3) was the most common morphotype, making up over of 50% of all samples.

![SEM image of morphotype 1 of C. bulloides. Example of the most common G. bulloides morphotype extracted for all analyses carried out in this project.](image)
Fig. 2.4. SO 136-005/02. Morphotype 2 of *G. bulloides*. Note the flattened appearance and an aperture which is smaller than that found on most examples of *G. bulloides*.

Fig. 2.5. SO 136-005/03. Morphotype 3 of *G. bulloides*. This specimen has an open aperture and is similar in appearance to *G. bermudezi*, the morphotype of *G. bulloides* as shown by Spero and Lea (1996).
Fig. 2.6. SO 136-005/04. Morphotype 4 of G. bulloides. Note the narrow, tightly arched aperture. This specimen was not cleaned in a sonic bath and so contains some detrital material inside the aperture and on the surface (indicated by arrows).

2.3 Growth and Life History of G. bulloides

The life span of individual planktonic foraminiferers varies from two weeks to one year (Be et al. 1979; Hemleben et al. 1989; Martinez 1994b), and reproduction occurs at depths where water density enhances the possibility of zygote formation (Be 1977; Thunell and Reynolds 1984; Reynolds and Thunell 1985; Hemleben et al. 1989). Foraminiferans have been shown to secrete additional chambers in a matter of hours (Spero and Lea 1996). An entire test can be formed in just a few days, with chambers added one at a time each usually proportionately larger than the preceding chamber (Hayward 1983; Martinez 1994b; Spero and Lea 1996). Spero and Lea (1996) describe the processes and stages observed during chamber formation as G. bulloides
tests take shape and calcify. They conclude that the life cycle lasts between 14 and 21 days, with maturity being achieved after the first 9 chambers have been precipitated. *G. bulloides* has a trochospiral chamber arrangement (asymmetrically coiled, with one side evolute and the other involute), which may be coiled either to the left or to the right (Hayward 1983; Spero and Lea 1996).

*G. bulloides* is symbiont-barren and has significantly shorter spines (1-1.5mm), than symbiont-bearing species (2.5mm) for reasons apparently unknown (Spero and Lea 1996). The soft protoplasm of the live *G. bulloides* is partly enclosed within the chambers, but may also stream out through the apertures as pseudopodia (Hayward 1983; Spero and Lea 1996). Approximately 24-48 hours prior to gametogenesis, *G. bulloides* gradually shortens its spines and withdraws its rhizopodial network, a short time later (hours), numerous gametes are observed streaming out of the apertures into the surrounding water (Spero and Lea 1996).

The tests of planktic foraminiferids have a wide variety of surface textures and are also pierced by many pores, the density and diameter of which vary from species to species. In 2 of the 3 families of planktic foraminifera, species have elongate spines around the outside of the test, but these usually drop off soon after death (Be 1977; Kennett and Srinivasan 1983; Spero and Lea 1996). There are two ways in which planktic foraminifera gain food; there are symbiont-bearing species that rely on photosynthetic bacteria to provide them with food in return for a place to live and there are symbiont-barren species that prey on microscopic marine organisms found in the water column.

### 2.4 Habitat

Variation in the relative abundances of planktonic foraminiferal species in the Tasman Sea is not only controlled by the position of the thermocline/mixed layer, but by variations in sea surface temperature (SST) and the availability of nutrients, as well as other ecological factors (Martinez 1994b). Symbiont-barren species such as *G. bulloides* occur preferentially in eutrophic (upwelling) areas where the thermocline is
shallow or, underneath the photic zone. In contrast, symbiont-bearing species occur in oligotrophic areas and in the photic zone (Sautter and Thunell 1991a; Martinez 1994b; Little et al. 1997). Martinez (1994b) presented a table, which outlined the dominant planktonic species in different regions of the Tasman Sea and placed G. *bulloides* as one of four dominant species in the Transition zone between 33° and 45° S.

*G. bulloides* is a symbiont-barren species, which generally lives in the upper 50m of the water column, but which may migrate vertically down to 400m (Spero and Lea 1996; Little et al. 1997). Such species are usually heterotrophic consumers, preying on dinoflagellates, diatoms and coccolithophores (Theide 1975; Hemleben et al. 1989). Such ecological requirements indicate why deep-dwelling species like *G. bulloides* occur commonly in upwelling areas where the thermocline is shallow and nutrients are abundant. Theide (1975) and Little et al. (1997) described a linkage between the density of *G. bulloides* in the water column and coastal upwelling zones and noted that there was an increase in abundance of *G. bulloides* in sediments representing glacial stages off the coast of West Africa. This increase in abundance during glacial times was linked to increased upwelling as a result of lower sea level and the reorganization of ocean currents and water-mass boundaries (Theide 1975).

Kustanowich (1962) identified a foraminiferal assemblage between 32°S and 37°S (the 'north-central fauna'), south of which faunas are dominated by *G. bulloides*, *G. truncatulinoides*, *G. inflata* and *G. pachyderma*. Zooplankton and associated planktic foraminiferal distribution in a localized upwelling zone northwest of the South Island was studied by Foster and Battaerd (1985). They concluded that copepods and euphasid larvae increase in number at the center of the upwelling zone, whereas *Orbulina universa* and *G. bulloides* increase at the margins of the upwelling plume. This distribution pattern was also found to occur in the Benguela upwelling system of the coast of West Africa and reflects the grazing habits of planktonic foraminifera and their response to phytoplankton and zooplankton blooms (Foster and Battaerd 1985; Little et al. 1997).
2.5 Conclusions

Because *G. bulloides* is a globally dominant species in cool-temperate waters it has been widely used for oxygen isotope analysis from deep-sea cores, and it is largely for this reason that *G. bulloides* was chosen as the target species for the present study. As stated in this chapter there are a number of difficulties in the identification of *G. bulloides* such that it is necessary in any work to clearly state what it is that has been incorporated in the species for comparison of studies. The occurrence and vertical migration of *G. bulloides* in upwelling zones is another problem area in that a single specimen may live in waters of different temperature at various life stages. This will have the effect of modifying the resultant isotopic signal of that specimen.
Chapter Three

Carbonate solution and the Sea Water Carbonate System

3.1 Introduction

Since the beginning of the industrial revolution carbon dioxide has become a molecule of immense importance to the human race. We now know that globally, industry produces millions of tonnes of CO\textsubscript{2} annually and it would appear to many that this is having a significant effect on Earth’s climate in the form of global warming (Chester 2000). The CO\textsubscript{2} concentration of the atmosphere can now be measured and compared year to year and fluctuations recorded. In order for these measurements to have any meaning it is necessary to relate them to a record, which spans millions of years. Paleoceanography is a tool that enables scientists to indirectly measure past changes in the CO\textsubscript{2} concentration of the atmosphere and place modern measurements in context (Murray and Riley 1971; Volat et al. 1980; Bearman 1989; Boyle 1988; Broeker and Denton 1989; Varney 1992; Chester 2000). The ways in which CO\textsubscript{2} reacts in nature, be it in the biosphere, the atmosphere or hydrosphere, are aspects important to our understanding of paleoceanography and subsequently paleoclimatology. By studying how marine organisms utilize CO\textsubscript{2} and how CO\textsubscript{2} behaves in the oceans we gain insight into the nature of the relationship between hydrosphere, biosphere and atmosphere. The marine carbon cycle is of key importance in the story of life in the sea, dissolved CO\textsubscript{2} being the primary source of carbon for marine plant life, and the primary component (along with water) in the process of photosynthesis (Bearman 1989; Chester 2000). The carbonate system is also of vital importance in the study of paleoceanography in that many animal species in the marine environment use components of the carbonate system to construct skeletons, tests and valves (Fig. 3.1).

The focus of the present study is the oxygen isotope chemistry of the planktic foraminiferal species \textit{G. bulloides}. This species grows and secretes its test in the oceans of the world and as such is affected by the chemical properties of the water in
which it lives. It is therefore imperative that any study undertaken with regards to this species, and indeed any other marine species pay due attention to the dynamic nature of sea-water chemistry and how associated compositional changes impact on organisms such as *G. bulloides*. The chemical component most relevant to this study is carbonate because it is this molecule that contributes most to the formation of CaCO$_3$. The following is an outline of the CO$_2$ cycle and the role CO$_2$ plays in the preservation and corrosion of calcareous tests deposited on the floor of the oceans.

3.2 **Ocean CaCO$_3$ Chemistry**

3.2.1 **Dissolved CO$_2$ Cycle**
Carbon dioxide is incorporated into the biosphere via photosynthesis, soft-tissue formation and by the construction of hard, skeletal material. In life and death these act as biological carriers of CO$_2$ to the sea floor. Most of the mass flux of material is carried down the water column in association with large-sized aggregates such as faecal pellets and other components making up 'marine snow' (sinking biological material) (Bearman 1989; Chester 2000). As carbon dioxide is removed from near-surface waters by the biological processes listed above, it is being continuously replaced from both the atmosphere and the oxidative destruction of organic matter. Thus the concentration increases towards the sea floor, with maximum concentrations in very deep water below the carbonate compensation depth (Chester 2000; Varney 1992; Cai et al. 1997). There is still enormous debate over the actual quantities of CO$_2$ in the oceans and the rates at which it is relocated and removed. The processes controlling CO$_2$ quantities are:

1) Removal of CO$_2$ by photosynthesis
2) Removal of CO$_2$ by formation of CaCO$_3$
3) Removal of CO$_2$ by solar heating
4) Addition of CO$_2$ by oxidation of plant material
5) Addition of CO$_2$ by dissolution of CaCO$_3$
6) Addition by increases in CO$_2$ in the atmosphere from fossil fuel burning
7) Addition by the poorly understood process of recharging and upwelling producing significant local CO$_2$ input.
Clearly such factors also affect both the chemistry and volume of material being deposited on the sea floor and as a consequence also play a large part in influencing the chemistry and physical characteristics of deep-sea sediments.

Fig. 3.1 The cycling of carbon between the Atmosphere, Hydrosphere and Biosphere (from Bearman 1989).

Carbon dioxide gas is more soluble in cold water than in hot water, hence it is present in highest concentrations in cold water masses such as Antarctic Bottom Water and Antarctic Intermediate Water (Murray and Riley 1971; Bearman 1989). A combination of decreasing temperature and increasing pressure also produce increased concentrations of CO₂ in solution at depth in the oceans such that the concentrations of all carbonate chemical species in the oceans can be seen as a
function of temperature and pressure (Chester 2000; Varney 1992). Concentrations of carbon dioxide gas in seawater are very low; in surface waters, only about 1 atom of carbon in 200 is in the form of dissolved CO\textsubscript{2}, and even in the deep ocean this figure only rises to about 3 atoms in 200 (Bearman 1989). This low concentration can be accounted for by the fact that in seawater CO\textsubscript{2} combines with water molecules to produce a weak acid (carbonic acid), which then dissociates to produce hydrogen and bicarbonate ions as in the following equation (1).

\[ \text{CO}_2 \text{ gas} + \text{H}_2\text{O} = \text{H}_2\text{CO}_3 = \text{H}^+ + \text{HCO}_3^- \]

This equilibrium equation, combined with the following factors affecting the Pco\textsubscript{2} (partial pressure of CO\textsubscript{2}) of surface waters, makes measurement of CO\textsubscript{2} in the oceans extremely difficult. Pco\textsubscript{2} is measured in mol/kg of seawater; typical oceanic concentrations are about 2.0-13.0 \times 10^{-6} \text{ mol/kg} (Chester 2000) and values are recorded relative to atmospheric CO\textsubscript{2} partial pressure (Fig. 3.2).

The levels of total CO\textsubscript{2} and Pco\textsubscript{2} in surface waters are related to the exchange of CO\textsubscript{2} across the air-sea interface with differing conditions (namely the rate of photosynthetic draw-down) causing either sluggish or rapid exchange (Varney 1992; Millero 1991). Sluggish exchange near the equator causes Pco\textsubscript{2} of seawater to be greater than atmospheric values, whereas more rapid exchange in polar waters causes Pco\textsubscript{2} of seawater to be lower than the atmospheric value. When rapid exchange occurs the Pco\textsubscript{2} in water and air are similar, and total CO\textsubscript{2} is higher in polar waters as a result of greater draw down by photosynthetic organisms (Millero 1991). There is also a significant fossil CO\textsubscript{2} signal caused by the transfer and dissolution of marine snow via a global conveyor belt. Enormous quantities of CO\textsubscript{2} are transferred to the deep-ocean circulation system as water, rich in biogenic matter, plunges to bathyal and abyssal depths off the north-east coast of North America (Bearman 1989). This water then begins a southward journey through the Atlantic, and is eventually carried past Australia and New Zealand (Bearman 1989). Some of that fossil CO\textsubscript{2} can be reintroduced into shallower water masses as a result of topographic damming and upwelling.
Fig. 3.2. Depth profile for the partial pressure of carbon dioxide in the Atlantic and Pacific Oceans. Surface values are similar to atmospheric values and increase to a maximum at 1 km owing to the oxidation of plant material. The deep-water values are higher in the Pacific because the waters are older and because of the higher primary productivity in the surface waters. From Millero (1991).

The calcium carbonate content of sediments is influenced by many variables operating at or near the sediment/water interface. These include temperature, water depth, salinity and hydrogen ion concentration of the water, the degree of saturation of the water with calcium carbonate, the activity of living organisms, sea water/pore fluid circulation and the proportion of terrigenous debris in the sediments (Trask 1936; Chester 2000). Most of the factors that affect the formation and deposition of calcium carbonate operate simultaneously, and their relative importance varies in different parts of the ocean (Trask 1936; Peterson 1966; Parker and Berger 1971; Volat et al. 1980; Peterson and Prell 1985; Varney 1992).
3.2.2 Ocean O$_2$ Content

Truly anoxic waters, where sediments are initially deposited under anoxic conditions, prevail over only a small area of the oceans (Bearman 1989; Chester 2000). The majority of sea floor environments at all depths are oxidizing and there is usually a layer of oxic material at the sediment surface where interstitial waters are still saturated with regards to dissolved O$_2$ (Emerson and Bender 1981; Chester 2000). The reason for this state of oxidation is explained by oxygen being transported to deep water by oxygen-rich, high-latitude surface waters, which sink and start on the ‘global grand tour’ (Fig. 3.4). Once the oxygen has been transported to deep water it is removed from contact with the atmosphere and is also taken out of the euphotic zone where photosynthetic reactions occur (Varney 1992; Chester 2000). Nonetheless, some oxygen utilization by animals and bacteria occurs in deep water and this oxygen cannot be replaced by exchange with the atmosphere or by plant activity (Bearman 1989; Chester 2000). Therefore dissolved oxygen becomes depleted during the ‘grand tour’, with the overall result that concentrations decrease from the waters of the deep Atlantic to those of the deep Pacific. This is the reverse of the situation for nutrients, which increase in concentration from the Atlantic to the Pacific (Chester 2000; Millero 1991). As a result of the consumption of dissolved oxygen in the interstitial waters through the oxidation of degrading organic matter, the sediment (including interstitial water) can become reducing and ultimately anoxic (Chester 2000).

3.2.3 Ocean pH

The pH of seawater varies over a surprisingly narrow range, centred at 8±0.5 (Boyle 1988; Chester 2000; Varney 1992). The most important aspect of ocean pH for this study is that the dissociation of carbonic acid (H$_2$CO$_3$) forms a buffering system. This may be summarized by the general weak acid-conjugate base equilibrium equation (2).

\[
H_2CO_3 \rightleftharpoons H^+ + HCO_3
\]
Small additions of acids or bases alter the ratio of anion (HCO$_3^-$) to acid (H$_2$CO$_3$) only slightly, and have little effect on the pH of the solution (Varney 1992).

