LA-ICP-MS TRACE ELEMENT ANALYSIS OF PLANKTONIC FORAMINIFERA AND APPLICATION TO MARINE ISOTOPE STAGE 31 IN THE SOUTHWEST PACIFIC OCEAN

ΒY

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Even if it's so tiny you can't see it, it is designed with ornament and elegance, down to the fractal, down to the quark, down to the emptiness of an electromagnetic field, there is still design and elaboration.

--Jan Haag, 2000

Abstract

Trace element/Ca ratios were measured by LA-ICP-MS in *Gs. ruber* and *N. incompta* from a wide range of core top and plankton tow samples in the Southwest Pacific Ocean, with particular focus on linking measured Mg/Ca ratios to observed (near-) surface ocean temperatures. Mean Mg/Ca ratios measured in the ultimate chamber F of *Gs. ruber* are significantly lower compared to chambers F-2 and F-1, which show no statistical difference. These observations led to the development of three new Mg/Ca – ocean temperature calibrations that can be used to reconstruct SST from LA-ICP-MS trace element analysis of *Gs. ruber* over a temperature range of 14.7-28.8°C. In contrast to the LA-ICP-MS study of *Gs. ruber*, the planktonic species *N. incompta* shows no systematic difference in Mg/Ca between the final four visible chambers at one core top site, nor between the F-3 and F chambers at any sites. In addition, there was no correlation between Mg/Ca ratios and ocean temperature in either reticulate or crystalline forms. This may reflect migration of this species within the water column that is not uni-directional, that this species does not dwell at the same depths at each core top site, or point towards further unidentified controls on Mg incorporation into *N. incompta* that require further study.

The chamber specific calibrations developed for *Gs. ruber* in this study, and a calibration developed using the same techniques for *G. bulloides* [*Marr et al.*, 2011] were applied down core to Mg/Ca ratios measured from ODP Site 1123. The SST derived from Mg/Ca ratios reveal that during the MIS-31 interglacial, SSTs were approximately 4-5°C warmer than today and 8-9°C warmer than those from MIS-29 and 30. A comparison of SSTs measured from *Gs. ruber* and *G. bulloides*, suggests that they are responding to local insolation changes. *G. bulloides* records colder temperatures than *Gs. ruber*, which reflects differences in their relative depth in the water column. Paired Mg/Ca and δ^{18} O data reveal significant changes in ice volume over the sampling period. Increases in SSTs recorded by the planktonic foraminifera lead the seawater stable isotope record by 10 kyr suggesting a significant influence from changes in Northern Hemisphere ice sheet volume during MIS-31. In some intervals, the SST leads the benthic stable isotope record by 8 kyr and shows deviations in benthic δ^{18} O from synchronous planktic samples.

In *G. bulloides* and *Gs. ruber*, Mn and Mg were the only trace elements to show systematic glacial-interglacial changes from MIS-34 to MIS-29. This correlation could imply that Mn/Ca ratios in the foraminifera are recording changes in ocean chemistry related to changing water mass circulation at ODP Site 1123 as past ocean temperatures changed.

Size-normalised weights (SNW) of *G. bulloides* tests show systematic variations from MIS-34 to MIS-29. For much of the record, SNW is anti-correlated with SST in a manner similar to the modern relationship between SNW and SST in the Southwest Pacific Ocean. However, immediately prior to the MIS-31 Southern Hemisphere insolation maxima, SNW increase with SST suggesting a fundamental change in surface ocean carbonate chemistry occurred that is unique to this time.

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List of Abbreviations

ACC	Antarctic Circumpolar Current
ANU	Australian National University
Aphelion	Furthest distance from the sun
Asymbiotic	An organism that does not have symbionts (see symbionts)
BP	Before Present
CTD	Conductivity, Temperature and Density (device)
DIC	Dissolved Inorganic Carbon
DWBC	Deep Western Boundary Current
Gametogenic (calcite)	Calcite formed at the end of the life cycle
G-IG	Glacial to Inter-glacial (cycles)
GNS	Geological and Nuclear Sciences
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
kyr	Thousand years
LA	Laser Ablation
LA-ICP-MS	Laser Ablation Inductively Coupled Plasma Mass Spectrometry
Lamellar	A thin layer (of calcite), or test-wall built of layers of calcite formed at consecutive instars and covering exposed surfaces of previously formed test
Lysocline	Denotes the depth in the ocean below which the rate of dissolution of calcite increases dramatically
Ma	Million years
mbsf	meters below sea floor
mbsl	meters below sea level
mcd	meters composite depth
µg/g	micro-grams per gram
mmol/mol	milli-moles per Mole
µmol/mol	micro-moles per Mole

MIS	Marine Isotope Stage
MS	Mass Spectrometer
n	number of determinations
NH	Northern Hemisphere
Non-spinose	Those foraminifera that lack spines
NIWA	National Institute of Water & Atmospheric Research
ODP	Ocean Drilling Program
Ontogenetic (calcite)	Calcite originally formed as part of the normal life cycle
Perihelion	Closest distance to the sun
Reticulate	Having ornamental features arranged in a network
SAF	Subantarctic Front
SAW	Subantarctic Surface Water
s.d.	standard deviation
s.e.	standard error
SEM	Scanning Electron Microscope
SH	Southern Hemisphere
SMOW	Standard Mean Ocean Water
SNW	Sized-normalised Weight
SST	Sea Surface Temperature
STF	Subtropical Front
STW	Subtropical water
Symbiont	An organism in a symbiotic relationship
TE	Trace Element (to Ca)
VUW	Victoria University of Wellington
WOA05	World Ocean Atlas 2005
WOCE	World Ocean Circulation Experiment

Chapter 1

Introduction

The study of past interglacial periods warmer than today can provide important perspectives on how Earth's ocean-climate system might respond in a world that may become several degrees Celsius warmer than the present, based on projected future anthropogenic increases of atmospheric carbon dioxide [*IPCC*, 2007]. This thesis utilises the geochemistry of planktonic foraminifera to establish modern calibrations between the trace element chemistry of their carbonate tests, seawater temperature and chemistry. Subsequently, these calibrations are applied to a high temporal resolution study of foraminifera from Marine Isotope Stage 31 (MIS-31), an interglacial period that occurred *ca.*, 1.1 Ma, which has been postulated to have been warmer than the present interglacial [*Scherer et al.*, 2008].

This introductory chapter outlines the objectives and structure of this thesis, and reviews the controls on the global climate system, the use of foraminiferal chemistry as palaeoenvironmental proxies, and the regional oceanography of the Southwest Pacific which is the region of focus in this study.

1.1 Objectives of this thesis

This thesis has two main objectives that both primarily involve the trace element analysis of planktonic foraminifera by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). The first part of this study investigates the trace element chemistry of modern individuals of two species of planktic foraminifera (*Globigerinoides ruber* and *Neogloboquadrina incompta*) from core top samples taken at various localities in the Southwest Pacific. This part of the thesis was designed to answer the following questions: (a) Can Mg/Ca ratios in these species measured by LA-ICP-MS be used to reliably reconstruct sea

surface temperatures (SST) in the Southwest Pacific?; (b) Assess whether other trace elements (e.g., Mn, Zn and Ba) measured in the foraminifera tests are potentially useful palaeoclimate and palaeoceanographic proxies in these species of planktonic foraminifera?; (c) What additional information can be gleaned from the *in situ* LA-ICP-MS analytical method as opposed to traditional bulk solution methods for analysing foraminifera? For example, the extent to which *intra-* and *inter-*individual chemical heterogeneity exists in foraminifera from a given core-top and identifying the process(es) responsible for this. (d) To examine the potential relationships between foraminiferal shell weights, size, Mg/Ca ratios and environmental variables such as ocean carbonate ion concentration and sea surface temperature.

The second part of this study aimed to utilise the LA-ICP-MS trace element chemistry of three species of planktonic foraminifera (*Globigerinoides ruber*, *Neogloboquadrina incompta* and *Globigerina bulloides*) to reconstruct the ocean-climate conditions of MIS-34 to MIS-29. The modern Mg/Ca – ocean temperature calibrations established for *Globigerinoides ruber* and *Neogloboquadrina incompta* in the first part of this thesis were used to reconstruct past SSTs from these species, and a comparable study of modern *Globigerina bulloides* [Marr et al., 2011] was used to reconstruct past SSTs from this species. This work also involved the acquisition of conventional stable oxygen and carbon isotope data.

MIS-34 to mid-MIS-29 occurred 1.00 to 1.15 Ma and during this period global average surface temperatures changed in response to orbitally-driven changes in solar insolation that are modulated by atmospheric composition, oceanic circulation and other factors that reflect the complexities of the Earth system. To date, the MIS-31 interglacial (*ca.*, 1.07 Ma), has received little attention as a key climate event. However, during this period there is sufficient evidence from both low and high latitude records to indicate significant ocean circulation and ice volume changes occurred and that this interglacial may have been considerably warmer than the present interglacial [*Naish et al.*, 2009]. The palaeo-environmental reconstruction of MIS-31 in this thesis is based on a deep marine sediment core form ODP Site 1123, retrieved on Leg 181 by the Ocean Drilling Program (ODP) offshore of New Zealand (Figure 1.1) [*Carter et al.*, 1999; *Carter et al.*, 2004b].

This palaeo-environmental reconstruction of MIS-31 is aimed to address the following research questions: (a) To compare the Mg/Ca derived SST results of this study to other SST data from ODP Site 1123 obtained from other archives or proxies *e.g.*, foraminiferal assemblages (Artificial Neural Networks), Ba/Al ratios from sediments, sortable silt

fraction. (b) How did the ocean and its planktic foraminiferal assemblages, in the vicinity of the Subtropical Front, respond to a period of peak insolation? (c) Given that this period was the most recent time in the past when Antarctica underwent a major loss of ice [*Pollard and DeConto*, 2009], what climatic effect resulted in the Southwest Pacific in the New Zealand region? (c) Is MIS-31 suitable as an analogue for projected future climate change and if so, what climatic and oceanographic changes can be expected in the coming centuries?

1.2 Structure of this thesis

This thesis comprises six chapters encompassing work from method description, technique development, Mg/Ca – ocean temperature core-top calibrations through to palaeo-environmental reconstruction of MIS-31 as follows:

Chapter 1: An introduction to this thesis, its objectives and background material relevant to this study (Earth's climate system, foraminiferal geochemistry and regional oceanography).

Chapter 2: A description of the materials and analytical methods used in this study.

Chapter 3: The development of the LA-ICP-MS analytical method and application to *Gs. ruber* from core-top sites from the Southwest Pacific to establish a LA-ICP-MS calibration between Mg/Ca and SST. This chapter was submitted for publication to the journal *Paleoceanography* and accepted for publication on February 22nd 2011. AB wrote the paper with contributions from each of the authors, in particular LC and GD commented on the introduction, JB and GD commented on the methods sections, EC contributed to the statistical modelling and all authors contributed to the discussion.

Chapter 4: The development of the LA-ICP-MS analytical method and application to *N. incompta* from core-top sites from the Southwest Pacific to establish a LA-ICP-MS calibration between Mg/Ca and SST.

Chapter 5: Application of LA-ICP-MS trace element analyses of *Gs. ruber* and *G. bulloides* to reconstructing the palaeo-environmental conditions during MIS-31 (MIS-33 to -29).

Chapter 6: The final chapter closes with a summary of the main conclusions of this thesis and suggestions for further work.

All of the data in this thesis was produced by me, except for the stable isotope data, which was prepared by myself and analysed at either NIWA or Stanford University. Other contributions were from Kylie Christiansen who worked with me as a summer research assistant under my supervision. Ms. Christiansen contributed to some of the preparation tasks such as weighing samples and measuring lengths and heights of individual foraminifera for the MIS-31 Chapter 5 study.

All of the data reported in this thesis have been copied to a DVD, which is attached to the back cover.