In both the Pacific and Atlantic Oceans, the maximum pH is recorded in surface waters because of the removal of CO$_2$ by photosynthesising components of the biota. Below that horizon, the pH decreases as a result of the oxidation of decaying organic matter (which produces CO$_2$), reaching a minimum of about 7.5 at 1000m depth in the Pacific (Fig. 3.3) (Bearman 1989; Millero 1991). This pH minimum coincides with the O$_2$ minimum and the maximum in Pco$_2$. Increasing pH in deeper waters is a result of the dissolution of CaCO$_3$ owing to increasing Pco$_2$, as a result of the oxidation of organic matter (Fig. 3.2). The pH in very deep waters (>4000m) may reach a maximum of 8.0 owing to the effect of pressure on the ionisation of carbonic acid (Fig. 3.2) (Millero 1991; Varney 1992; Chester 2000).
Fig. 3.3 Depth profile of pH in the Atlantic and Pacific Oceans. The higher pH in Atlantic waters above 1000m result from CO₂ loss as a result of high productivity relative to the Pacific. From Millero (1991).

Changes in pH as a function of depth in both the water column and the sediment pile have been attributed to the summation of two factors (Millero 1991).

- \( \Delta pH = \Delta pH(a) + \Delta pH(b) \)
- \( \Delta pH(a) = -2.0 \) AOU, (apparent oxygen utilization) the decrease in pH owing to the oxidation of organic material.
- \( \Delta pH(b) = 2.4 \Delta Ca \) (change in Ca\(^{2+}\) owing to the dissolution of CaCO₃)
This basically indicates that CO$_2$ from organic matter breakdown is lowering pH causing the dissolution of calcite, which leads to the counteracting rise in pH. Dissolution of calcium carbonate skeletons (CaCO$_3$) occurs where increased acidity of the water results from the release of hydrogen ions (equation 3) (Bearman 1989). Where ΣCO$_2$ concentrations are high CaCO$_3$ is more likely to dissolve than where they are low (Bearman 1989).

(3) \[
\text{CaCO}_3 + \text{H}^+ \rightarrow \text{Ca}^{2+} + \text{HCO}_3^-
\]

Fig. 3.4. Generalised map of deep water flow (dark grey) and surface water return (mid grey) in the oceans. Large ellipses designate sources of North Atlantic Deep Water (NADW) and Antarctic Bottom Water (AABW); small mid-grey circles indicate areas of localized upwelling. Water becomes depleted in O$_2$ as it flows through this cycle starting in the North Atlantic. From Bearman (1989).

More than 90% of the organic carbon that reaches the deep-sea floor is oxidized by O$_2$ (Chester 2000). Oxygen may therefore be regarded as a primary oxidant involved in the destruction of organic matter. In a closed system, the destruction of organic matter will continue until sufficient oxygen has been consumed to drive the redox potential low enough to favour the next most efficient oxidant (Emerson et al. 1980; Millero 1991; Chester 2000). Thus, as dissolved oxygen becomes depleted, organic
matter decomposition can continue using \( \text{O}_2 \) from secondary oxidant sources (suboxic diagenesis). Such secondary oxidants include nitrates, \( \text{MnO}_2 \), \( \text{Fe}_2\text{O}_3 \) and sulphates (Emerson et al. 1980; Chester 2000). Consequently, \( \text{CO}_2 \) is continuously being produced by the ongoing organic decomposition, affecting both the \( \text{Pco}_2 \) and local \( \text{pH} \) of the ocean water.

Pelagic sediments generally have organic matter concentrations of only 0.1-0.2\%, (Berelson et al. 1990; Chester 2000). As a result, the oxidizing layer can extend several tens of metres below the sediment/water interface simply because dissolved oxygen concentrations are affected only slightly by the low rate of organic matter oxidisation.

Much of the above system describes biologically driven decomposition of organic matter. The diagenetic part of the equation, which affects the sediment (and hence foram tests), is a result of that organic breakdown and the effects of ambient interstitial water chemistry and increasing depth of burial (Bearman 1989, Millero 1991). The alteration of sediments and the valves/tests of living organisms at the sediment/water interface is considered a syndiagenetic process. It is from this interface that the core used in the present study was extracted and so samples herein have largely been subjected to syndiagenetic processes.

3.3 Carbonate Solubility

Carbonate solubility is key in the preservation of calcareous material in the oceans and as such bears immense relevance to the present study. The rate at which tests constructed of calcite dissolve in both in the water column and on the seafloor is dependant upon a number of factors. These factors include the initial crystal structure of calcite making up tests, the \( \text{pH} \) of the water in which the tests are submerged (equation 3) and most importantly the calcite saturation state of the surrounding water (Emerson and Bender 1981; Volat et al. 1990). The following section outlines these and other factors important in the preservation and/or solution of calcite in the oceans.
3.3.1 Carbonate Compensation Depth

A major portion of CaCO$_3$ formed in the oceans is precipitated by pelagic organisms in the upper ocean where the waters are supersaturated with respect to calcite and aragonite (Martin and Fitzwater 1988; Morse and MacKenzie 1990). Post-mortem carbonates formed in the upper ocean become an integral part of ‘marine snow’ and as a result are deposited on the seafloor along with organic matter. The combined affect of 1) decreasing temperature, 2) increasing pressure, and 3) fluctuating P$_{CO_2}$ result in water in the deeper parts of the oceans becoming undersaturated, first with respect to aragonite and then with respect to calcite (Millero 1991; Varney 1992). The depth at which dissolution begins is called the lysocline (Emerson and Bender 1981; Martin and Fitzwater 1988; Bearman 1989; Morse and Mackenzie 1990; Millero 1991; Chester 2000). The carbonate compensation depth (CCD) is the depth in the oceans at which water is so undersaturated with CaCO$_3$ that none remains undissolved (Bearman 1989; Millero 1991; Chester 2000). This also applies to aragonite, however, aragonite is more susceptible to dissolution than CaCO$_3$ and therefore the aragonite compensation depth is shallower than the CCD.

The increase in P$_{CO_2}$ with ocean depth is primarily the result of oxidation of organic matter. The spatial/temporal contrasts in the rates at which this reaction proceeds establish the enormous variation in saturation state evident in the deep ocean (Boyle 1988; Morse and MacKenzie 1990). These same factors also affect the quantity and preservation state of CaCO$_3$ when it reaches the sea floor, and as a result, only a small fraction of the total amount of CaCO$_3$ produced in surface waters is deposited on the seafloor. It is important to keep in mind that the formation and preservation of both pelagic and benthic CaCO$_3$ is intimately tied to ocean productivity, circulation and chemistry. The complex interactions associated with the cycling of organic carbon within the oceans and the effects of dissolution and burial at the sediment/water interface affect the preservation of calcite (Bearman 1989; Berelson et al. 1990; Millero 1991).

The metabolisation and decomposition of organic matter at the seawater-sediment interface plays an important role in determining the pattern of calcium carbonate preservation in the deep sea (Volat et al. 1990; Emerson and Bender 1981; Chester
Emerson and Bender (1981) presented a model, which predicts that in deep-sea sediments calcite dissolution should begin at a depth that is 500-1000 metres above the calcite saturation horizon in the water-column. The model also predicts that near the sediment-water interface, in a sediment at the saturation horizon, 40-80% of the calcium carbonate rain from surface waters is dissolved by metabolic CO_2 produced in the surface pore.

In fact calcite dissolution occurs at all depths and the effects of dissolution/recrystallisation have been described for ostracod shells recovered from littoral depths (Swanson and van der Lingen 1997). An increase in the particulate carbon to carbonate ratio displaces the onset of CaCO_3 dissolution at the CCD upward with respect to the water column saturation horizon (Emerson and Bender 1981). If the rain of particulate organic carbon is equal to that of CaCO_3 the model predicts that the CCD should lie near the saturation horizon. As the organic carbon : CaCO_3 rain ratio increases, there is a tendency to preserve less calcite above the saturation horizon (Emerson and Bender 1981). This, again is simply a response to increased oxidation of organic carbon resulting in increased CO_2, higher acidity and CaCO_3 dissolution. Peterson (1966), Berger (1967, 1970), and Peterson and Prell (1985) all conducted tests on the solubility of calcite with increasing ocean depth. They noted a slight dissolution of calcite tests, from a single assemblage on the sea floor between 300 and 4000m depth, followed by rapidly increasing dissolution below this depth. Observations of changes in the vertical oceanic chemical structure indicate that during glaciations metabolic CO_2 and nutrients are shifted from intermediate waters into deeper waters, thus raising Pco_2, increasing calcite dissolution, and effectively raising the lysocline (Boyle 1988; Labracherie et al. 1989).

When calcareous tests reach the seafloor and are incorporated into the sediment pile there are a number of diagenetic processes that control the preservation or destruction of the tests. Dissolution, overgrowth and recrystallisation have all been identified as diagenetic factors that affect foraminifera tests after deposition (Collen & Burgess 1979; Murray 1989). Dissolution may result in the enlargement of pores and perforations and the stripping of layers from the test surface. Overgrowth of calcite on foraminiferal test surfaces is initiated by growth of small crystals on the plates making up the test wall, and these crystals progressively increase in size and merge
with one another (Collen & Burgess 1979; Boltovskoy and Totah 1992). Walter and Morse (1984) state that dissolution rates are a function of both grain size and microstructure. They defined an empirical roughness factor that quantifies the difference in reactive surface area between rhombic calcite and a given biogenic grain of equivalent size. This roughness factor increased with grain microstructural complexity but was independent of grain size over the grain-size range studied (51-513 microns) (Walter and Morse 1984). Their findings indicate that both microstructure and grain size can play important roles in controlling reactivity of biogenic carbonates during diagenesis. It is known for example that calcite laths preferentially dissolve along the c-axis (Henrich and Wefer 1986). Thiede (1975) made the observation that planktonic species dwelling in upwelling zones are highly resistant to dissolution relative to other species and stated that methods used to delineate the lysocline (such as preservation indices) should be applied with caution in upwelling, coastal, and possibly equatorial regions.

3.3.2 Dissolution and Etching

Dissolution of foraminiferal tests has been recognized mostly among planktonic species (Collen and Burgess 1979). With these it is most important below the lysocline, but also occurs at shallower depths where it selectively removes thinner-shelled species and may alter the character of the assemblage (Berger 1967, 1968; Parker and Berger 1971; Adelseck et al. 1973; Murray 1989; Boltovskoy and Totah 1992; Wu and Berger 1991). Partial dissolution, or etching, of the test surfaces of calcareous foraminifera has been recorded by Murray (1967), who found that most fossils examined showed some etching effects which made the tests opaque and sometimes altered the surface extensively. Effects were most pronounced on topographically higher parts of the test and hence were possibly aided by abrasion prior to burial. If a foraminiferid is buried in sediment in which the interstitial water has a pH 7.0 or less, etching of that test will take place (Murray 1967). Lowering of the pH below 7.0 will, however, etch and weaken the tests of calcareous foraminiferids in a much shorter period of time. Significant to paleoecological studies is the possibility that thinner-walled or otherwise more susceptible species may be
dissolved first, thus altering the character of the assemblage (Murray 1967; Boltovskoy and Totah 1992; Dittert et al. 1999).

Dissolution of foraminiferal tests on the sea floor is enhanced by the action of migrating pore waters, which are presumed to be undersaturated with respect to calcium carbonate (Lorens et al. 1977; Collen & Burgess 1979; Emerson and Bender 1981). This process is often progressive, proceeding from initial etching of a test, to its total dissolution, and eventual collapse and fragmentation. The usual effects of partial dissolution on foram tests are that smooth surfaces are roughened, component crystals are made visible by preferential dissolution along crystal boundaries, and pores are enlarged (Fig. 3.5) (Collen & Burgess 1979; Dittert et al. 1999). High porosity and permeability are characteristics important in the processes of dissolution, overgrowth and recrystallisation as they provide fluid pathways and greater surface area for reactions to proceed. It is also possible that porous foraminifera often become infilled with fine-grained carbonate detritus (especially nannofossils), and that such particles may preferentially dissolve (Paull et al. 1988) and in effect locally buffer or neutralize corrosive interstitial waters, at least temporarily.

Boltovskoy and Totah (1992) carried out a series of experiments in which planktic and benthic foraminiferal species were exposed to buffered distilled water of pH 6.7 to assess their preservation potential. Over a period of 160 days the specimens were observed and the amount of dissolution each species had endured was recorded. From this data they were able to derive an “Index of Preservation”, which characterized the state of preservation of a given species within 5 preservation states (5 = all specimens completely preserved to, 1 = all specimens completely destroyed). By ranking species on a scale of susceptibility to dissolution, these authors were then able to calculate the preservation state of a sediment horizon based on presence/absence of those species in the sedimentary pile. The lower the number of species the greater the level of dissolution. One obvious weakness of this method is that it is based on an assumption that all species presumed missing were actually present originally.
Fig. 3.5 *G. bulloides* test exhibiting dissolution and etching around crystal boundaries. Note also the preferential dissolution of topographic highs; this may be aided by physical abrasion of these highs during and after deposition.

However, despite these deficiencies, this technique and a modified version of the same are still routinely used as a method for calculating mass accumulation rates (MAR’s) for carbonate-rich, deep-sea sediments. *G. bulloides* was found to be more resistant than several benthic species, although, taken as a whole, planktonic foraminifers have a lower preservation potential than benthic forms (Bolotovskoy and Totah 1992). Dissolution of different specimens of the same species also show variable effects, presumably owing to morphologic differences between specimens (Hetch and Savin 1972; Emiliani 1974; Healy-Williams 1985; Bolotovskoy and Totah 1992; Houston et al. 1999). Bolotovskoy and Totah (1992) also discovered that a few tests often remain in very good condition, owing perhaps to intraspecific differences in shell robustness or even to recrystallisation processes that strengthen them internally. Only the exteriors of tests were examined in their study.
Dissolution experiments undertaken by Henrich and Wefer (1986) indicate that skeletal structure is as important a factor as mineralogy and crystal size in affecting the rate of disintegration of biogenic carbonates. For their experiment, particles of aragonite and high Mg-calcites (representing a wide spectrum of mineralogies and types of skeletal framework) were exposed to seawater at different depths on a mooring in the Drake Passage for 52 days. They concluded that the breakdown of biogenic carbonates is not only controlled by carbonate mineralogy and particle size, but also strongly influenced by other skeletal features (Henrich and Wefer 1986). These include crystal size, resistance of organic coatings to decomposition, and organisation of the skeletal framework, especially the pore space between individual skeletal crystals and the overall permeability within the skeletal structure. As a result, intraparticle permeability is strongly variable for skeletons of almost identical mineralogy and chemical composition, and in many cases also differs within the same skeleton. The intraparticle permeability controls and often directs the flow of water through the test explaining the variety of dissolution features often observed in tests of a single species selected from the same sample (Henrich and Wefer 1986).

Berelson et al. (1990) also concluded after similar experiments that dissolution rate is dependent on shape and size of the individual skeletal crystals and how those laths are arranged within the skeleton and, that organic matter oxidation supplies the acid to account for 60-100% of the total calcium carbonate dissolution in seafloor sediments. The chemistry of interstitial waters immediately around the test surface appears to have had little evaluation. It is possible that the chemistry of the interstitial water immediately surrounding tests may alter over distances of only a few microns from the test surface. The irregular nature of foram test surfaces could create microenvironments in which water becomes trapped and saturated with respect to CaCO$_3$ because it is not being replenished. Thus a progressive shift may occur to a carbonate-saturated state as a result of test-wall dissolution in the area confining the trapped fluid.
3.4 Conclusions

This chapter has outlined the ways in which the mineral calcite is formed and how calcareous tests are affected by ocean chemistry whilst falling to and post-deposition on the sea-floor. The subjects of most relevance to the present study are the factors affecting dissolution and precipitation of calcite at or near the sediment/water interface. It is apparent that there are a number of factors controlling the eventual preservation or dissolution of foram tests at this interface. The most important of these factors are 1) amount of organic matter in the sediment 2) original crystal structure of the tests and, 3) the depth to the CCD and exposure to undersaturated fluids Each of these factors are vary greatly over the worlds sea-floors.
Chapter Four

Preservation Index and Fragmentation Analysis

4.1 Preservation Index

Indices of preservation and dissolution have been developed and used by a number of authors as a means for quantifying dissolution in deep-sea cores (Parker and Berger 1971; Thiede 1973; Thompson and Saito 1974; Thunell 1976; Teh-Lung and Tadamichi 1977; Peterson and Prell 1985; Henrich and Wefer 1986; Paull et al. 1988; Boltovskoy and Totah 1992; Martinez 1994a; Swanson and van der Lingen 1994, 1997; Dittert et al. 1999; Dittert and Henrich 2000). Dittert and Henrich (2000) devised a dissolution index for *Globigerina bulloides* and provided evidence for 1) progressive *G. bulloides* ultrastructural breakdown with increasing carbonate dissolution even above the lysocline, 2) a sharp dissolution increase at the sedimentary lysocline and 3) the total absence of that species at the lysocline. Their “bulloides dissolution index” (BDX) was based on dissolution characteristics as observed with a SEM and describes a sequence ranging from the best-preserved specimens (R1) still having spines intact, through break down in spines and pores to specimens not even preserved as fragments (R5). A complementary crystal structure index was also devised which outlined the alteration in crystal appearance with increasing dissolution. Dittert and Henrich (2000) found that their dissolution index was useful in locating the lysocline in the Southern Atlantic Ocean as values of dissolution increased with depth and carbonate undersaturation.

Swanson and van der Lingen (1994) devised an ostracod dissolution index based on six arbitrary classes ranging from 0 (transparent, perfectly preserved test) to 6 (chalky, collapses when manipulated or wet). Swanson and van der Lingen (1994) were also able to prove that the dissolution indices developed for podocopid ostracods from the Tasman Sea could be used as a proxy signal for surface productivity, which contrasted with many of the results presented by foram workers where dissolution intensity was related to regional fluctuation of deep-ocean, carbonate saturation.
4.1.1 Objectives

The main focus of research for this thesis was the development of a protocol for the selection and sub-grouping of morphotypes for the planktic foraminifer *Globigerina bulloides* based on physical characteristics readily recognizable using a transmitted light microscope. A preservation index was developed in this study that enables the distinguishing of preservation state of tests under the transmitted light microscope, thus enabling overall preservation indices to be calculated from core samples without the need for SEM examination. The “preservation index” consists of a series of five grades representing a series of preservation states (best, grade 1; to worst grade 5) for those tests. Such a classification system is qualitatively useful, although somewhat arbitrary and artificial in the sense that any foram assemblage undergoes progressive and continuous degradation. However the intensity with which that dissolution process proceeds varies both temporally and geographically as a result of changing ocean chemistry. Swanson and van der Lingen (1994) derived a similar index for ostracod preservation state. Swanson’s index, however, differs to the index devised here as ostracods moult 7-8 times in their lifetime unlike forams and because the ostracod carapace is an architectural solution to a life spent entirely on the sea-floor. Many valves have surface features that have evolved to reduce the effects of dissolution and thus economies with respect to the metabolic stress associated with calcite precipitated have been achieved (Swanson and van der Lingen 1994).

It was hoped that by sub-dividing the species *G. bulloides* and analysing $^{18}$O values from the resultant sub-groups, it would be possible to determine if there are significant $\delta^{18}$O variations between morphotypes of this species selected from classes representing the most extreme preservational states (i.e. grades 1 and 5).

Another reason for establishing a downhole preservation curve was to see if there was any link between overall dissolution, fragmentation, $\delta^{18}$O values and core sample depth.
4.1.2 Methods – Sampling and Microscope/SEM Work

All specimens of *Globigerina bulloides* used in this study were extracted from TASQWA multicore SO 136-005 and dredge sample SO136-002 (see Ch 1 and appendices 3 and 4). The original core sample was split into a down-hole series of 23, 1 cm thick, washed subsamples. For each subsample, the sediment was washed in distilled water then, dry-sieved through a fine (250μm mesh) sieve, the >250μm fraction being retained for analysis. The sieve was thoroughly cleaned using a sonic bath and left to dry between each sample. The >250μm fraction was then spread in a thin layer (one grain deep) on a picking tray and specimens of *G. bulloides* were removed with a fine, moist brush under a reflected-light microscope and placed in mounting trays. Adhesives were not used to secure specimens to the trays because of the probability of contamination of specimens destined for geochemical analysis. Additionally adhesives obscure much of the test microfabric, detail essential to the SEM part of this investigation.

The characteristic used to differentiate degrees of preservation under the binocular microscope was an assessment of transparency when the test was wet. Those tests showing minimal transparency were classified as grade 1, whilst completely transparent tests were grade 5. Samples were also examined with a Scanning Electron Microscope (SEM) in order to establish that the classes described above could also be discriminated on the basis of observable alterations to the microfabric of the surface of the test.

4.1.3 Creation of Preservation Index

In order to establish a 'preservation index' for each core sub-sample, the following procedure was adopted. 100 forams were removed from each of the 23 core subsamples. These forams were divided into 5 grades based on test transparency. The number of specimens belonging to each grade was then counted, and these totals were entered in a table as shown below (Table 4.1). The number of specimens in each
grade was multiplied by the grade number e.g. the 15 specimens in grade 1 were multiplied by 1 and the 35 specimens in grade 3 were multiplied by 3. These numbers were then totalled and the total divided by 50 to give a value of between 1 and 10 (= the ‘Preservation Index’). This calculation method was devised during the present study, as methods derived for other studies did not seem appropriate to the present study.

Table 4.1

<table>
<thead>
<tr>
<th>Preservational Grade</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>Totals</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of specimens</td>
<td>15</td>
<td>25</td>
<td>35</td>
<td>15</td>
<td>10</td>
<td>100</td>
</tr>
<tr>
<td>Grade Total</td>
<td>15</td>
<td>50</td>
<td>105</td>
<td>60</td>
<td>50</td>
<td>280</td>
</tr>
<tr>
<td>Preservational index</td>
<td>280/50</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>5.6</td>
</tr>
</tbody>
</table>

Shows method for calculation of ‘preservation indices’ from core SO 136-005.

The higher the preservation index value, the lower the overall level of preservation exhibited by specimens in that sample; and the lower the value, the better overall preservation. Numbers are generally between 4.0 and 5.2 as a result of this method of calculation and, thus a difference of greater than 0.2 is considered a significant change when looking at the contributions made to the sample by different grades in the raw data (appendix 2).

The preservation index grades documented below, were derived using specimens from dredge sample SO 136-002, with the assumption that this sample should contain specimens showing all stages of preservation found in the neighbouring multicore SO136-005. Those specimens most recently deposited into the ‘active’ layer at the sediment/water interface were also important because they would provide examples of least corrosion. Each sample within the multicore SO136-005 was graded as to its preservation state down the entire core (23cm) following the procedure outlined below. Both SO136-002 and SO136-005 were taken from approximately the same point on the Challenger Plateau, west of the South Island of New Zealand in 1998 (Fig. 1.1).
4.1.4 Description of Grades for *G. bulloides* Preservation Index (PI)

The following are descriptions of the five grades into which specimens of *G. bulloides* were categorized for the present study.

1) Clean white test, occasionally with some transparency around lip of final chamber.
2) Transparent around lip of final chamber and other minor transparent spots over remainder of test (<30% of surface).
3) Transparent around lip of final chamber and many transparent spots over remainder of test (30% to 70% of surface).
4) Test almost entirely transparent (>70% of surface).
5) Test entirely transparent.

The SEM images presented on plates 1-5, illustrate the surface texture of specimens typical for each of the grades. Clearly, scanning electron microscopy cannot assess transparency, however, equivalent alterations to crystal fabric and texture are apparent using that instrument. These images indicate a general smoothing of test surfaces with decreasing preservation state and confirm the use of test transparency with a binocular microscope.

4.1.5 Results

As illustrated by Fig. 4.1 there is a slight decrease in preservation state downhole with an \( R^2 \) value of 0.2. Whilst the broad scatter of preservation index counts is acknowledged, this slight downhole increase in degradation of *G. bulloides* tests is apparent (Fig. 4.1). The object of this 'preservation index' is to indicate any difference in preservation state between horizons and scattered results were anticipated as a result of differences in the amount of diagenesis between horizons.

The dredge sample SO 136-002 is also plotted (Fig. 4.1) and gives a value toward the worst preserved end of the spectrum. This sample contains a mixture from all horizons of the sediment pile in core SO 136-005. As such it will contain specimens more perfectly preserved than grade 1 and, more importantly, a proportion of
specimens at or near the extreme end of degradation (i.e. grade 5). The latter are very quickly destroyed as diagenesis and compaction proceed.
Plate 1. SEM images of a Grade 1 *G. bulloides* specimen at 5000, 10 000 and 15 000 times magnification.
Grade 2 specimen
*G. bulloides*
Note slightly less topographic relief than in plate 1, with more pores and overall smoother appearance. X 5000

Note calcite crystal boundaries in topographic lows as in plate 1. X 10 000

Note transition from smooth highs to defined crystal boundaries in lows. Also note nannofossil incorporation in lows. X 15 000

Plate 2 SEM image of a Grade 2 *G. bulloides* specimen at 5000, 10 000 and 15 000 times magnification.
Grade 3 specimen

G. bulloides

Note dissolution and worn down appearance of topographic highs and smooth and rough areas in lows.

X 5000.

Note general smoothing of test surface with defined calcite crystals in topographic lows.

X 10000.

Defined calcite crystals in lows are becoming incorporated in test surface in what may be a secondary calcite layer.

Plate 3  SEM image of a Grade 3 G. bulloides specimen at 5000, 10000 and 15000 times magnification.
Plate 4  SEM image of a Grade 4 *G. bulloides* specimen at 5000, 10 000 and 15 000 times magnification.
Grade 5 specimen *G. bulloides*.
Note smoothing of entire test. Some pores contain detrital material. X 5000.

SO 136-005/09

Note outlines of crystal boundaries, pores and material within pores. X 10000.

SO 136-005/09

Again note smooth surface, crystal boundaries and pores. X 15000.

*Plate 5*  SEM image of a Grade 5 *G. bulloides* specimen at 5000, 10000 and 15000 times magnification.
4.2 Fragmentation Analysis

Thiede (1973) observed that the preservation of planktonic foraminiferal assemblages in sediments could be characterized by their degree of fragmentation. Foraminiferal test fragmentation has been found to be one of the best indices for monitoring changes in dissolution intensity (Martinez 1994b; Dittert et al. 2000). Additionally, Thiede (1973) proposed a model for the calculation of absolute carbonate dissolution of pelagic sediments rather than merely grading the dissolution state of sediment relative to other sediments or standards and this technique has been used by a number of workers since. The ides (1973) carbonate dissolution technique is used to identify downhole changes in preservational state compared to cores from other areas. However, for this study the object was to find changes in preservation between horizons of the on core (SO 136-005) and comparison with other cores was not required.

4.2.1 Objectives

A fragmentation ratio is the proportion of whole to fragmented tests, where a fragment was defined as any particle with a surface area of less than 50% of a whole test. Fragmentation ratios were calculated for all 23 samples taken from core SO 136-005 following the method outlined below. This method was used in an attempt to determine any possible relationship between depth of burial of a foram assemblage/taxa and the breakdown of foraminifera in that assemblage as a result of physical and/or chemical alteration. Under normal circumstances it is expected that foram preservation will decline with depth in a core as length of exposure to, and intensity of diagenetic processes (especially compaction and corrosion by interstitial waters) increases.

4.2.2 Methods

The present study used a common method of calculating foraminiferal fragmentation as described in Martinez (1994a). A small (<1cc) sample of sediment was extracted from each washed core residue (includes all particles >250μm). Each sample was sieved and the >180μm fraction kept for the analyses. These fractions were then subdivided using a micro-splitter, until a total sample of approximately 300 individual
“whole” (more than half the test remaining) and “fragmented” forams (less than half the test remaining) were retained in one splitter tray. Forams were then evenly spread on a picking tray and placed under a transmitted light microscope set at 32x magnification. The numbers of whole and fragmented forams were recorded, with every specimen on the tray counted. The calculated fragmentation percentage of a sample is the proportion of fragmented specimens relative to the total number of specimens counted.

4.2.3 Results

The values calculated from fragmentation analyses were entered on a spread sheet (see appendix 2) and graphed as points on a xy scatter plot (Fig. 4.2) with depth in core on the x-axis. A trend line has been added (Fig. 4.2) to indicate the slight increase in fragmentation with depth ($R^2 = 0.15$, mean = 25.2, standard deviation = 3.1). Whilst the broad scatter of points is acknowledged, the evidence of a slight downhole increase in foram fragmentation is anticipated. The multicore SO 136-005 is only 23cm in length so it was not expected that extreme breakdown/diagenesis would have affected constituent sediments.

4.3 Discussion and Comparison of Results

As outlined above, a preservation index and fragmentation percentage was recorded for all 23 samples from the core SO136-005. The reason for undertaking these analyses was to profile the overall preservation state of assemblages throughout the core and to compare the preservation index developed herein with commonly used fragmentation ratios. The results of the preservation index (Fig. 4.1) indicate a slight overall decrease in level of preservation with depth in the core. Percentage fragmentation follows a similar slight trend (Fig. 4.2) as could be predicted, since at depth, less-well preserved forams are more common and more likely to contribute fragments to the assemblage as diagenetic processes take effect. Both physical and chemical breakdown are generally accepted as being interrelated as, they complement one another during the process of test degradation (Corliss and Honjo 1981; Berelson et al. 1990).
When preservation index (PI) and fragmentation percent (FP) are plotted on the same graph (Fig. 4.3) it becomes apparent that slightly increasing dissolution is reflected in the downhole increase in FP from a PI = 4.65 and FP of 24 at 1-2 cm, to PI = 5.4 and FP 27% at 22-23 cm. It was anticipated that the preservation index developed for this study should duplicate fluctuations calculated for fragmentation of tests of *G. bulloides* from the same horizon yet the lines do not exactly parallel each other. There is an apparent lack of compatibility between fragmentation percent and preservation indices calculated for core SO 136-005 at the individual horizon level. For example, in some cases (e.g. core depth 14 cm) highest fragmentation values were calculated for horizons at which preservation indices were low (best preserved).

One possible reason for the discrepancy between PI and FP for individual horizons may be the small sample size used in this study. Owing to time constraints, only approximately 100 specimens were extracted from each core sample and as such the results must be seen as indications only. Statistically robust results would only be achieved if populations of 300 specimens or more were isolated for equivalent analyses.

Another reason might be that measures of fragmentation include both whole and broken tests whereas the dissolution index measures the state of preservation of whole tests only. Those specimens in the 'worst' state of preservation are likely to be the first to fragment and as a result the 'worst' preserved tests are quickly removed from possible inclusion in that group used to calculate the preservation index. These same tests are then incorporated as fragments in the fragmentation percent count for the same horizon, thus a high FP values will coincide with a low PI value.

A third reason for the lack of relationship may be that the preservation state of tests is controlled by both the way in which the calcite was originally crystallised and by subsequent dissolution. Dissolution may occur not only in surface-waters whilst the foram is still alive, but also as the test is settling to the sea floor and later as part of the active nepheloid layer close to the sediment/water interface (Bearman 1989; Chester 2000). Post-mortem dissolution effects occurring in the water-column and at or near the sediment/water interface are usually described as syndiagenetic processes, which
contrast with normal calcite diagenesis associated with burial and incorporation into the sedimentary pile. Fragmentation is normally seen as a syndiagenetic process and reworking may modify that signal. Strong current action may remove most fragments and thus significantly reduce the assessed fragmentation percentage for that population once buried.