1.3 Earth's climate – an overview

Reconstruction of Earth's past climate throughout the Quaternary and Cenozoic can be used to examine natural climate variability, warming and cooling of the oceans and atmosphere, and from the response of Earth's cryosphere to this, at a time when there were no anthropogenic influences. This section reviews the factors that are responsible for driving natural climate variability *i.e.*, without anthropogenic influence.

1.3.1 What drives Earth's climate system?

The energy that drives natural climate/ocean variability comes primarily from the sun. Given that Earth is an oblate sphere, different amounts of heat fall on different parts of the planet's surface, less at the poles, and most at the equator. Thus the equator is warmer than the poles, and heat is redistributed from the equator to the poles gives rise to weather, climate and oceanic circulation.

On average, about a quarter of incoming solar radiation is used to evaporate water, which carries with it a large amount of that energy (as latent heat) through the atmosphere. It is effectively this energy, and the pole-equator variation in energy balance, which powers atmospheric circulation and winds, and with it the associated water that is the source of what is characterised as weather. The effect of winds is mostly confined to the upper several hundred metres of the oceans, and these winds redistribute energy and moisture around the globe [*Andrews*, 2000; *Rahmstorf*, 2002]. The wind also causes upwelling (referred to as Ekman divergence) near coasts and the Equator, which changes sea surface

temperatures. This mechanism plays an important role in the El Niño/La Niña Southern Oscillation cycle.

The other way that heat is transported away from the equator is by the oceans. Although oceanic circulation is also influenced by the morphology of the ocean basins, differences in seawater density aided by wind-driven upper ocean currents primarily drives ocean circulation and, in particular, the deep thermohaline circulation system [Munk and Wunsch, 1998]. It is this system that delivers most heat from the equator to high latitude polar regions.

1.3.2 Thermohaline circulation

The term thermohaline circulation is often used to describe the movement of temperature and salt (or freshwater) in the ocean. This was further defined by Wunsch [2002] who argued that as both heat and salinity operate in three-dimensions they should be viewed separately and therefore used the definition of ocean circulation as that of its [water] mass, sustained primarily by the wind, and secondarily by tidal forcing. In the Atlantic Ocean, during the winter, this warmer water is transferred to the overlying atmosphere, greatly supplementing that received from the sun. This extra heat results in warmer than expected winters in Europe [Broecker, 1997]. This water loses heat as it cools, and is subsequently converted into cold water that sinks and flows equatorward at depth [Toggweiler and Key, 2001]. The thermohaline circulation system is thought to be a key component in the climatic records that indicate significant changes in the mode of this circulation occurred in this past [Clark and Mix, 2002]. Figure 1.1 shows a highly simplified schematic of the thermohaline circulation system in the modern ocean [Rahmstorf, 2002]. It shows the Pacific equatorial near surface waters, driven westward by atmospheric winds where it slowly moves into the South and then North Atlantic. Here the upper water cools due to ambient temperatures and increases in salinity and density. Initially the dry atmosphere increases evaporation and hence seawater salinity, and then ice formation increases that salinity further. This cold saline dense water then sinks and is pushed south at depth forming one of four main deep-water production regions. In the Southern Hemisphere these are in the Ross Sea and the Weddell Sea. These regions also re-circulate the ocean at depth. Most of this dense, cold water is slowly circulated northward into all three major oceans via the Antarctic Circumpolar Current. This cycling water eventually becomes warmer and less saline, and is upwelled in the Pacific where the cycle continues.



Figure 1.1: Schematic of the global thermohaline circulation system. Red lines = near surface water currents; yellow ovals = main deep-water formation regions; blue lines = deep water currents; purple lines = bottom currents; green shading = salinity above 36‰; blue shading = salinity below 34‰. Figure from *Rahmstorf* [2002].

1.3.3 Why does global climate vary?

The factors that cause global climate to vary can be divided into two broad types:

- extraterrestrial (orbital variations, solar output) and,
- terrestrial (atmospheric chemistry, tectonics, volcanism and biological factors).

Terrestrial factors are a complex interplay of atmospheric chemistry, ocean-atmosphere circulation, continent-ocean basin configurations, volcanism and life. The latter three are not discussed as they are controlled largely by plate tectonics (with the exception of life), and thus tend to change gradually, and for the most part, uni-directionally, on million-year (My) time scales [*Ruddiman*, 2003].

In response to external forcing are changes in ice volume and greenhouse gases that interact with the climate system. These variations in ice-volume produce ice-proximal changes in SST, dust fluxes, and deep water flow, and some combination of these responses controls the 41,000-year atmospheric CO_2 signal [*Ruddiman*, 2003]. An increase in CO_2 and other greenhouse gases, provides a positive feedback on the size of the ice

sheets by amplifying ice-volume changes. Atmospheric circulation is also an important component as large-scale anomalies of (SST) induces heating or cooling of the atmosphere, changing wind on the ocean surface (wind stress) and heat exchange between the ocean and the atmosphere (heat fluxes) [*Samelson et al.*, 2006; *Wyrtki*, 1973], see also Section 1.5.1.

In this section, it is considered that extraterrestrial factors caused by variations in the Earth's orbit are the main driver of climate change; these factors are discussed further below.

Variations in Earth's orbit and attitude were first proposed by scientist James Croll, and later advanced by the Serbian physicist Milutin Milankovitch who identified three modes of variation and predicted that these modes should leave climatic evidence. The three modes are referred to as eccentricity (orbital stretch), obliquity (axial tilt), and precession (axial path wobble) (Figure 1.2). Furthermore, *Milankovitch* (1941) hypothesised that summer insolation in the northern hemisphere at the periods of obliquity and precession directly forced ice sheets through changes in summer ablation.



Figure 1.2: The three modes of the Earth's orbital variation. Source: www.eoearth.org/article/Milankovitch_cycles.

Eccentricity: Earth's orbit about the sun is elliptical and, therefore, the global mean average energy received by the Earth varies with the long axis of its ellipse which is maximal approximately every 100,000 and 400,000 yr [*Paillard*, 2010]. When the Earth is closest to the Sun, it is called perihelion and when furthest, the aphelion. The difference between the maximum and minimum long axis is about 5 million km. Hence, this 'eccentricity' of Earth's orbit around the Sun leads to regular changes in the amount in solar radiation reaching Earth, which in turn affects global climate.