Fig. 4.1 Graph of 'preservation index' for SO 136-005 and SO 136-002. There is a slight trend toward decreasing preservation with depth downcore.

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average</td>
<td>4.9</td>
</tr>
<tr>
<td>Median</td>
<td>4.9</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>0.3</td>
</tr>
<tr>
<td>R squared</td>
<td>0.2</td>
</tr>
</tbody>
</table>
Fig. 4.2  Graph of fragmentation percent for SO 136-005. There is a slight trend towards greater levels of fragmentation with depth downcore.

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Average</strong></td>
<td>25.2</td>
</tr>
<tr>
<td><strong>Median</strong></td>
<td>25.0</td>
</tr>
<tr>
<td><strong>Standard Deviation</strong></td>
<td>3.1</td>
</tr>
<tr>
<td><strong>R squared</strong></td>
<td>0.15</td>
</tr>
</tbody>
</table>
Fig. 4.3 Graph of 'preservation index' and fragmentation percent for SO 136-005. Note the opposite trends in the bottom half of the core.

<table>
<thead>
<tr>
<th>Preservation Index</th>
<th>Fragmentation %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average</td>
<td>4.9</td>
</tr>
<tr>
<td>Median</td>
<td>4.9</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>0.3</td>
</tr>
<tr>
<td>R squared</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Finally a fourth reason may be the secondary precipitation of calcite on the surface of tests. This syndiagenetic process is caused as a result of metabolic CO₂ altering the alkalinity of the ambient seawater; it may also be a diagenetic process caused by changes in the alkalinity of interstitial water (Adelseck 1973; Collen and Burgess 1979). The presence of a secondary layer of calcite has the effect of making the test appear thicker and better preserved under the transmitted light microscope (acknowledging that it also results in a smoothing of test surface texture in SEM). It is therefore possible that the precipitation of calcite onto tests after deposition may
result in a low preservation index value for what was originally a highly fragmented assemblage.

4.4 Summary

While the PI and FP graphs may give contradictory information at the detailed level of a particular horizon, their overall trends indicate decreasing preservation with depth. These data are not as statistically robust as would be liked, however this is likely a result of the short length of the core and the fine level of detail at which the core was analysed (every 1cm). For a longer core diagenetic effects would be expected to be greater as a result of greater burial and a more significant decrease in preservation index and increase in fragmentation percent would be anticipated. For this study it was more important to derive a 'preservation index' than to actually discover trends in the core used for the study.
Measures of the relative abundance of light ($^{16}$O) to heavy ($^{18}$O) oxygen isotopes in calcareous tests of some marine organisms have been used as a proxy indicator of fluctuations in global ice volume, sea level, and ocean temperature through time since oxygen isotope paleoceanographic reconstruction began in the 1940s. The fundamental basis for oxygen isotope analysis is that the lighter $^{16}$O isotope is preferentially evaporated from the oceans with respect to the heavier $^{18}$O. As a result, during global glaciations when sea level was low, isotopically lighter water was stored in ice caps and the oceans were proportionally enriched in heavy ($^{18}$O) oxygen. During intervening interglacial stages the ice caps melted, raising sea level and resulting in the restoration of oxygen isotope concentrations in seawater to ‘normal’ with respect to global atmospheric and oceanic temperatures (Bearman 1989; Broeker and Denton 1990). There are three forms in which natural oxygen can exist, with the following abundances: $^{16}$O = 99.763%, $^{17}$O = 0.0375% and $^{18}$O = 0.1995%. Of these isotopes only $^{16}$O and $^{18}$O are used in the oxygen isotope analysis of marine sediments. The $^{18}$O/$^{16}$O ratio has been adopted as the standard for calcium carbonate, with that value being expressed as $\delta^{18}$O (depleted or enriched relative to a standard) rather than measured quantities of each isotope. $\delta^{18}$O is normally reported as per mil (‰) difference from the reference standard, Pee Dee Belemnite (PDB). Individual laboratories use an internal reference standard for purposes of calibration, but for the purpose of regional/global contrasts, the PDB standard is used (Brasier 1995; Williams et al. 1989). The following equation indicates how the $\delta^{18}$O value is derived from raw isotope data.

$$\delta^{18}\text{O}_{\text{PDB}} = \frac{1000 \times ^{18}\text{O}/^{16}\text{O}_{\text{Sample}} - ^{18}\text{O}/^{16}\text{O}_{\text{Standard}}}{^{18}\text{O}/^{16}\text{O}_{\text{Standard}}}$$
Translation of $^{18}O/^{16}O$ ratios, derived through the above equation into approximate temperature values is affected by the combination of three factors, 1) the temperature of the water at the time of formation, and 2) the fractionation of isotopes by the foram in question, and 3) the fractionation by evaporation. Fractionation of oxygen ($^{16}O$ and $^{18}O$) in relation to temperature results in deeper, colder waters having more of the heavy isotope $^{18}O$, while shallow, warmer waters tend to have more of the light isotope $^{16}O$ (Brasier 1995). Positive $\delta^{18}O$ values (i.e. enrichment in the heavy isotope $^{18}O$) would be predicted during episodes of upwelling, which bring cool, $^{18}O$-rich waters to the surface (Brasier 1995). Because downhole fluctuations in marine oxygen-isotope records from forams result in part from changes in ice volume and in part from changes in ocean temperature core profiles of the marine oxygen-isotope record are a composite of two independent signals and as such cannot be interpreted as a perfect proxy for ice volume (Anderson et al. 1989; Broeker & Denton 1989, 1990).

Marine organisms such as foraminifera incorporate oxygen into their tests in ratios in equilibrium with, or fractionated relative to, the water in which the tests formed. Temperature dependant oxygen-isotope fractionation (the rate at which a particular species incorporates the different isotopes at different temperatures) by foraminifera has been shown to influence both the phasing and the amplitude exhibited in oxygen-isotope records if the temperature at the sea surface changes through time at a given locality (Moore et al. 1980; Mulitza et al. 1998). Under normal circumstances sea-surface temperature changes with time as dictated by seasonal variation and this may also be incorporated into the isotope record. After foraminifera die, their tests settle to the sea floor thus transferring to the sedimentary pile an isotopic record of the water in which they formed.

5.1.1 The glacial cycle
Marine oxygen-isotope records provide clear evidence for a 19 000, 23 000 and 41 000 year cyclicity coincident with orbital forcing and associated oscillations in Earth's climate system (appendix 4). This evidence has been used to support Milankovich's theory of orbital eccentricity, which is considered the driving force behind periods of glacial maxima and minima on Earth through geological time.
Deep sea cores, collected from most parts of the globe but largely concentrated in the northern hemisphere as part of the Deep sea Drilling (DSDP) and Ocean Drilling Programs (ODP), have been used to build up a composite picture of earth's Cenozoic climatic history, with special emphasis and highest resolution in the Quaternary (Weaver 1993). This high resolution is the case for the simple reason that these sediments are the youngest and therefore least altered by post-depositional processes. Oxygen isotope stratigraphy can be used to divide the Quaternary into 63 stages representing alternating glacials and interglacials (Hodell and Ciesielski 1991; Weaver 1993). Other data such as taxonomic diversity, foraminiferal fragmentation ratios and benthic : planktonic foraminiferal ratios also show distinct shifts between glacial and interglacial times and these data are also often used to supplement that derived using oxygen isotopes (Martinez 1994a, 1994b; Nelson et al. 1993; Weaver, Carter and Neil 1998). Combined, such analyses may also provide proxy information on fluctuations of ocean chemistry, productivity and migration of water masses through time.

5.2 Carbon isotope analysis

Carbon 13 is another isotope that can be used to indicate past ocean conditions in the form of a productivity indicator. Carbon has two stable isotopes (\(^{12}\text{C}, {^{13}\text{C}}\)) that are distributed through the water column according to three mains factors. The first factor is primary productivity at the surface, which preferentially incorporates the lighter isotope \(^{12}\text{C}\) into biomass, leaving surface waters relatively enriched in the heavier isotope \(^{13}\text{C}\). The second factor is organic decomposition in mid waters releasing \(^{12}\text{C}\) and nutrients from decaying organic matter back into the water column. The third factor is ventilation by polar bottom waters in which the influence of different bottom waters returns the isotopic balance a little more towards positive values (Brasier 1995). The advection of cold, nutrient-rich waters into the upper water column should leave its imprint in the stable isotopic composition of fossils with \(\text{CaCO}_3\) skeletons. As with oxygen, carbon is measured as \(^{8}\text{C}\) (the ratio between \(^{12}\text{C}\) and \(^{13}\text{C}\)) relative to the PDB standard (Williams et al. 1989).
If $^{13}$C isotopes are incorporated into CaCO$_3$ skeletons in equilibrium with the environment then they should give some indication of the seawater chemistry in which they were secreted (Brasier 1995). However, it is clear from the studies of modern skeletons that ‘vital effects’ can overprint the environmental signal, producing values that are much lighter than ambient seawater (Dudley and Nelson 1989; Brasier 1995). These vital effects are little understood but seem to involve the utilization of metabolic carbon in the secretion of carbonate. Some groups of organisms are known to have large vital effects, whereas others are thought to incorporate stable isotopes into their carbonate skeletons largely in equilibrium with seawater, G. bulloides is thought to belong to the latter group (Lee and Anderson 1991; Murray 1991; Brasier 1995).

In living planktonic foraminifera, more negative $^{13}$C values (i.e. enrichment in the light isotope $^{12}$C) would be predicted during episodes of upwelling, which bring cool, $^{12}$C-rich waters to the surface (Brasier 1995). However, $\delta^{13}$C values have often proved contradictory between taxa and between areas (Kroon and Ganssen 1989; Thunell and Sautter 1992). Globigerina bulloides has been shown to be paradoxical in recording a significant depletion in $^{13}$C during upwelling episodes off California (Thunell and Sautter 1992) but enrichment in $^{13}$C in the northern Indian Ocean (Kroon and Ganssen 1989). A suggested reason for this anomaly is the probability that there is an ecological succession during the upwelling cycle in which successive species migrate upwards or downwards through the water column. However, these patterns of species migration appear to differ between areas, so that a given species may therefore give contrasting isotopic signals (Thunell and Sautter 1992). Another explanation may be the $\delta^{13}$C of organic carbon produced by photosynthesis, which varies naturally between different groups of phytoplankton; a 10% change from -20‰ to -22‰ could enrich the surface water $\delta^{13}$C of CO$_2$ by approximately 0.2‰ (Curry et al. 1992). The outcome, therefore, is that patterns of $\delta^{13}$C change are complex and cannot easily be used to indicate the onset of upwelling over short time periods (Brasier 1992).
5.3 Factors affecting Isotope Signals

The principal axiom of isotope paleoceanography is that the mechanism of isotope incorporation utilised by the foraminiferal species targeted for proxy paleoenvironmental information is consistent throughout the geographic and stratigraphic range of that taxon (Williams et al. 1988). In reality, however, this is not always the case, and a number of studies (including the present project) provide evidence that refutes this assumption (Emilianai 1974; Healy-Williams et al. 1985; Darling et al. 2000). The following sections present how some intra-specific variation in isotope values may originate.

5.3.1 Morphological variation

Both environmental and genetic influences contribute to the phenotypic expression of foraminifera (Robbins and Healy-Williams 1991; Darling et al. 2000). As a consequence, there is considerable difficulty in distinguishing between intraspecific morphologic variation that is purely ecophenotypic and that which results from genetic differentiation either in concert with, or caused by, environmental differences (Robbins and Healy-Williams 1991). For example the species *Globigerinoides ruber* exhibits considerable morphological variation yet it remains unresolved whether those morphotypes represent separate species or environmental variants (Parker 1962; Hetch and Savin 1972; Robbins and Healy-Williams 1991). Robbins and Healy-Williams (1991) sub-divided *G. ruber* into six morphotypes based on test elongation and analysed two end-member groups for $\delta^{18}O$ values. The more elongate forms were found to be enriched in $\delta^{18}O$ and $\delta^{13}C$ by 1.4% and 1.25% respectively compared to the less elongate forms. That range of isotopic values may be the result of seasonal temperature changes at the site of collection; however, this does not exclude the possibility there is a genetic component to the differentiation of the morphotypes of *G. ruber* (Robbins and Healy-Williams 1991). It is also possible that each morphotype is utilizing a particular niche in the water column and as a consequence each morphotype could register the $^{18}O$ signature of the differing water mass in which it lived. (Reynolds and Thunell 1986; Williams et al. 1988; Robbins and Healy-Williams 1991; Sautter 1998).
The tests of foraminifera exhibit a wide range of morphological traits, some of which are an expression of the effects of fluctuations between optimal and stressful environmental conditions (Healy-Williams et al. 1985). Shell morphology of *Globigerinoides rubra* has been found to change with environmental conditions from large, thin-walled specimens with large apertures to small, compact shells with small openings (Emiliani 1974). The larger forms are predominant in post-glacial sediments and the smaller forms dominate during glacial times (Emiliani 1974). The morphology of a foraminiferal species is often taken as including the overall variation in a sample population with unimodal distributions of morphological variables (Healy-Williams et al. 1985). Because of this assumption, populations are often characterized by arithmetic averages (by average diameter, average length and height ratios) (Healy-Williams et al. 1985). Use of means, however, can lead to misinterpretations if the population’s true, underlying structure is strongly asymmetric or polymodal (Healy-Williams and Williams 1981; Healy-Williams et al. 1985). Healy-Williams et al. (1985) demonstrated the existence of isotopic variation between three morphotypes of the foraminiferal species *G. truncatulinoides* in the Indian Ocean. δ¹⁸O differences of 0.5 to 1.0‰ found between two of those morphotypes extracted from the same size fraction from the same sample clearly suggest that the “morphological effect” may induce significant variations of isotopic concentration (Emiliani 1974; Healy-Williams et al. 1985; Bijma et al. 1998). These three morphotypes of *G. truncatulinoides* are now considered sub-populations, which occupy different niches within the water column.

Williams et al. (1988) used Fourier shape analysis to differentiate morphotypes of foram outlines for *Uvigerina peregrina, Globorotalia truncatulinoides*, and *Neogloboquadridna pachyderma*. The accumulation rates of marine sediments suggest that sediment samples 1-2 cm thick might have accumulated in tens, hundreds or thousands of years depending on the rate of accumulation and extent of bioturbation (Williams et al. 1988). Because of these factors, the intrasample polymorphotypic structure observed in planktonic foraminifera could arise from post-depositional reworking of specimens from different climatic periods (e.g. glacial and interglacial periods), seasonal changes in faunal composition, the occurrence of morphotypes in ecological sub-niches in the water column, or genetic differentiation between the
morphotypes (Williams et al. 1988). Again, between morphotypes of the same species taken from the same sample and size range those authors found isotopic differences in the order of 0.5-1.0\%o. If the proportion of morphotypes in a sediment assemblage changes through time, then these morphotypic-isotopic changes become a significant barrier to achieving higher resolution in isotope paleoceanography (Williams et al. 1988).

$\delta^{18}O$ vs. $\delta^{13}C$ plots for planktonic foraminifera from plankton tows, sediment traps and seafloor sediments in the central North Atlantic show a clear separation of species and genera. Erez and Honjo (1981) indicate that different species fractionate isotopes at different rates. This suggests that their isotopic composition is controlled to a certain extent by biological factors (Erez and Honjo 1981).

Darling et al. (2000) reported on DNA variation within three bipolar species of planktonic foraminifera, including *G. bulloides*. The aim of their research was to examine genetic variation between Arctic and Antarctic subpolar populations of the target species. Surprisingly it was discovered that there were two bipolar morphotypes and one subpolar, Antarctic morphotype, with a fourth transitional morphotype occurring around the South California Bight (Fig. 5.1).

![Globigerina bulloides phylogeny](image)

**Fig. 5.1** Foraminiferal SSU rDNA phylogeny, highlighting the genotypic variants identified for *G. bulloides*. From Darling et al. (2000).

Distribution patterns for the above genotypic variants indicate that different genotypes may inhabit different hydrographic or trophic environments (Darling et al. 2000). *G. bulloides* type IIa was distributed from the Falkland Islands to the Polar Front but type
Ilb was found only at the Polar Front in the Antarctic subpolar region (Darling et al. 2000). A similar segregated distribution pattern was observed in the Arctic subpolar region (Darling et al. 2000). For paleoclimatic reconstructions, an assumption is made that each ‘morphospecies’ represents a variant conditioned by environmental/habitat preference but is still a legitimate part of a continuous morphologic gradient, which defines ‘the species’. If this is not the case, then stable isotope and geochemical analyses of planktonic foraminiferal shells, and census-based transfer-function techniques derived from such pooled data, must include significant noise, and in all probability, error (Williams et al. 1988; Sautter 1998; Darling et al. 2000). However, if genetic differences can be correlated with specific environment and habitat preferences and those genotypes are able to be differentiated in the fossil record, then a new level of precision for climate modelling could be achieved (Darling et al. 2000).

Sympatric speciation, or the formation of more than one species from an original parent species without geographical isolation has been studied by a number of authors in many organisms (Healy-Williams et al. 1985; Tregenza and Butlin 1999; Kondrashov and Kondrashov 1999; Dieckmann and Doebeli 1999; Darling et al. 2000). Dieckmann and Doebeli (1999) state that speciation is a likely outcome of competition for resources. The most straightforward scenario for sympatric speciation requires disruptive selection favouring two substantially different phenotypes (Kondrashov and Kondrashov 1999). Tregenza and Butlin (1999) gave the following analogy for the need for sympatric speciation. “If a lake contains two potential resources—say, large or small prey—then large or small predatory fish will do well while medium-sized fish will be at a disadvantage. This disadvantage to intermediates, termed ‘disruptive selection’, creates pressure for divergence into two populations of distinct ecological types (Tregenza and Butlin 1999 p.312). In sexual populations, the stumbling block preventing sympatric speciation is that mating between divergent ecotypes constantly scrambles gene combinations creating intermediate phenotypes (Tregenza and Butlin 1999). This mixing can be prevented only if there is assertive mating, in which pairings between similar individuals are more common (Tregenza and Butlin 1999). With disruptive selection, this pairing pattern is selectively favoured because it reduces the production of offspring that are less well adapted to their environment (Tregenza and Butlin 1999; Dieckmann and
Morphologic variation is especially relevant to the present study because isotope values have been shown to vary between morphotypes of the same planktic foraminiferal species. Oxygen isotope signals may vary between morphotypes occupying different niches and hence different water masses and genetic differences between these morphotypes may cause fractionation of isotopes at different rates. Therefore it is important that morphotypes be identified and separated when preparing samples for isotopic analysis.

5.3.2 Incremental test growth

Foraminiferida form their tests by the secretion of calcite (CaCO$_3$), and this process incorporates oxygen and carbon atoms from the seawater in which they grow. As that CaCO$_3$ is precipitated $^{16}$O and $^{18}$O are incorporated, either in equilibrium with seawater or at a fractionation rate that generally reflects the influence of metabolic CO$_2$ on the 'primary' seawater isotopic concentration. Some species appear to have a temperature-dependent fractionation such that, their rate of isotope fractionation varies with respect to the temperature of the water in which they are growing.

Depths at which foraminiferids secrete their tests appear to be determined by seawater density and ultimately by osmotic equilibration with surrounding sea water (Martinez 1994b) and consequently, different size fractions would be expected to have isotopic values representative of the different water masses in, which they lived. There is considerable evidence that a number of foraminiferal species occupy different depths in the water column during ontogeny. Representative life stages of the same species commonly present contrasting isotopic signals because the test CaCO$_3$ was precipitated in waters in which temperature/depth-related gradients resulted in a fractionation of $^{16}$O:$^{18}$O in the seawater.
Isotopic variation in foraminiferal species observed today is most likely to reflect the growth of individuals during different phases of the seasonal cycle and/or the kinetic effect of intraspecific variation in shell calcification rates (Houston et al. 1999). In general, δ¹³C and δ¹⁸O values of planktic foraminifers covary with shell size, with larger shells typically becoming enriched in ¹³C and ¹⁸O (Kahn and Williams 1981; Erez and Honjo 1981; Bouvier-Soumagnac and Duplessy 1985; Deuser 1987; Kroon and Darling 1995). Spero and Lea (1996) found an δ¹⁸O increase of 2.6‰ between the small (chambers 1-9) and large (chamber 14) chambers when the ambient temperature, δ¹⁸O (water), and δ¹³C of total CO₂ are kept constant. From their results, they concluded that for paleoceanographic applications, shells in the size range 270-320 µm are optimal for paleoenvironmental reconstructions.

*G. bulloides* has one of the largest reported isotopic deviations from equilibrium with seawater of extant species for both carbon and oxygen isotopes and the different isotope values covary with test size (Deuser and Ross 1989; Sautter and Thunell 1991b; Kroon and Darling 1995). The first successful laboratory experiment in which non-symbiotic planktic foraminifera where grown was conducted by Spero and Lea (1996). Small specimens of *G. bulloides* were hand collected by scuba divers from north Pacific surface waters and subsequently grown in culture until they released gametes (tests with 13-14 chambers). Between 4 and 10 chambers from identical test whorl positions 10 through 14 were combined and analysed for ¹⁸O and ¹³C. The results of these samples were compared with δ¹⁸O and δ¹³C from the first nine chambers from the same tests. Under controlled conditions, chamber δ¹⁸O values increase 0.7 and 0.8‰ in 16°C and 22°C (culture water temperature) groups respectively as shell development proceeds from the juvenile chambers to the laying down of the final chamber (Spero and Lea 1996). This depletion emphasizes the importance of strict size control when utilizing *G. bulloides* for oxygen isotope studies of deep-sea sediments (Spero and Lea 1996). The ability to interpret the paleoenvironmental information contained within the *G. bulloides* stable isotope record is also limited by the ability to filter out the factors contributing to disequilibrium fractionation during calcification (Fairbanks et al. 1982; Spero and Lea 1996).
Along with *Globigerina bulloides*, the planktonic foraminiferal species *Neogloboquadrina dutertrei* and *Globigerinoides ruber* and have all been found to show variation in stable isotope composition with size (Kroon and Darling 1995). For larger tests, $\delta^{18}O$ values are more positive, which again indicates that adult specimens sank from the surface waters in the final stages of their life prior to gametogenesis or that they lived in deeper waters during most of their adult stage (Duplessy and Blanc 1981, Erez and Honjo 1981, Kroon and Darling 1995). The species *Planoglobulina multicamerata* has also been found to have positive adult $\delta^{18}O$ values believed to be the result of moving into deeper, $^{18}O$ enriched water as the forams age (Houston et al. 1999). This species is also believed to have no symbionts (photosynthetic microorganisms that produce food for the foram), thus it is not restricted to the photic zone and may migrate into deep waters. *G. bulloides* is also believed to be non-symbiotic and may also have more positive $\delta^{18}O$ values with age related to change in habitat depth.

Bijma et al. (1998) also recorded differences in both carbon and oxygen isotopic values for *G. siphonifera* and as a result of laboratory culturing attributed these results to variance in the rate of test formation. They found that the more rapid the growth the lighter the isotope signature that results.

### 5.3.3 Metabolic CO$_2$ incorporation

Labracherie et al. (1989) claim that unpublished results from their group, indicate that in the north Atlantic the Holocene $\delta^{18}O$ values for *G. bulloides* are close to equilibrium if they accept the generally acknowledged premise that *G. bulloides* growth occurs during late spring and summer in surface temperate and subpolar waters. Therefore *G. bulloides* has commonly been used in oxygen isotope analyses because its values are believed to be unaffected by temperature dependant fractionations. However, results from work by Spero and Lea (1996) suggest that oxygen and carbon isotope values derived for *G. bulloides* may not be in equilibrium with seawater. Isotope values out of equilibrium with ambient seawater have been attributed to the incorporation of metabolic CO$_2$ in the foram tests (Spero and Lea 1996). By feeding *G. bulloides* with *Artemia nauplii* of known organic $\delta^{13}C$ values,
direct evidence for the incorporation of respired CO₂ into tests was established, as chambers laid down after feeding were depleted in ^13^C relative to chambers formed prior to the controlled experiment (Spero and Lea 1996). However, despite the large non-equilibrium stable isotopic signal, those authors still concluded that *G. bulloides* has the potential to yield valuable paleoceanographic information in temperate and sub-polar regions as its δ^{18}O values still fluctuate with respect to the water in which they live.

5.3.4 Test calcite crystallinity

The rates at which foraminiferers precipitate their tests, and the degree of encrustation obtained (thickness of tests) appear to contribute significantly to resultant oxygen isotope signals. The preservation potential of planktic foraminifera is to a large degree dependent on the internal wall structure and microfabric. In general, this consists of small, anhedral crystals on the proximal side, larger crystals toward the distal side, and in some cases large crystals forming a calcite crust (Adelseck et al. 1973; Be' et al 1975; Boltovskoy and Totah 1992).

Sautter (1998) selected a number of morphotypes of the genus *Neogloboquadrina* from Ocean Drilling Project core 769A collected from the Sulu Sea. Morphotype selection of specimens in the size fraction 150-350 µm was strictly based on chamber number and periphery morphology and the degree of calcite encrustation (reticulate=thin-walled or, crystalline=thick-walled). Comparison of oxygen isotopic signatures between morphotypes from interglacial samples revealed complete isotopic separation between crystalline and reticulate types of between 0.5 and 1.35 ‰ in the three species sampled, regardless of the number of chambers. Surface samples from the Sulu Sea also show separation between crystalline and reticulate δ^{18}O composition, although the difference of 0.28‰ was less than that observed for interglacial samples (Sautter 1998). Enriched δ^{18}O values in crystalline forms were attributed to the presence of a secondary calcite crust present only on crystalline tests, interpreted as indicating that the heavily encrusted morphotype subpopulations calcify in cold water (Sautter 1998). Crystalline morphotypes may be viewed as separate sub-populations of *Neogloboquadrina* that inhabit waters that are 3.0 to 6.5°C colder
than waters inhabited by reticulate sub-populations (Sautter 1998). Such colder conditions may occur either at greater depth in the water column or alternatively, reticulate and crystalline morphotypes may reflect responses to different seasonal hydrographies (Reynolds and Thunell 1986; Sautter 1998).

5.3.5 Solution effects

The surfaces of calcareous foraminiferal tests may be altered after burial by the diagenetic processes of dissolution, overgrowth and recrystallisation (Adelseck et al. 1973; Collen and Burgess 1979; Dittert and Henrich 2000). Dissolution usually results in enlargement of pores and perforations and stripping of layers from the test surface. It destroys thin-walled chambers and, because of differential effects on the ornament and on the rest of the test surface, may alter the appearance of the species, thus affecting identification and classification (Collen and Burgess 1979; Dittert et al. 1999; Dittert and Henrich 2000).

Long-term carbonate dissolution patterns indicate more intense dissolution during glacial stages and improved preservation during interglacial stages in the Atlantic and South Indian Oceans, which contrasts with the North Indian and Pacific Oceans where this pattern is reversed (Te-Lung and Tadamichi 1977; Martinez 1994b). This change in dissolution patterns is linked to migrating water masses, altering currents and subsequent changes in the water chemistry with fluctuations in sea level. The Tasman Sea has greater population abundance of foraminifera during glacial stages, presumably as a result of increased productivity associated with greater input of cold, nutrient rich waters (Stanton 1972; Martinez 1994b).

Solution effects at or near the sediment/water interface preferentially dissolves those species having thin-walled tests, which results in a selective concentration of the thicker walled foraminifera in the sedimentary pile (Berger 1970; Parker and Berger 1971; Thiede 1973;). With isotopic values varying between different size fractions and different wall thickness of the same species this selective dissolution can also bias the isotopic record in favour of the heavier isotopes (Boltovskoy and Totah 1992). It is possible that differences in the way calcite was originally laid down in tests as they
formed (owing to growth rate and other factors) controls the way in which the tests react when placed under conditions with potential to dissolve them.

Empty shells of planktonic foraminifera on the seabed have been found to be significantly enriched in $^{18}O$ when compared with the shells of their living counterparts collected in surface waters (Duplessy and Blanc 1981). This suggests that syndiagenetic/diagenetic dissolution or secondary precipitation may also alter the isotope signals. Therefore selective dissolution of more susceptible tests may result in misinterpreted data and incorrect interpretations of paleotemperatures. Isotopic temperatures of many species become progressively colder as the sampled sediment water-depth increases because the weaker, isotopically lighter specimens have been preferentially dissolved. Dissolution increases with depth and more resistant tests are usually $^{18}O$ enriched (Duplessy and Blanc 1981).

Variation in the original calcite structure in forams may make some morphotypes more susceptible to dissolution; hence the isotopic signal of sediments exposed to solution effects will be biased towards the most resistant form (Adelseck et al. 1973; Collen and Burgess 1979; Dittert and Henrich 2000). Where this is not taken into account, erroneous conclusions may result from the comparison of isotopic temperatures of samples from different locations. Savin and Douglas (1973) found that species giving the warmest isotopic temperatures in the Pacific Ocean, that is those that live at the shallowest depths, are most susceptible to dissolution. The effects of preferential removal of such individuals may lead to one bias in isotopic paleothermometry which to date has been the focus of minimal research. Susceptibility of foraminiferal tests to selective solution after death also increases with magnesium content of the test, as the aragonite compensation depth is shallower than for calcite (Savin and Douglas 1973; Chester 2000).

5.4 Summary

It is obvious from the work discussed here that there are a large number of ways in which 'primary' isotope values from a selected species may be 'adversely' affected. Factors such as morphological variation, test wall thickness, test size and selective dissolution have been proven to result in variable isotope values between specimens of the same foraminiferal species (Parker 1962; Heitch and Savin 1972; Thiede 1973;
Emiliani 1974; Erez and Honjo 1981; Fairbanks et al. 1992; Healy-Williams et al. 1985; Reynolds and Thunell 1986; Williams et al. 1988; Robbins and Healy-Williams 1991; Kroon and Darling 1995; Spero and Lea 1996; Bijma et al. 1998; Sautter 1998; Houston et al. 1999; Darling et al. 2000). The results of these authors and others give clear evidence for a large number of factors having influenced the isotope signal of an individual foram test by the time it is recovered from the sea floor by coring or dredging. It is possible for a foram test to be affected by one or many of the factors reported by the above authors and it is because of this fact that recognised protocols for sample selection for isotope analysis are necessary for consistent gathering and comparing of isotope data. It is because of this fact that a set of internationally recognised protocols for sample selection should be established. Without such guidelines, comparisons of isotopic data from horizons in the same core or more importantly from projects sited in other oceans or hemispheres are difficult and equivocal.
Chapter Six

Nannofossil (Coccolith) incorporation

6.1 Introduction

It has been noted in the present study that a number of specimens of G. bulloides have calcite overgrowth on their surfaces. The precipitate may appear as a grainy layer spread over the surface of the test, obscuring spines and pores and incorporating coccolith plates, two species of which were identified by comparison with other work (Adelseck 1973; Bearman 1989). Alternatively, the precipitate may occur as a layer of well-developed, angular, irregular, calcite crystals, which occasionally also contain coccolith plates and which often obscure original surface features on the foram test. These secondary layers vary from small, localized pockets to extreme cases where the entire surface of the test is covered. Exactly what effect this layer has on the isotope chemistry of the tests is not known but it is likely that it causes some deviation from the primary isotope values incorporated into the chemical fabric of the test during its construction.