Precession: The third orbital effect on Earth's climate is that of precession of the equinoxes. Precession is the 'wobble' that occurs on a 19,000 to 24,000 yr cycle in Earth's spin on its rotational axis. It is caused by the gravitational pull of the Sun and Moon on Earth. The amplitude of this cycle is modulated by eccentricity. Changes in precession result in incident changes in intensity of solar radiation at the equator; but this also decreases the length of the summer as the pass around the sun will be shorter. Thus, high precession correlates to hotter, shorter summers.

Tilt/Obliquity: Earth's axis relative to the plane of its orbit has also changed through time between (21.5 to 24.5°) with a period of about 41,000 yr. A change in the axis changes the angle of solar radiation with respect to the poles. The current tilt of 23.5° is what gives the Earth its seasons where, for example, the northern hemisphere is tilted toward the sun during June, and hence receives more solar energy than the south. At the same time, the southern hemisphere is tilted away from the sun, which results in winter. These changes in tilt produce long-term variations in seasonal solar energy, particularly at the poles. If the axial tilt of the Earth were 0°, then there would be no seasons.

Thus, eccentricity affects climate by modulating the amplitude of precession, influencing the total annual/seasonal solar energy budget, whereas obliquity changes the latitudinal distribution of insolation [Zachos et al., 2001]. Together the combined effect of these parameters are called insolation, which is the amount of solar radiation expressed in kWh/m^2 impinging on the earth in any given region or area.

Evidence of the above external variations is increasingly more apparent in sedimentary archives. For example Zachos et al., [2001], show Earth's climate system last 65 million years

and beyond, has experienced continuous change, shifting from expansive warmth with icefree poles, to extremes of cold with massive continental ice-sheets and polar ice caps.

1.4 Foraminifera as archives of palaeoclimate and palaeoceanographic change

Foraminifera are unicellular marine micro-organisms (single-celled protistids) capable of fossilisation that constitute only a minor percentage of the total living zooplankton [*Hemleben et al.*, 1989]. The name "foram" comes from the 'formamen', which is a tube-like opening that connects all the chambers of the test together. The Class Foraminifera can be separated into groups by their morphology based on wall structure and chemistry [*Gupta*, 1999]. The first group build their test or outer membrane with organic material. The second group are agglutinated, where the tests are made up of particles from the surrounding environment. The third group are made of calcium carbonate (CaCO₃). This third group is further separated into two polymorphs, calcite and aragonite. Finally, the fourth group has tests that are composed of opaline silica. Within each of these groups are one or more orders. This study focuses only on those foraminifera that secrete tests made of calcite, of which there are eight orders.

Fossil foraminifer shells or tests preserved in the marine sediment record are important because species assemblage data, test weights and shell chemistry can be used to reconstruct information about past oceanic and climatic conditions such as SST, ocean productivity, global ice volume, and seawater salinity, carbonate ion concentration $[CO_3^2]$ and pH *e.g.*, [*Fischer and Wefer*, 1999]. The next section reviews the physico-chemical factors that control foraminifers' ecology, which are pertinent to their use as archives of palaeo-environmental conditions.

1.4.1 Modern planktonic foraminifera

Calcium carbonate tests of foraminifera are either aragonite or calcite, and the shell can be milky white (*porcelaneous* taxa), grey (*microgranualar* taxa) or glassy (*hyaline* taxa), [*Wilkinson*, 1997]. Foraminifera can be separated into two types based on their habitat: planktonic (upper ocean) and benthic (seafloor). Planktonic foraminifera live in the upper surfaces of the oceans passively floating within a depth range of about 0-400 m, but are often found at deeper depths towards the end of their life cycle (*e.g.*, Erez *et al.*, 1991; *Huang et al.*, 2008). Benthic foraminifera are adapted to living in or on the seabed in most water depths. Those

that live in deep-water can contain information about the abyssal circulation of the ocean [*Curry and Lohmann*, 1982; *Miller et al.*, 1987]. Benthic foraminifera that are composed of calcite are limited to waters which are thermodynamically supersaturated or near saturation with respect to $CaCO_3$ *i.e.* above the carbonate compensation depth [*Archer*, 1996]. This is also true for aragonitic foraminifera and other organisms that precipitate aragonite. In this case, it is the aragonitic depth which controls whether these tests are preserved in sediments [*Berger*, 1978]. However, most calcium carbonate foraminifera have calcite tests [*Todd and Blackmon*, 1956].

The lifespan of foraminifera is known to be short, ranging from anything between a few days to several months [Goldstein, 1999]. Foraminifera have been known to reproduce in relation to the lunar calendar and the semi-lunar calendar [Bijma et al., 1990a; Armstrong and Brasier, 2005]. Other researchers have found reproduction (gametogenesis) coinciding with full moons [Erez et al., 1991].

Current available knowledge on the foraminiferal lifespan has mostly been obtained from laboratory culture studies, which have shown variations (*e.g.*, morphology, size, amounts of gametogenic calcite produced) between the same species, thus giving rise to uncertainties and obvious limitations [*Bé et al.*, 1977; *Bijma et al.*, 1990b; *Caron et al.*, 1990; *Bijma et al.*, 1992]. Obtaining reliable data on the lifespan of foraminifera is essential when extrapolating palaeoclimatic data, as such data will represent the duration and depth location in which foraminifera tests record the physico-chemical conditions of seawater in which they were living *e.g.*, temperature, salinity [*Nigam et al.*, 2003].

1.4.2 Life processes and calcification

The actual formation of a foraminferal test is thought to reduce biological, physical and chemical stress. For example, providing the organism with protection from predation, provision of shelter from unfavourable physical or chemical conditions, a receptacle for excreted matter, an aid to the reproductive process, control of buoyancy, possible assistance with cell growth and support for pseudopods and the body cell [*Marszalek et al.*, 1969; *Armstrong and Brasier*, 2005].