Fig. 6.1. Image of intact coccolithophore (Coccolithus huxleyi). Cocosphere is approximately 6 μm in diameter. Individual plates from this species and others are found attached to G. bulloides tests in the present study. Image from Bearman (1989).
It is possible that a significant proportion of the donor chemicals making up these 'secondary' layers are in fact derived from nannofossils. These also selectively dissolve (Adelseck 1973) such that specimens seen under the SEM may represent resistant forms buried in the dissolution products of their less resistant cohorts. Adelseck et al. (1973) experimented with dissolution and overgrowth of calcareous nannofossils during diagenesis in an attempt to simulate, in a short-term experiment, the long-term diagenetic changes commonly observed in continuous downhole sections of calcareous ooze. The authors concluded that crystal size plays an important role in the growth or dissolution of the tests. For crystals smaller than 1μm, the excess free energy of the surface ions and atoms becomes important and total free energy of the crystal is increased with diminishing size (Adelseck et al. 1973). As a result, it was predicted that for samples containing a range of crystal sizes from 1μm to several μm, the smallest particles would be selectively destroyed while the larger ones would form secondary overgrowths with the calcite donated by the destruction of smaller crystals (Adelseck et al. 1973; Dudley et al. 1980; Walter and Morse 1984; Wu and Berger 1991). This therefore indicates that it is not only possible for dissolution and precipitation to occur in the same sample, but that they can simultaneously affect different sized crystals on or within the same specimen.

It is possible that fine fraction material such as nannofossils trapped in the interior of forams can cause interference with isotope signatures. The water chemistry within a foram test may vary from undersaturated to supersaturated with respect to calcite and as such, fine fraction nannofossils trapped inside foram tests could be corroded preferentially and then, when fluids within the chamber become saturated, reprecipitated as a thin layer on the inside of the foram test (Adelseck et al. 1973; Walter and Morse 1984). This important factor should be evaluated as nannofossil calcite incorporation could significantly affect the overall isotope signal derived from foram tests. The degree to which foram test signals could be altered by such nannofossil inclusion would depend upon the difference in isotopic signature between the foram and nannofossil calcite, as well as the relative proportions of foram and nannofossil calcite.
The degree of secondary calcification on tests is also another factor that was noted in the present study as a likely control over the incorporation of coccoliths on foraminiferal tests. Tests from the same sample may have a complete overgrowth of secondary calcite incorporating coccoliths, or may have no overgrowth at all and hence no attached coccoliths. Comparison of δ¹⁸O values from tests with a coccolith inclusive secondary overgrowth and tests, which have had this layer removed (through etching) would provide some indication of the effect coccoliths and this secondary layer are having on overall test isotope chemistry.

Dudley et al. 1986 and Dudley and Nelson (1989, 1994) studied the δ¹⁸O values of coccoliths and found them to differ from equivalent δ¹⁸O values for *G. bulloides* from the same site on the Chatham Rise. In general the uncorrected δ¹⁸O signal of the calcareous nannofossils is more positive (¹⁸O enriched) than that of planktic foraminifers from the same sample (Dudley and Nelson 1994). If both calcareous nannofossils and planktic foraminifers were precipitated in isotopic equilibrium with seawater at the same site, isotopic analysis of calcium from both species would indicate a colder habitat for coccolithophores. However, because live coccolithophorids are photosynthetic, they are restricted to the photic zone, and therefore either the coccoliths and planktic foraminiferal tests occupy different niches within surface water or biological differences cause the two species to fractionate ¹⁸O from seawater at different rates (Dudley and Nelson 1994).

Results of work by Dudley et al. (1980, 1986) indicate that the oxygen isotope composition of coccoliths grown in-vitro, though significantly affected by non-equilibrium fractionation, showed a strong correlation with temperature of calcification. By applying a ‘vital effect adjustment’ based on these in-vitro studies, Dudley and Nelson (1994) were able to produce nannofossil δ¹⁸O values, which were similar to, or depleted in, ¹⁸O relative to the planktic foraminifers. Different coccolithophorid species were studied in-vitro and it was found that some show positive ¹⁸O values relative to equilibrium whilst others produced negative values. Downcore alternation of these species groups has been found to correlate with isotope excursions in core from the Chatham Rise, indicating the isotopic signal may
represent species assemblage or selective solution effects rather than seawater temperature.

6.2 Removal of Nannofossil Contamination

6.2.1 Objectives

Whilst extracting forams for isotope and preservational analyses, SEM examination indicated that a number of foram specimens appeared to have a secondary layer of calcite on the outer surface of their tests. This layer often contained nannofossils (coccoliths) either partially or completely submerged in the microcrystalline fabric, such that only the faintest surface expression of these nannofossils remained (Figs. 6.2, 6.3). The presence of such a layer could have significant implications for the δ18O composition of tests, as it is likely the δ18O value of the precipitated layer reflects that of the source material for this layer rather than that of the foram test it is attached to. If this is the case, then any values obtained from the test will not represent the primary foram signal (that of the living test), but a mixture of both the test and the nannofossil bearing secondary layer. By selectively removing the ‘secondary’ layer from tests of *G. bulloides* it might then be possible to calculate the contribution that layer makes to any ‘anomalous’ isotopic signal derived for a population of secondarily altered specimens of that species.

One objective of this research was to determine whether selective etching was effective in removing the outer surface and what protocols might best ensure the loss of that ‘contaminant’ layer without significant damage to the primary layer. Three methods of selective etching were trialed and evaluated, glycerol etching, acetic acid etching and distilled water etching.
Fig. 6.2 Nannofossils can be seen over much of the test surface; in many instances they have been incorporated into the surficial layer of the test. Arrows indicate some examples of the attached/embedded nannofossils.

Fig. 6.3 Close up of test surface showing incorporation of coccoliths in the secondary calcite layer. Arrows point out the most obvious examples and the remains of other coccoliths can also been seen submerged in the secondary layer.
Fig. 6.4. Examples (from Adelseck 1973) of nannofossils species observed incorporated on the exterior of *G. bulloides* tests in the present study. All bar scales equal 1 μm  A) *Coccolithus pelagicus*, B) *Coccolithus pelagicus*, C) *Cycloccolithina leptopora*, D) *Cycloccolithina leptopora*, E) *Cycloccolithina leptopora*, F) *Cycloccolithina leptopora*. 
6.3 Glycerol Etching

6.3.1 Method

In an attempt to investigate the degree of cementation of the outer nannofossil-bearing layer and to expose the 'primary' layers of the test, 60 specimens of *G. bulloides* were divided evenly among three vials, each containing various concentrations of glycerol (10%, 30% and 50%) diluted in distilled water. Glycerol was chosen as a corrosive agent because it has been found that this reagent dissolves the tests of ostracods exposed to the fluid for up to 14 days (K. Swanson pers. comm. 2001). In order to determine the optimum length of time for foram samples to be submerged, two specimens were removed from each vial every second day and their surfaces examined in detail using the SEM.

6.3.2 Results

Glycerol was found to have little effect on the surface structure of the tests used in this study (terminated after 21 days of exposure). This suggests that either the foram test of *G. bulloides* is more dissolution-resistant than the ostracods studied by K. Swanson, or that the secondary precipitates increase the resistance of the tests to a level higher than normally anticipated for living representatives of the same species. Whatever the reason, rates of dissolution were so slow that no optimum length of time for exposure could be determined. On that basis it was decided to use the more aggressive acetic acid as the corrosive agent.

6.4 Acetic acid etching

An attempt was made to remove the nannofossil bearing layer from *G. bulloides* tests using acetic acid because it is highly corrosive with respect to calcite and because accurate diluted solutions of acetic acid can be easily achieved and maintained by buffering or constant monitoring of pH.

6.4.1 Method

Four beakers were filled with acetic acid solutions with pH increasing in 0.5 increments from 5.0 to 6.5. 20 forams were added to each beaker, 2-3 specimens
being removed every two days until all specimens had been withdrawn from the solutions. The pH of the solutions was monitored throughout the experiment by using an electronic pH meter and where indicated, by adding more acid to bring the solution to the required acidity.

6.4.2 Results

It became rapidly apparent that acetic acid of pH 5 attacks *G. bulloides* tests very aggressively. All specimens placed in the pH 5.0 solution were largely destroyed within the first two days of the experiment. Thus the optimum treatment time to remove all nannofossils is a relatively short term (2 days) exposure to a pH 5.5 solution of acid. Specimens exposed to these solutions show total removal of the nannofossil layer (Fig. 6.5), however, this is also combined with severe etching of the primary test layer itself. For longer exposure periods at higher pH (6.5) the primary test itself undergoes severe dissolution, but the nannofossils remain unaffected (Fig. 6.6). I therefore recommend that an acetic acid solution of pH 5.5 be used with an exposure time of 2 days for optimum nannofossil removal.

6.5 Distilled water etching

6.5.1 Methods

A beaker containing only distilled water was also used to test the corrosive properties of distilled water (pH = 6) on calcareous tests. The procedure followed was the same as that described for acetic acid.

6.5.2 Results

Distilled water with a pH of 6.0 was found to be mildly corrosive to the calcite over a period of 2 days (Fig. 6.6). Unfortunately samples prepared for SEM examination after 8 days exposure disintegrated upon coating. This indicates that distilled water is indeed a corrosive agent capable of dissolving and destroying foram tests. For this reason it is recommended that calcareous microfossils not be stored in distilled water, but should be stored in alcohol or some other medium that will not cause degradation of the tests. Clearly these results have implications for most laboratory procedures used for the disaggregation of calcareous sediments and the subsequent concentration and solution of released microfossils. Careful monitoring of distilled water pH is
advised prior to its use for routine laboratory procedures used for the concentration of calcareous-walled microfossils.

Distilled water is a good corrosive agent, however acetic acid reacts more vigorously and the secondary calcite layer is destroyed more comprehensively over a shorter time frame than for distilled water.

6.6 Discussion of Etching results
The etching experiments undertaken in the present study have shown that it is indeed possible to remove calcite from the exterior of foram tests with the use of a corrosive agent. The isotopic values of the secondary layer of such tests will reflect the chemical composition of the water in which the layer was precipitated and this in all probability will differ from the equivalent signal derived from the primary test. All of the nannofossil remains attached to foram tests are disarticulated, single plates (Figs. 6.2, 6.3) indicating the nannofossils where incorporated after their death. The most likely place for this to occur is on the seafloor or in the sediment pile where both nannofossil and planktic foram remains accumulate as a result of post-mortem sedimentation through the water column. Given that this process of secondary calcification and nannofossil incorporation is almost certainly taphonomic, the isotope signal of the secondary layer should reflect a combination of the deep water isotopic signature ($\delta^{18}$O enriched and $\delta^{13}$C depleted) and that of the surface-water in which the nannoplankton photosynthesised.
Fig. 6.5 A) view of entire test exposed to pH 5.5 acetic acid solution for 2 days.

Fig. 6.5 B) view of test surface in Fig. 6.5 A) at 5,000 times magnification
Fig. 6.6 A) view of entire test exposed to pH 6.5 acetic acid solution for 8 days.

Fig. 6.6 B) view of test surface in Fig. 6.6 A) at 1000 times magnification.
Fig. 6.7 A) View of entire test exposed to pH 6.0 distilled water for 2 days.

Fig. 6.7 B) View of test surface in Fig. 6.7 A) at 1000 times magnification.

6.7 Summary
In order to measure the contribution secondary calcite and nannofossil incorporation makes to overall foram test isotope values it is necessary to analyse and compare entire tests and tests with the external layer removed. The above etching results indicate that it is indeed possible to remove the external surface of tests and so it
should also be possible to prepare samples that allow such isotopic analyses. From this study it has been shown that acetic acid is a good corrosive agent to use for calcite dissolution as it reacts swiftly and strips away the surface entirely. Greatest precision with respect to determining the isotopic contribution made by the secondary calcite will be achieved when dissolution effects on the primary layer are minimised. One way that might be achieved would be to make detailed SEM/TEM (transmitted electron microscope) examinations of test-wall microfabric for specimens of *G. bulloides* representing selected rates of exposure to the acid.
Chapter Seven

**Oxygen and Carbon Isotope Analysis of the Multicore SO 136-005**

7.1 Objectives

A primary aim of this thesis was to determine if there was any variation in $\delta^{18}O$ signal generated by morphotypes of the foraminiferal species *G. bulloides*. To answer this question a number of foraminiferal samples selected from multicore SO136-005 were sent to the University of Waikato for oxygen and carbon isotope analysis. It was anticipated that samples of different preservation state from the same core horizon would produce contrasting oxygen and carbon isotope values.

7.2 Methods

7.2.1 Sample selection

Based on the preservation grades discussed earlier (chapter 4), populations of *G. bulloides* were isolated from each of 15 horizons throughout the multicore SO 136-005. These horizons were selected because they showed the greatest excursions from the trendline on the ‘preservation index’ graph (fig. 4.1). Specimens from the best preserved (grade 1) and worst preserved (grade 5) categories at each of these points in the core were removed for $\delta^{18}O$ analysis such that submitted samples each contained between 22 and 31 specimens. Originally it was thought that 30 specimens would be a minimum number for accurate results, but the author was later informed (H. Turner pers. comm. 2000) that samples of more than 20 forams would suffice. For this reason some earlier samples contained around 30 specimens and, some grade 5 samples were supplemented with grade 4 specimens in order that the target 30 specimens could be met. Specimens used in the present study were selected from a relatively narrow size range of between 350 and 400 microns, consequently size is not regarded as a factor likely to be contributing to isotopic variations in the present study. For more detail on how *G. bulloides* specimens were selected and prepared prior to being sent to Waikato University for isotopic analysis refer to appendix 1.
7.2.2 Isotope Analysis by Mass Spectrometer

The isotope samples were prepared for analysis by Helen Turner at the University of Waikato using the following procedure: 1) specimens were cleaned and vacuum roasted to ensure that an uncontaminated CO$_2$ gas sample would be obtained, 2) the generation and extraction of CO$_2$ by the Individual Acid Dosing Carbonate Reactor System (CAPS) (Fig. 7.1). 3) comparison of the isotope composition of the gas with that of a laboratory standard in the mass spectrometer (GEO 20-20).

In step 1, the cleaned foraminiferal concentrates were vacuum oven roasted to remove any residual organic contaminants. The roasting furnace consisted of a 25cm-long pyrex cylinder wrapped with a nichrome wire coil to form the heating element and covered with several layers of asbestos insulation cloth. One end of the furnace was connected to a vacuum line and the other end was sealed with a rubber stopper incorporating a vacuum release tap. The samples were transferred to small glass vials and placed in an aluminium sample holder, or piccolo tube, which consisted of a tube with holes to support the vials and a hook at one end to allow removal of the tube from the furnace. The piccolo tube was loaded with samples (capacity 72) and placed in the furnace, which was sealed with the stopper and evacuated to -1mm Hg. The samples were then roasted at 300°C for 1 hr to decompose any organic matter, which could interfere with the isotopic measurement by generating CO$_2$ through decarboxylation reactions. The samples were then left to cool under the vacuum.

The CAPS system of step 2 is a fully automated preparation device for determining $\delta^{18}$O and $\delta^{13}$C values in carbonate samples (fig. 7.1). The samples were loaded into individual quartz reaction vessels and placed in a 24-position carousel, which is housed in an oven maintained at a temperature of 80°C. Each sample was analysed sequentially. The reaction vessel was pumped down and a predetermined dose (~1ml) of 100% orthophosphoric acid dispensed. Orthophosphoric acid is used as it is the only known non-volatile water-free acid that does not exchange oxygen with the CO$_2$. As the acid is water-free, it is very viscous and as a result reaction times are slow. The reaction is temperature dependent and to allow adequate time for completion, the oven must be maintained at a consistent 80°C. While the reaction takes place
(-25mins) the evolved CO2 is frozen into a dedicated cold finger positioned close to
the dual inlet of the mass spectrometer to minimise sample transfer time. Water was
removed during the reaction by passing the CO2 through a loop (cold trap) immersed
in a ‘slush bath’, which consists of pure ethanol cooled with liquid nitrogen and
maintained at -81°C. Water must be removed to prevent elemental isotope exchange
with the CO2.