The last chamber of the test has one or more openings where protoplasm exudes to engulf the outer test [Goldstein, 1999]. This protoplasm, in the form of pseudopodia, are used to make long filaments that aid movement and trap food particles such as diatoms, algae,

bacteria and detritus, which after capture are withdrawn and ingested inside the test. The geographical patterns of planktonic foraminiferal abundances generally follow those of nutrient concentrations and plankton productivity, and are closely linked to water circulation patterns [*Bé and Hutson*, 1977].

The depths habitats of many foraminifera species are not well known and it is believed that some species live at different water depths at different times in their life cycles [*Bradley*, 1985]. Many forms of planktonic foraminifera, particularly *Globorotalia*, increase their test densities by forming a calcite crust (secondary calcification); the deepest-dwelling morphotypes having the thickest tests. Thus, planktonic foraminifera control their buoyancy by using the density of the protoplasm, the amount of calcite in the test (by test growth and secondary calcification) and by absolute test size [*Kennett*, 1982]. Calcification depth has been estimated from depth-stratified plankton tows, sediment traps and stable oxygen isotope ratios (δ^{18} O) (*e.g.*, *Mortyn and Charles*, 2003; *Bé and Ericson* 1963; *Regenberg et al.*, 2009). A sediment trap study from the Arabian Sea suggested that the lifecycle of planktonic foraminifera is probably of the order of several months due to periods of nil flux, which could not be explained by practical factors of the experiment [*Nigam et al.*, 2003].

1.4.3 Geochemistry of foraminiferal tests

Foraminifera secrete carbonate shells by a biochemical reaction whereby:

$$Ca^{2+} + 2HCO_3^{-} \Leftrightarrow CaCO_3 + H_2O + CO_2$$
 [Eq. 1.1]

The formation of either aragonite or calcite depends on temperature and pressure. Most of the calcium carbonate foraminifera tests are composed of almost pure $CaCO_3$ (>99%) with the remaining 1% consisting of trace elements [*Lea*, 1999]. It is these trace elements within foraminiferal calcite, which make it a sensitive palaeoclimate indicator via various geochemical proxies.

1.4.4 Trace elements in seawater and foraminiferal calcite

On average, there is about five times more Mg than Ca in seawater (Table 1.1). The ratios of conservative elements (*e.g.*, Mg, Sr, B, Li, F, V, U) to Ca are broadly fixed in seawater, whereas those of nutrient (*e.g.*, Cd, Ba, Zn) or scavenging elements (*e.g.*, Al, Mn) to Ca have much larger and systematic variations [*Nozaki*, 1997; *Bruland and Lohan*, 2003]. In inorganic precipitation experiments, calcite is formed only under supersaturated conditions and trace elements such as Mg^{2+} and Sr^{2+} can either assist or inhibit nucleation. Sr^{2+} is a similar size and has similar co-ordination geometry to Ca^{2+} and will assist nucleation, whereas Mg^{2+} is much smaller and will hinder nucleation [*Williams*, 2008]. The Mg content of inorganic calcite was measured as *ca*. 80 mmol/mol at 25°C whereas it is much lower in aragonite (*ca*. 4 mmol/mol). Foraminifera have a considerable control on the bio-mineralisation of calcite and aragonite because they are able to internally control the pH, concentrations of ions and salts and calcification rate [*Erez*, 2003; *Bentov and Erez*, 2006; *Kisakürek et al.*, 2008; *Bentov et al.*, 2009]. Therefore trace element/Ca ratios in foraminiferal tests are influenced by the physiological and/or biological processes of calcification [*Elderfield et al.*, 1996].

The Ca^{2+} ion can be exchanged for other trace elements (TE) within the calcite lattice [*Lea*, 1999] whereby:

$$CaCO_3 + TE^{2+} \Leftrightarrow TECO_3 + Ca^{2+}$$
 [Eq. 1.2]

Element	Ion	Average ocean concentration	Ocean residence time (yr)
Mg	Mg^{2+}	52.7 mmol/kg	13,000,000
Sr	Sr ²⁺	89 μmol/kg	5,100,000
Ba	Ba ²⁺	109 nmol/kg	10,000
Ca	Ca ²⁺	10.27 mmol/kg	1,100,000
Mn	Mn^{2+}	360 pmol/kg	60
Al	Al ²⁺	1.11 nmol/kg	200
Zn	Zn^{2+}	5.4 nmol/kg	51,000

 Table 1.1: Residence times of trace elements in seawater adapted from [Nozaki, 1997; Bruland and Lohan, 2003].

1.4.5 Mg/Ca ratios as a palaeocean thermometer in planktonic foraminifera

The Mg/Ca ratio of planktonic foraminiferal calcite is an important tool for reconstructing past SST. Ca^{2+} ions in the calcium carbonate test lattice are substituted by Mg²⁺ ions in an endothermic reaction. Therefore, the higher the temperature at the time of calcification, the higher the carbonate Mg/Ca ratio.

This relationship is an exponential one described by the equation:

$$Mg/Ca = B \exp (A \times T)$$
 [Eq. 1.3]

Where B is the pre-exponential constant, A is the exponential constant (intercept) and T is temperature (°C). Most palaeo-ocean thermometry calibrations are based in specific latitudinal ranges such as equatorial/tropical, subtropical/transitional and polar because of the biogeographical distribution of individual foraminiferal species [*Arnold and Parker*, 1999]. Calibrations derived to reconstruct SST in polar regions are limited because, as latitude increases, the number of planktonic species decreases with only one planktonic species found at both poles [*Pearce*, 1991]. Notwithstanding this, calibrations from higher latitudes are important as temperature changes over geological timescales will be more prominent at polar regions, compared to the equatorial regions.

An important aspect of Mg/Ca palaeo-ocean thermometry is that the relationship between the Mg/Ca ratio and temperature is also modified internally by different species of foraminifera (*i.e.* A and B in equation 1.3 are species-specific). Some of these differences can be explained by other environmental and biological factors that include salinity, dissolution, test size and seasonality. Some studies have found salinity has little effect on core-top foraminiferal Mg/Ca ratios [*Sadekov et al.*, 2008], although it appears to be more pronounced in regions with high salinity gradients such as the Red Sea [*Ferguson et al.*, 2008; *Mathien-Blard and Bassinot*, 2009]. Others have found that increased test size is coupled with increased Mg/Ca ratios in several species [*Elderfield et al.*, 2002]. Dissolution on the other hand, can alter carbonate Mg/Ca ratios by the preferential dissolution of high Mg bands found within the calcite lattice. This is further complicated as some species appear to be more susceptible to dissolution than others [*Dekens et al.*, 2002] and, although the majority of dissolution, is related to those fossils that are beneath the calcite compensation depth, there is evidence to suggest that dissolution can also occur at shallower depths [*Brown and Elderfield*, 1996]. Therefore it is important to exercise caution in the interpretation of foraminiferal Mg/Ca ratios from deep marine sediment cores (*i.e.* > 3000 m); as derived temperatures can be erroneously lower than actual calcification temperatures. Seasonality can also affect the Mg/Ca ratios where the dominant signal (SST) is biased towards a particular season [*Kawahata*, 2005; *Wilke et al.*, 2008; *Wan et al.*, 2010]. This could affect the inferred SST, which is usually correlated to annual SST [*Fraile et al.*, 2009].

1.4.6 Stable Oxygen isotopes (δ^{8} O)

The development of high-resolution deep-sea oxygen (δ^{18} O) and carbon (δ^{13} C) isotope records have been pivotal in resolving the rates and scales of Cenozoic climate change [Shackleton, 1987].

There are three stable isotopes of oxygen (¹⁶O, ¹⁷O and ¹⁸O) with relative abundances of 99.76% (¹⁶O), 0.04% (¹⁷O) and 0.20% (¹⁸O), respectively. Most applications in palaeoclimatology concern only the ¹⁸O/¹⁶O ratio. The fractionation of oxygen (and carbon) isotopes results from isotopic exchange reactions and kinetic effects, where the lighter isotope either reacts or evaporates more easily than the heavier one. This temperature-dependent fractionation can be large (0.25‰/°C) in biogenic carbonate so that oxygen isotopes can be used to examine past changes in seawater temperature [*Ravizza and Zachos*, 2003].

However, application of stable oxygen isotopes to palaeo-ocean thermometry is complicated by the fact that the oxygen isotope ratios in seawater ($\delta^{18}O_{sw}$) have not been constant over relatively short geological timescales. In seawater the lighter isotope ¹⁶O is preferentially partitioned into water vapour during evaporation, leaving the heavier ¹⁸O isotope in the seawater. Condensation and precipitation result in the reverse, where the heavier ¹⁸O condenses into liquid water, and the lighter ¹⁶O remains as a vapour. This can result in large differences between global ice sheets and mean seawater δ^{18} O values (-35 to 40‰ versus 0‰, respectively). During interglacial periods, the evaporation-precipitation cycle generally maintains an overall balance in oxygen isotope ratios in seawater due to the returning of most of the snow and ice to the oceans via summer ice and snow melt [*Katz et al.*, 2010]. During glacial periods, however, the oceans become increasingly depleted in ¹⁶O and enriched in ¹⁸O as precipitation (snow/rain) on land becomes trapped in ice sheets, and cannot return to the ocean, also resulting in a global fall in sea level. For example, at the last glacial maximum, global sea level fell by *ca.* 120 m (*e.g., Clark and Mix,* 2002; *Siddall et al.*, 2003).



Figure 1.3: Schematic of changes in δ^{18} O in oceans during glacial and interglacial periods. (A) Represents a warmer climate with low ice volume. (B) Represents a colder climate with high ice volume. Modified from [*Jager and Hunziker*, 1979].

Therefore the ¹⁸O/¹⁶O ratios can be of importance climatically as they reflect the shifts from glacial (colder climate with high ice volume) and interglacial (warmer climate with low ice volume) periods (Figure 1.3). In foraminiferal tests the ¹⁸O/¹⁶O ratios or δ^{18} O, is a function of the ratio in the seawater in which the foraminifera lived and the temperaturedependent calcification process [*Urey*, 1947; *Epstein et al.*, 1953]. Individual species of foraminifera have been shown to fractionate oxygen isotopes differently during metabolism [*Kennett*, 1982], with some species showing differences in isotopic ratios giving lighter than expected (*ca.*, 0.5‰) values in comparison to non-biological thermodynamic calculations. A 0.5‰ lighter value is equivalent to a *ca.* 2.5°C temperature error [*Shackleton et al.*, 1973] and these differences are species-dependent. The oxygen (δ^{18} O) and carbon (δ^{13} C) incorporated into biogenic calcite is quantified by comparison of results to those of a known standard, such as Vienna Pee Dee Belemite (vPDB).

For oxygen isotopes the equation would be:

$$\delta^{18}O(\%) = 1000 \text{ x } \{ [(^{18}O/^{16}O)_{samble} - (^{18}O/^{16}O)_{standard}] / (^{18}O/^{16}O)_{standard} \}$$
[Eq. 1.4]

Therefore, foraminiferal tests can be used to examine changes in global hydrological resources *e.g.*, ice volume ($\delta^{18}O_{sw}$), local changes in evaporation/precipitation, and changes in temperature. An additional complexity lies in the fact that the chemical composition across the oceans is not uniform. When seawater evaporates it also increases in salinity so that empirical relationships within different oceanic regions have been developed in order to derive estimations of palaeosalinity (*e.g., LeGrande and Schmidt*, 2006). However, changes in $\delta^{18}O_{sw}$ also vary seasonally so that one equation may not necessarily define a region [*McConnell et al.*, 2009].