![Diagram of Europa Penta 20-20 Stable Isotope Ratio Mass Spectrometer]

Fig. 7.1 Schematic overview of the Europa Penta 20-20 Stable Isotope Ratio Mass Spectrometer.

The oxygen and carbon isotopes released by the reaction are then measured by mass
spectrometer. The results are then compared with the laboratory standard and this
compared with the international standard (PeeDee Belemnite) and presented as either
positive or negative δ¹⁸O and δ¹³C values calculated according to the following
equation.
\[ \delta^{18}\text{O}_{\text{FBDB}} = \frac{1000 \times {^{18}\text{O}} / {^{16}\text{O}}_{\text{sample}} - {^{18}\text{O}} / {^{16}\text{O}}_{\text{standard}}}{^{18}\text{O}} / {^{16}\text{O}}_{\text{standard}} \]

A description of the Europa Penta 20-20 mass spectrometer machine is attached in appendix 5.

7.3 Results of isotope analyses

Results of oxygen and carbon isotope analyses undertaken as part of this study are presented in figures 7.2 to 7.5 and the raw data for these graphs are presented in appendix 2.

7.3.1 Oxygen isotopes

A plot of $\delta^{18}$O vs. depth in the core indicates that there is a consistent offset in $\delta^{18}$O between the two grades sampled (Fig. 7.2). In general, grade 5 (most poorly preserved) samples give lighter $\delta^{18}$O values lighter than grade 1 samples by a range of 0.2 to 1.2‰. An offset in $\delta^{18}$O of more than 0.3 per mil is considered sufficiently significant to have a bearing on the accurate interpretation of $\delta^{18}$O values derived from deep-sea cores (P. Cooke pers. comm. 2001).

One exception to the overall trend occurred at the 8-9 cm horizon in a grade 5 sample (Fig. 7.2). The reason for this extremely enriched value is most likely a sampling error. Anomalous excursions such as this are known to occasionally occur as a result of sample contamination or owing to machine error during the Mass Spectrometer operation (P. Cooke pers. comm. 2001). In the case indicated above, machine error is unlikely since this usually causes results to appear depleted in $\delta^{18}$O relative to the predicted value. The highly enriched value here is most likely to have resulted from a benthic foram being accidentally incorporated into the sample and producing a $\delta^{18}$O value well outside the range normally expected for planktic foraminifers. It is also possible that fine fraction material lodged within tests could have an adverse effect on values. Modern pelagic sediments usually contain $>50\%$ silt-sized material (Paull et
al. 1988) and this is not always possible to make sure it is entirely removed from tests during cleaning. It is therefore recommended that this anomalous value be ignored in the interpretation of the results presented herein and as such while still plotted on this value has been removed from the curve and a dashed line placed where the true value is likely to have been (Fig. 7.2).

Another anomalous value occurs at the 17cm horizon where there is a reverse in the isotope patterns between grades for both oxygen and carbon. The reason for this change could be any of the following: 1) the samples may be indicating a genuine reversal in the relative isotopic values between grades 1 and 5 or 2) the samples could have been accidentally mislabelled, in which case the graphs would show grade 1 as lighter than grade 5 as is the case for the rest of the core. Neither time nor funding was available to allow reruns of isotopic analyses for the anomalous horizons.
Fig. 7.2  Graph of $\delta^{18}O$ results for grades 1 and 5 specimens of *G. bulloides* from core SO 136-005 (Challenger Plateau). Note that grade 5 values are generally 0.2-1.2‰ lighter than grade 1 values. Mean and median values for the two grades are shown in the following table. The mean difference between the grades is 0.4 ‰.

<table>
<thead>
<tr>
<th>Grade 1</th>
<th>Grade 5</th>
<th>Offset of Grades 1 and 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean</td>
<td>1.0‰</td>
<td>0.6‰</td>
</tr>
<tr>
<td>Median</td>
<td>1.0‰</td>
<td>0.6‰</td>
</tr>
</tbody>
</table>
The heavier δ\(^{18}\)O for grade 1 relative to grade 5 in the present study may be related to syndiagenetic/diagenetic effects such as precipitation of secondary calcite after deposition or the inclusion of nannofossils on the exterior of the tests. Although all specimens used in this study were ultrasonically cleaned, it is also acknowledged that some ‘contamination’ may have arisen as a result of entrapment or recrystallisation of nannofossil-rich, biogenic debris within the internal cavity of the foraminiferal tests. It is also possible that precipitation of calcite on the interior of tests could explain the enriched signal of grade 1 tests over grade 5. This signal would be consistent with the oxygen isotope signal of deeper water where calcite precipitation likely took place.

The morphotypes examined in the present study may represent populations that occupied different niches in the water column, thus contributing to the δ\(^{18}\)O and δ\(^{13}\)C differences between grades 1 and 5. The thicker walled, grade 1 specimens may have lived at greater depth than their thin walled counterparts. Alternatively each of the two morphotypes may be a dominant component of the assemblage at different times of the year and thus represent a seasonal variation.

The isotope offset observed in this study may well be one or a combination of the factors described above. However, discrimination of the contribution each of those factors may have on derived foraminiferal oxygen isotope signals is beyond the scope of the present study. Despite all these different possible causing factors the connection between preservation and δ\(^{18}\)O signal is strong regardless of what the cause is.

### 7.3.2 Carbon isotopes

A plot of δ\(^{13}\)C vs. depth in the core indicates that for carbon there is also a consistent offset in δ\(^{13}\)C between the two grades samples (Fig. 7.3). In general grade 5 (worst preserved) samples give lighter δ\(^{13}\)C values than grade 1 (best preserved) samples by an average value of 0.2‰ with a range from 0.1 to 0.7‰. In three instances grade 5 samples give δ\(^{13}\)C values of 0.2 to 0.3‰ heavier than grade one samples from the same horizon. While offset between the two grades is generally towards grade 5 being lighter than grade 1, neither the consistency nor amounts of offset are as significant as for oxygen. It is documented that the behaviour of carbon isotopes is
less predictable and more poorly understood than for oxygen (Curry et al. 1992; Brasier 1995). As such no major conclusions are drawn from the data presented in the present study.

Fig. 7.3  Graph of $\delta^{13}C$ for grades 1 and 5 specimens of *G. bulloides* from core SO 136-005 (Challenger Plateau). Note: grade 5 values are generally 0.1-0.7%o lighter than grade 1 values. Mean and median values for the two grades are shown in the following table. The mean difference between the grades is 0.4 %.

<table>
<thead>
<tr>
<th>Grade</th>
<th>Mean</th>
<th>Median</th>
<th>Offset of grades 1 and 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grade 1</td>
<td>-0.2%o</td>
<td>-0.1%o</td>
<td></td>
</tr>
<tr>
<td>Grade 5</td>
<td>-0.4%o</td>
<td>-0.4%o</td>
<td>0.2%o</td>
</tr>
<tr>
<td>Offset</td>
<td>0.6%o</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
7.4 **Comparison of oxygen and carbon graphs.**

$\delta^{13}C$ and $\delta^{18}O$ values usually display an inverse relationship with water depth, surface waters generally giving lighter oxygen values and heavier carbon values and deeper water giving heavier oxygen and lighter carbon values. However, this relationship has been shown to be paradoxical for *G. bulloides* when specimens have migrated vertically in upwelling systems (Kroon and Ganssen 1989; Thunell and Sautter 1992). Samples from non-upwelling areas, which had not undergone diagenesis, would be expected to produce plots of carbon and oxygen that show opposing shifts between horizons. This, however, is not the case in this study as illustrated by plots of carbon versus oxygen concentration. In fact the patterns of the curves are generally very similar (figs. 7.4 and 7.5). The reason for this similarity could be either vertical migration in an upwelling system or diagenetic effects.

In core SO136-005 carbon isotopes are offset by 0.1-0.7‰, an amount smaller than for oxygen; additionally this offset is not as consistent as that derived for oxygen. The comparison of $\delta^{18}O$ and $\delta^{13}C$ (Figs. 7.4 and 7.5) results from core SO 136-005 can give an indication as to the origin of the differences in $\delta^{18}O$ between preservation index grade 1 and 5 samples. Both carbon and oxygen are incorporated in the tests of living foraminiferids as they secrete their tests, however, the two isotopes do not behave identically, since carbon is not fractionated as readily in tests as oxygen. As a consequence, diagenetic processes do not significantly alter its concentrations. In other words, the $\delta^{13}C$ is more likely to be a primary signal. The fact that carbon values indicate offset between the preservational grades indicates that this is a primary phenomenon and the oxygen offset between preservational grades may have also have a primary component. However, the inconsistency of carbon offset means not all oxygen offset can be attributed to a primary signal.

If there was a consistent offset in $\delta^{13}C$ values between preservation index grades 1 and 5, as is the case for $\delta^{18}O$, this would indicate the offset pattern for oxygen values was caused by differences in the original calcite composition of the tests. Such a $\delta^{13}C$
offset would indicate an oxygen signal inherited as a result of alterations to the hydrologic character of the water mass in which the forams being analysed lived. On the other hand a lack of consistent δ^{13}C offset with preservational grades would indicate that the oxygen offset is associated with other processes such as diagenesis. Therefore I conclude there are two probable causes for this similarity in δ^{13}C and δ^{18}O trends; 1) the heavy δ^{13}C values illustrated in grade 1 specimens may originally have been accompanied by lighter δ^{18}O values that were subsequently altered through secondary inclusion of ^{18}O-rich calcite and/or nannofossils after deposition or 2) the lighter grade 1 δ^{13}C values may have originally been accompanied by heavier δ^{18}O values that have subsequently been altered through preferential removal of heavy isotopes during diagenesis.

When comparing horizons 1 and 4 with 15,17 and 23, for δ^{18}O and horizons 1-10 with 12, 17 and 23 for δ^{13}C it is apparent that there is some reduction in the consistent offset between grades with respect to δ^{18}O and δ^{13}C downcore. δ^{13}C values show a reasonably consistent offset in the uppermost 11cm of the core with grade 5 samples being consistently depleted relative to grade 1 (Fig. 7.3). Beneath this depth, the two δ^{13}C curves still exhibit an offset in values, but with more scatter in the data, with some grade 5 samples exhibiting a heavier signal than that derived for grade 1 samples. This may be a result of one of the following: 1) where numbers of grade 5 specimens were insufficient to make up the volume of calcite required for analysis, individuals from grade 4 were incorporated (appendix 2). In all cases this required the addition of no more than 4 (15% contribution) specimens to the total required for the isotopic analysis. The need to adopt this strategy increased with depth in the core, which means more grade 4 specimens were included in the grade 5 samples toward the bottom of the core. The obvious consequence of this would be the increasing enrichment of δ^{18}O values with increasing numbers of lower grade individuals. 2) It is also possible that diagenetic effects have contributed to the observed narrowing of offset with depth. Specimens recovered closer to the base of the core have been exposed to interstitial waters for a longer period of time and consequently to a greater potential for oxygen fractionation. Syn-diagenetic processes are initiated at or near the sediment/water interface and result from both the metabolic decomposition of organic materials and alterations to chemical gradients/reactions in interstitial waters. Below the 'active' layer in the sediment, diagenetic alterations of carbonates usually
increase with depth, however, because of the fact that SO 136-005 was a predominantly active-layer sample, diagenetic affects normally attributed to pressure, temperature interactions between carbonate grains and interstitial fluids are not considered of great significance to the present discussion.

Fig. 7.4 Graph of δ¹³C and δ¹⁸O for grade 1 samples of *G. bulloides* from core SO 136-005 (Challenger Plateau). Note the similarity in shifts between horizons for the two lines. For carbon and oxygen opposing shifts are usually anticipated.
Fig. 7.5 Graph of $\delta^{13}C$ and $\delta^{18}O$ for grade 5 samples of *G. bulloides* from core SO 136-005 (Challenger Plateau). Note the opposing shifts of the two lines between horizons for the top 7-8cm and the similarity in shifts between horizons for the bottom 15cm of the core.
7.5 Discussion

It is concluded from the above data that there is indeed significant offset for $\delta^{18}\text{C}$ and slightly less significant offset for $\delta^{13}\text{C}$ isotope values between samples from preservation index grades 1 and 5. Offset in both oxygen and carbon is interpreted as an indication that the measured offset has a primary component. However, patterns of $\delta^{13}\text{C}$ change are complex and cannot easily be interpreted. The decreasing offset in oxygen isotope concentration downcore is taken as indicating increasing syn-diagenetic effects with depth. Post-mortem dissolution and/or secondary calcite precipitation either as the tests descend through the water column or post-deposition may also be altering the oxygen isotope values of tests.

The general level of deviation in $\delta^{18}\text{O}$ values between times of glacial maxima and minima for *G. bulloides* is on the order of 1.0 to 2.0% (Hodell and Ciesielski 1991, Labracherie et al. 1989; Martinez 1994b). Martinez (1994b) provides a $\delta^{18}\text{O}$ curve for Deep Sea Drilling Programme site 593 approximately 400km NE of SO 136-005 on the Challenger Plateau (Fig. 7.6). A curve for SO136-003 on the Challenger Plateau is also presented (Fig. 7.7). The Martinez graph indicates a maximum change in values between stages 11 and 12 of about 4% with mean changes between 0.5 and 2%. The Challenger Plateau curve gives similar shifts between glacial and interglacials.

As stated above the magnitude of offset in $\delta^{18}\text{O}$ values between grades 1 and 5 of *G. bulloides* in this study ranges from 0.2 to 1.2%. The consequences of this artificially induced isotopic deviation with respect to the derivation and interpretation of oxygen isotope signals is obvious. It is possible that a bias in the selection of specimens for stable oxygen isotopic analysis could significantly influence interpretations of the resultant data set with respect to a number of paleoceanographic scenarios, especially those relating to glacial-interglacial excursions and paleothermometry. In reality, these excursions may simply represent the effects of changes in preservation state of components of the foraminiferal assemblage.
Fig. 7.6 Oxygen 18 curve for DSDP site 593 in the Tasman Sea. Note the large (4‰) change between stages 11 and 12 otherwise shifts between glacial and interglacial are on the order of 0.5 to 2‰. From Martinez (1994).
Fig. 7.7  Oxygen isotope curve for core SO 136-003 from the Challenger Plateau. Horizontal lines indicate glacial stages. Note the shift of 0.5 to 2‰ between glacial and interglacial stages.
Chapter Eight
Conclusions

8.1 Summary

It was the primary objective of this study to ascertain if there was any variation in the ratio of oxygen isotopes between morphotypes of the planktic foraminiferal species, *Globigerina bulloides* from the same deep-sea sediment sample. In order to answer this question, an artificially induced 'preservation index', was devised, which subgrouped specimens of *G. bulloides* on the basis of the preservation state of tests (from grade 1 = best preserved, to grade 5 = worst preserved) as seen under a transmitted light microscope. The best preserved specimens were identified under the microscope as those tests exhibiting no transparency and, the worst preserved specimens were entirely transparent tests. The consistent appearance of test surface, microfabric features, associated with the 5 preservation grades was qualified using the Scanning Electron Microscope.

Once the 'preservation index' had been devised it was used to create a measure of overall preservation state in each of the 23 horizons down the multicore SO 136-005. As stated in chapter 3, this gave a general trend toward decreasing preservation state with depth. Fragmentation analyses were also completed for all horizons of the same core and these gave a general trend towards greater fragmentation with depth. These two independent measures of preservation state were not, however, always synchronous in individual horizons. The possible reasons for this were discussed in chapter 4 and it is likely that as a horizon becomes more dissolved, the weaker specimens are fragmented and so cannot be included in a count for preservation index (as only whole specimens are counted).