In the deep ocean, changes in temperature recorded in benthic foraminifera over glacial to interglacial timescales are much smaller (*ca.* 1-2°C) than the much larger amplitudes recorded in planktonic foraminifera in the upper ocean. In order to unravel the concomitant changes in temperature and ice volume recorded by δ^{18} O, an independent measurement of temperature (*e.g.*, Mg/Ca) can be used to remove temperature from the δ^{18} O signal. By substitution into a suitable palaeotemperature equation (*e.g.*, *Bemis et al.* 1998; *Shackleton et al.* 1973) based on that proposed by *Epstein et al.*, [1953] (Eq. 1.5), the changes in ice volume can be estimated.

$$T = 16.5 - 4.3 \left(\delta^{18}O_{c} - \delta^{18}O_{sw} \right) + 0.14 \left(\delta^{18}O_{c} - \delta^{18}O_{sw} \right)^{2} \quad [Eq. 1.5]$$

1.4.7 Complexities of using Oxygen isotopes as a palaeoclimate proxy in foraminiferal calcite

The estimation of temperature and global ice volume/salinity from foraminiferal δ^{18} O is complicated as the δ^{18} O in most foraminiferal tests is not in equilibrium with the surrounding seawater. These offsets are referred to as *vital effects* and can include:

- (1) Photosynthetic activity of algal symbionts. Experiments on foraminifera that harbour symbionts have shown that the photosynthetic activity of the algal symbionts can modify test δ^{18} O values. For example, they can lower pH or change the carbonate ion concentration $[CO_3^{2-}]$ of immediately surrounding seawater [*Bé et al.*, 1982; *Spero et al.*, 1997; *Wolf-Gladrow et al.*, 1999; *Eggins et al.*, 2004];
- (2) Regional variations, seasonal fluxes or depth habitats of different species that vary regionally [*Fairbanks et al.*, 1980; *Reynolds and Thunell*, 1986];
- (3) Vertical migration of species within the water column where a surface-to-deep temperature gradient may result in different δ^{18} O values (*e.g.*, *Mortyn and Charles*, 2003);
- (4) Differences within the test chambers (e.g., the production of gametogenic calcite, (e.g., [Ravelo and Fairbanks, 1992; Kozdon et al., 2009]);
- (5) Although not strictly a vital effect, post-depositional diagenesis where deep-burial diagenesis can decrease δ^{18} O values due to re-calcification of fossil tests in equilibrium with sediment temperatures [*Katz et al.*, 2010]. Likewise, diagenesis in planktonic foraminifera as opposed benthic foraminifera may result in 'colder overprinting' due to precipitation of calcium carbonate on the foraminiferal tests cold bottom waters.

In considering these issues, careful selection of fossil samples such as those preserved in clay-rich sediments, as well as the study of the species and/or associated vital effects can help overcome these problems.

1.4.8 Stable Carbon isotopes ($\delta^{I3}C$)

There are two stable isotopes of carbon (¹²C and ¹³C), with relative abundances of 98.89% (¹²C) and 1.11% (¹³C), respectively. In the oceans, the distribution of carbon (δ^{13} C) is

controlled by air to sea gas exchange, biological uptake at the sea surface and organic decomposition at the seafloor [*Mackensen et al.*, 1993]. The oceanic inorganic carbon pool is governed by carbonate reactions such that the dissociation of atmospheric CO_2 into the surface oceans produces bicarbonate (HCO₃):

$$H_2O + CO_{2(atm)} \Leftrightarrow H^+_{(aq)} + HCO_{3(aq)}$$
 [Eq. 1.6]

The exact composition of the HCO_3^{-1} and CO_3^{-2-1} ions is pH dependent (Eq. 1.6), but at normal marine pH (7.8 to 8.3), the HCO_3^{-1} ion is the dominant species. The sum of HCO_3^{-1} , CO_3^{-2-1} and $CO_{2(dissolved)}$ is termed the total dissolved inorganic carbon (DIC).

$$HCO_3^{-} \Leftrightarrow H^+ + CO_3^{-2-}$$
 [Eq. 1.7]

Foraminifera use the HCO_3^- fraction of the DIC to produce calcium carbonate (CaCO₃). Planktonic foraminifera use carbon from the DIC in the photic zone to a depth of *ca.*, 200 m in the surface open ocean [*Kroopnick*, 1985]. However, because photosynthesis strongly favours the lighter ¹²C isotope, surface waters are isotopically enriched in ¹³C as marine phytoplankton produces organic matter (Figure 1.4).



Figure 1.4: Schematic of the generation of a carbon isotope gradient between the sea surface and deep water due to export production and interactions between marine organic and organic cycles. This figure also illustrates the cycling of carbonate species. With foraminifera it is the bicarbonate (HCO₃⁻) ion that is used to construct tests. Figure modified after *Rohling and Cooke* [2003].

These organic carbon particles eventually sink into deeper water where they become remineralised, causing a gradient in δ^{13} C between surface and deep water. The release of the isotopically lighter δ^{13} C into deep water equilibrates with HCO₃⁻, and benthic foraminifera use this lighter δ^{13} C to construct their tests. Benthic foraminifera tests therefore give a carbon isotope signal that is complicated, affected by the exposure time of decaying organic matter, the amount of organic matter and the rapidity of organic matter delivery (this is temperature-dependent), and basin-to-basin fractionation caused by different source regions and deep water circulation patterns [*Kroopnick*, 1985; *Raymo et al.*, 1990; *Robling and Cooke*, 2003].

The δ^{13} C in benthic foraminifera has been used to distinguish water masses derived from different sources as the δ^{13} C that has sunk from the surface is slowly moved through the ocean basins [*Bostock et al.*, 2004]. This means that as deep waters age, DIC and nutrient contents increase so that the δ^{13} C becomes depleted. Over longer timescales, for example Quaternary climate cycles, some of the changes in δ^{13} C from glacial to interglacial timescales will also be the result of change in surface ocean productivity.

1.4.9 Vital effects

The 'vital effect' refers to biologically controlled processes that affect the fractionation of trace metal and isotope chemistry in foraminiferal tests away from isotopic and elemental equilibrium [Nürnberg et al., 1996; Eggins et al., 2003; Erez, 2003; Sadekov et al., 2005; Bentov and Erez, 2006].

These vital effects include calcification rate, respiration and photosynthesis (of symbiotic algae) [*Duplessey et al.*, 1970; *Spero et al.*, 1991] and large interspecies, inter-individual and intra-test variability, and deviation of the apparent distribution coefficients from that of inorganic calcite and its variable temperature dependence [*Lea*, 2003; *Bentov and Erez*, 2006]. In many cases, the vital effect between species can be avoided by constructing records based on single species.