The 'preservation index' was also used for the selection of samples for oxygen and carbon isotopic analyses. Separate samples, from both the best (grade 1) and worst (grade 5) preservation states were selected from 15 horizons down core SO 136-005, giving a total of 30 samples, which were then sent to Waikato University for Mass
Spectrometry isotope analysis, the results of, which were presented in chapter 6. Interpretation of the resultant isotope data, indicate very strongly that there is indeed a very significant and consistent offset in $\delta^{18}O$ between grade 1 and grade 5 specimens from the same sediment horizon. The magnitude of the offset is such that, bias in the selection of samples for isotope analysis toward grade 1 or 5, could result in the collection of erroneous data.

8.2 Cautionary Note and Recommendations for Future Work

The discovery herein of significant offset in both $\delta^{18}O$ and $\delta^{13}C$ between morphotypes of the planktic foraminiferid *Globigerina bulloides* leads to the following recommendations for the accurate selection of samples of this species for isotopic analysis in the future. In order to be confident that the fluctuations in isotope values down a deep-sea core, (spanning centimetres or metres) are accurately indicating change in the isotope ratio of the water in which, forams were living, one of the following must be done. Firstly all samples could be chosen from one grade outlined in the preservation index derived herein. If this procedure were followed for each horizon throughout a core it would reduce the possibility that changing preservation state throughout a core is affecting the isotope values derived for these horizons. Such changes in the state of preservation between individual horizons have been shown to exist in core SO 136-005 in the present study (Fig. 4.1). An alternative to merely selecting from one preservation grade would be to collect a selection ranging through all preservation grades, perhaps selecting 20% of every sample from each of the five preservation grades would also give a more accurate indication of changes in $\delta^{18}O$ throughout a core. This would hopefully have the effect of giving an overall isotopic value for each horizon and should reasonably accurately indicate fluctuations in $\delta^{18}O$ between horizons. The most important factor is to make certain that the same types of specimens are being selected for analysis from each horizon Downcore.

An area of future research, recommended as a result of this thesis is an investigation into the effect nannofossil incorporation in a secondary calcite layer has on the isotope signal of forams. Research undertaken by other authors (Dudley et al. 1986; Dudley and Nelson 1994), indicate that alteration of the isotopic signal by nannofossil incorporation could be significant. As chapter 4 states, experiments were undertaken
as part of the present study to ascertain the ability of this secondary layer to be removed through acid etching. This resulted in the recommendation that tests should be by exposed to an acetic acid solution of pH 5.5 for 2 days. However, owing to restraints it was not possible in the present study to prepare etched samples for isotope analysis and quantify variation in isotope signals between them and specimens with the external, nannofossil-bearing layer intact. As discussed in chapter 5, it is also possible that nannofossils are incorporated inside foram tests, either intact or as part of a layer precipitated on the interior of the foram test. Recrystallisation of such nannofossils on the interior of the foram test could again have profound implications for the isotopic signature of a given test. Research should therefore be undertaken with the aim of quantifying the contribution nannofossil derived calcite (on both the interior and exterior of foram tests) has on isotope values derived for those tests.

The aims of this thesis have been successfully carried out and, satisfactory answers to the questions posed, found. An index for the preferential selection of *G. bulloides* morphotypes for $\delta^{18}O$ analysis based on characteristics observable under the transmitted light microscope has been derived, and found useful for sample selection. At the same time the herein derived 'preservation index' has been used successfully to rate the preservation state of *G. bulloides* assemblages in individual horizons within a deep-sea core. As such, the results of this study have been positive and have led to the asking of a number of further questions regarding the accurate selection of isotope samples that require future research.
Acknowledgements

The following is a tribute to all those people who have directly supported and encouraged me through my university years, especially those who helped me in the completion of this thesis.

Firstly to Mum, Dad, Maree and Deane I say thank you for your support over the last 5 and a half years, I couldn't have made it this far without you.

Thanks to Kerry Swanson for being the best supervisor I could have hoped for. You were always interested in my progress and genuinely had my best interests at heart throughout my time at Canterbury, for that I am eternally grateful.

To Gerritt van der Lingen and Kari Bassett, thank you for your time, interest and input. A special thank you to Gerritt and GRAINZ for providing me with my scholarship, it made life a lot easier.

To 'Team Baldoyle' I say thanks for being such awesome flatmates and friends, you have all made the last 18 months far easier than it could have been. I'll never forget the late night discussions with David and the frothy milk miros with the girls. Special thanks to Sam for constantly reminding me how slack I was; to Rob for taking advantage of my drained mind at the chess board; and Geoff for being a great mate.

Thank you Hannah for constantly refreshing my motivation every time I sent a complaining e-mail, and for critiquing my work.

Finally and most importantly I would like to say an enormous thank you to Charlotte. All those innocent nights spent sipping milo and talking by the TV will stay with me forever; you're my best friend and I couldn't have finished off this thesis without you.
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Appendix One

Experimental Methodologies

Introduction
This appendix documents methods used sample preparation for isotopic analysis, and techniques associated with the preparation of materials for scanning electron microscopy.

Preparation of Samples for Isotopic Analysis

A total of 30 samples of G. bulloides were extracted from 15 points throughout core SO 136-005 for $\delta^{18}$O and $\delta^{13}$C isotope analysis at the isotope laboratory at the University of Waikato. Two sub-samples, each representing extremes with respect to the preservation index (grades 1 and 5 described in chapter 3 were taken from each of the 15 points. These 15 points were selected because they represent locations of maximum excursion with respect to preservation and fragmentation graph trendlines presented in figures 4.1 and 4.2. Each of these sub-samples was prepared and foram specimens selected in the following manner.

1) Core sample was sieved through a 250µm sieve with the larger size fraction kept for picking.

2) 25-35 individual tests belonging to grade 1, and 25-35 individual tests belonging to grade 5 were selected from each sample and placed into glass vials. Where there were insufficient numbers of preferred specimens, individuals belonging to adjacent grades were used to make up numbers. In all cases these other specimens were selected from grades as close to the end members as possible. Notes were kept of the contributions made by supplementary specimens to grade
5 (appendix 3). In all cases such contributions represented less than 15% of the total population isolated for analysis. In order for isotope samples to be accurate it is necessary to have enough sample tested and that is why supplementary tests from neighbouring grades were used.

3) The samples were cleaned in the following manner. Vials containing the grade 1 and 5 G. bulloides concentrates were filled with ethanol and placed in a sonic bath for one second after which time the ethanol was removed with a 1ml disposable pipette and replaced with fresh ethanol. This process was repeated three times for each sample and a new pipette used for each of the 30 samples. It was found that 3 seconds was the optimum exposure time for each sample to be in the sonic bath. For periods longer than this, an unacceptable number of tests were corroded and eventually shattered. By refreshing the ethanol between exposures it was hoped that most fine, contaminating material trapped within and on the test wall would be removed.

4) After cleaning, the samples were placed in an oven set at 40°C where they remained until all remaining ethanol was driven off.

5) The dry samples were then placed on a picking tray and any loose fragmentary material removed before the intact forams were placed in new vials, packaged and sent to Waikato University for isotope analysis.

**Scanning Electron Microscopy**

**Specimen Mounting**
All specimens were mounted on 12mm aluminum SEM stubs using carbon dots as a conductive adhesive. Specimens were usually mounted with apertures uppermost. It is important not to touch the stubs or specimens with the fingers as organic contaminants reduce the quality of SEM images and resultant oily vapours often precipitate on the
inner surfaces of the SEM vacuum column. All mounted stubs were stored in an airtight container with fresh silicon gel to absorb moisture.

Photography / Digital Imaging

Mounted, gold-palladium coated specimens were placed in a Leica SEM and photographs and digital images were taken using a High Resolution Recording Unit. Operating conditions were an EHT of 15kV with probe values ranging from 40-120 pA. Images were records of secondary electron scans taken at magnifications ranging from a few hundred up to approximately 20 000 times. An effort was made to take images of different specimens at a standard series of magnifications (500, 5000, 10 000 and 15 000 times) for ease of comparison. Both photographs and stored digital images were taken of specimens. Photographic images were originally preferred over digital images because of their higher resolution, however problems with photographic quality produced by the microscopes record unit meant digital images became the format of choice. Hard copies of digital images were produced using Corel PHOTO-PAINT 9 and the only alterations to those images were the adjustment of brightness and contrast.
Appendix Two

Raw Data

Fragmentation Percent Data for multicore SO136-005.

Fragmentation % equals the percentage of test fragments with less than half the test remaining out of the total number of fragments counted for each horizon downhole.

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**Preservation Index Data for Multicore SO136-005 and Dredge Sample SO136-002.**

Number of specimens equals the total number of specimens selected for each sample. Preservation index grades are the 5 categories selected specimens were assigned to. Preservation index values are the numbers calculated to give relative overall values of preservation for each horizon. The higher the preservation index value the less well preserved the sample is.

Preservation total = e.g. \( (1 \times 16) + (2 \times 46) + (3 \times 30) + (4 \times 5) + (5 \times 3) \) = 233

Preservation Index = e.g. preservation total

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Oxygen and Carbon Isotope Data for Multicore SO136-005

Sample numbers prefixed with NBS and CAR are control samples used for calibration.

Sample numbers beginning with 4 numbers (e.g. 0102ONE) are samples from multicore SO136-005. The ONE means that is a sample of grade one specimens. The numbers 0102 refers to the horizon from which the sample was extracted. For example 0102ONE is from the sample between 1 and 2cm depth in the core and is from the same sample as sample# 2 in the fragmentation and preservation index data tables.

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NBS1956 0.272 -4.849 1.889 0.009 -2.28 0.01
NBS1957 0.25 -5.024 1.871 0.005 -2.456 0.02
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Mass Spectrometer Sample Selection Data for Multicore SO136-005

This table gives the total number of specimens selected for each sample prepared for Mass Spectrometer analysis and the percentage of grade 4 specimens in each sample.

Mass Spec. # corresponds to the sample runs from the raw isotope data on the previous 2 pages.

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Appendix Three

Challenger Plateau Lithology
(summary from page 43, GEOMAR Report 89 (1998))

The cores show a rather monotonous lithology. The sediment consists of silty foraminiferal ooze to foraminiferan bearing clayey silt. The predominant grain-size of the sediment lies within the fine silt fraction. Some medium sand sized grains are present. These grains are planktic foraminifers and black angular clasts. Whether these clasts are charcoal or volcanic glass could not be determined. The major variations that are apparent in the cores are the style of bioturbation and sediment colour. Two types of bioturbation are present: (1) large burrows filled with sediment with a distinct other colour and (2) small *Planolites* burrows with a clear layer parallel to bedding orientation, a preferential horizontal orientation. Within the latter, clear burrowing directions can be seen. The maximum vertical extent of the burrows is 20cm. The sediment colour varies between light greenish grey to greenish grey and very dark grey. Black pyrite streaks frequently occur.

The following is the core log for core SO 136-003GC (gravity core)
Site 1, Challenger Plateau

42°17'74" S, 169°52'66" E, W.D. 926 m

**Soil Profile**

**Horizon A**
- **A1**: Dark grey (7.5Y 2/1) illuvial horizon, showing signs of weathering.

**Horizon B**
- **B1**: Dark grey (7.5Y 2/1) illuvial horizon, showing signs of weathering.

**Horizon C**
- **C1**: Dark grey (7.5Y 2/1) illuvial horizon, showing signs of weathering.

**Horizon D**
- **D1**: Dark grey (7.5Y 2/1) illuvial horizon, showing signs of weathering.

**Horizon E**
- **E1**: Dark grey (7.5Y 2/1) illuvial horizon, showing signs of weathering.

**Horizon F**
- **F1**: Dark grey (7.5Y 2/1) illuvial horizon, showing signs of weathering.

**Horizon G**
- **G1**: Dark grey (7.5Y 2/1) illuvial horizon, showing signs of weathering.

**Horizon H**
- **H1**: Dark grey (7.5Y 2/1) illuvial horizon, showing signs of weathering.

**Horizon I**
- **I1**: Dark grey (7.5Y 2/1) illuvial horizon, showing signs of weathering.

**Horizon J**
- **J1**: Dark grey (7.5Y 2/1) illuvial horizon, showing signs of weathering.
Appendix Four

Oxygen isotope curve for gravity core SO 136-003 correlated with SPECMAP isotope chronology. Lines indicate some stage correlations. SO 136-005 is assumed to be represented by the upper 23 cm of SO 136-003, giving an age for the bottom of core SO 136-005 of approximately 10 000 yrs old. Diagram supplied by G. van der Lingen (2001).

Comparison of oxygen isotope record of Core 003 (Tasman Sea, West of South Island of New Zealand (1998 TASQWA Expedition), with the SPECMAP isotope chronology (from Bradley, 1999). Red lines indicate some stage correlations.
Dear Dr Van der Lingen,

Here are two AMS results for you. The final reports and an invoice will follow by mail.

With kindest regards
Dawn

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Age, delta-14C, DELTA-14C and absolute per cent modern are as defined by Stuiver and Polach. Radiocarbon 19: 355-363 (1977)

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Dawn Chambers (Ms)
Sample Coordinator
Rafter Radiocarbon Laboratory

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Institute of Geological and Nuclear Sciences Limited
PO Box 31312 Lower Hutt, New Zealand

Results of radiometric carbon analysis for core SO 136-003. The age for 52-54 cm is shown as 19-20 000 years B.P., again suggesting the bottom of core S)-136-005 is about 10 000 yrs old. Results supplied by G. van der Lingen (2001).
Appendix Five

Outline of Mass Spectrometer.

The following is an outline of the mass spectrometer used at Waikato University in the analysis of samples for the present study.

This outline was kindly provided by Penny Cooke (Waikato University).

The Europa Penta 20-20
The 20-20 is a magnetic sector mass spectrometer designed for measurements of the isotopic ratios of light gases (e.g. nitrogen and carbon dioxide). It consists of an ion source, which produces a beam of mono-energetic ions from the sample gas, a flight path which passes through a permanent magnetic field and a collector system which collects spatially separated components of the beam.

Source electronics is responsible for controlling the beam generation. A pumping system maintains a vacuum within the analyser through which ions can pass with a low probability of collision. The collector system and head amplifier converts the flow of separated ions into signals, which may be quantified by an integrator.

The major components of the module are:
The source, flight tube and collector system
A differential pumping system
Measurement, communication, pump control and source electronics.

The Major Analyser Components

The source of ions is designed to be at a pressure some 100 times higher than the analyser and its function is to impart energy to the maximum number of incoming neutral gas molecules. Individual molecules are first given an electric charge by stripping them of single electrons, a process known as ionization.

The charged molecules are then given a precise amount of energy (in the form of momentum) by an electric field, and ‘shot’ into a magnetic field, where they follow curved paths dependent on their mass.

The separated ‘beams’ of molecules are collected in Faraday ‘bucket’ collectors.

The beams are in effect, a flow of current (an electric current is defined as a flow of charge, usually electrons). This is of the order of $10^{-9}$ Ampere for a common isotope, and a head amplifier converts this into a low impedance voltage output.
The Differential Pumping System

In order for molecules to travel anywhere at all, the probability of them colliding with other molecules must be low, i.e. the mean free path between collisions must be high.

If measurable separation is to be achieved then the molecules must be enclosed in a system operating at pressures no higher than $10^{-6}$ mbar, i.e. a vacuum (mean distances between molecules increase as pressure is reduced).

This gives the first constraint for a real instrument -- an enclosure (called the analyser) at $10^{-6}$ mbar or better. The vacuum is provided by the pumping system.

Two stages of pumping are needed to achieve the level of vacuum required: a turbo-molecular pump (high speed turbine) provides the ultimate vacuum at the analyser, but the outlet of this must be held below $10^{-3}$ mbar. A multi-stage rotary vane pump provides this 'roughing vacuum'.

In order to monitor the operation of the pumping system, a vacuum gauge is normally mounted close to the throat of the high vacuum pump. A Penning gauge, which works on the basis that the electrical conductance of a gas varies with pressure, is used on the 20-20.