1.5 Regional oceanography

New Zealand and its submerged micro-continent are located midway between the equator and Antarctica at southern mid-latitudes. This section describes the oceanography of this region in the context of the sites of the core top and plankton tow material that were used in this thesis to establish Mg/Ca – ocean temperature calibrations for the planktic foraminifera *G. ruber* and *N. incompta*. An introduction is also given to ODP Site 1123, which was the sampling site of the sediment core used to establish a palaeoclimate and palaeoceanographic record for Marine Isotope Stage [MIS] 31.

The Southwest Pacific Ocean has three main elements to its circulation:

[i] The South Pacific Gyre (STG) which brings Subtropical surface waters via eastern Australia to northern New Zealand (Figure 1.5);

[ii] The Antarctic Circumpolar Current (ACC) which introduces Subantarctic surface waters to southern New Zealand (Figure 1.6);

[iii] at depth the ACC and Pacific deep western boundary current (DWBC) transport Circumpolar Deep Water from southern sources, with the ACC also carrying Antarctic Intermediate Water and Mode Water (Figure 1.7).

In the New Zealand region, the upper ocean supports several well defined but dynamic fronts that represent the boundaries between these tropical and polar water masses.
1.5.1 Surface waters in the Southwest Pacific Ocean

Surface ocean fronts are zones that are relatively narrow and separate broader zones with marked changes in water mass properties, in particular temperature and salinity, resulting in separate water mass types. In the Southwest Pacific, surface ocean circulation is strongly influenced by the STG which plays a crucial role in the climate system of exporting excess tropical heat and salt polewards [Trenberth and Caron, 2001; Belkin and Cornillon, 2003]. The STG is driven by the combination of low-latitude easterly trade winds and high latitude westerlies and rotates in a counter-clockwise direction. Recent observations have confirmed that the STG is part of a southern 'super-gyre' that connects the South Pacific Ocean with the Indian Ocean and thus creates a pathway for ocean-to-ocean transport of heat, salt and nutrients (Figure 1.5) [Roemmich, 2007; Roemmich et al., 2007]. Recent modelling and observational studies have confirmed a spin-up and southward shift of Southern Hemisphere subtropical ocean circulation forced by wind stress curl intensification associated with a pole-ward shift in the circumpolar westerly winds and a positive Southern Annular Mode [Gillett and Thompson, 2003; Cai et al., 2005; Cai, 2006; Hill et al., 2008]. In the New Zealand region the Subtropical Front (STF) locally approximates the southern limit of the South Pacific STG, and marks the boundary between subtropical water and Subantarctic water of the Southern Ocean.

In the northern reach of the South Pacific STG, the South Equatorial Current moves in an eastern direction where it bifurcates on reaching the Australian continent. There a weaker branch, the Subtropical Counter Current turns north-eastward whereas the main branch turns south to form the East Australian Current (EAC) [Hamon, 1965]. The EAC is a complex seasonal system [Ridgway and Godfrey, 1997] providing the western boundary of the Pacific STG that links with Indian STG [Speich et al., 2002]. Warm core eddies have been observed in the EAC [Boland and Hamon, 1970; Nilsson and Cresswell, 1980; Boland and Church, 1981; Ridgway and Dunn, 2007] and these perturbations can be up to 200-300 km in diameter with several generated each year. At 35°S part of the EAC leaves the coast and continues east as the Tasman Front [Andrews et al., 1980].

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Figure 1.5: Generalised chart of the Southern super-gyre (after *Roemmich* [2007] and *Hill et al.*, [2008]) showing ocean circulation and heat exchange (black arrows) between the Southern Pacific and Indian Oceans at a depth of 1,000 m. The orange band represents the area of super-gyre circulation, and the pink and red bands show the distinct inner gyres operating north of the ACC (blue band). The contour lines represent dynamic height ($m^2 s^{-2}$), which is generally derived from temperature and salinity profiles. EAC = East Australian Current, SEC = South Equatorial Current, EAC Ex = East Australian Current Extension, EAUC = East Auckland Current, TF = Tasman Front.

On decadal timescales the EAC is strongly influenced by wind stress curl, which has in turn been related to ENSO variability [*Ridgway and Hill*, 2009]. Increased warmth in the tropical Pacific associates with weaker South Pacific wind stress curl maximum, a weaker extension past Tasmania and a stronger TF [*Sasaki et al.*, 2008]. The eastward flow associated with the TF extends to northern New Zealand, where it part -forms the East Auckland Current (EAUC) together with three semi-permanent eddies—the North Cape Eddy, East Cape Eddy, and Wairarapa Eddy [*Roemmich and Sutton*, 1998; *Stanton*, 2001]. The EAUC extends to ~37°S before becoming the ECC which continues south to the Chatham Rise where it turns east.

Off western New Zealand, the STF intercepts the southernmost South Island where it is forced northward along the continental margin to eventually continue along the west-east crest of Chatham Rise. The flow associated with the STF along the South Island is locally termed the Southland Current, which carries mainly Subantarctic surface water, some of which passes through Mernoo Saddle onto Cook Straight and the eastern North Island with another branch extending along the southern side of Chatham Rise (Figure 1.6).



Figure 1.6: Chart of the surface ocean currents of New Zealand and surrounding regions. Blue arrows indicate the cold, fresher Subantarctic front (SAF) within the Antarctic Circumpolar Current (ACC), whilst the purple arrows show warmer, saltier subtropical water that is brought to the west of New Zealand from the East Australian current (EAC) and the Tasman Front (TF), which branches into the East (EAUC) and West Auckland Currents (WAUC). This Subtropical Front (STF) forms part of the South Pacific Subtropical Gyre that moves warm water in a counter -clockwise direction down the east coast of Australia. West of New Zealand the westerly winds force warm water via the Westland Current (WC) and Southland Current. Some of the former flow moves through the Cook Strait as the D'Urville Current (DC). The Southland Current reaches the south of New Zealand, and is diverted by Chatham Rise to the east. AUS = Australia, NZ = New Zealand, ANT = Antarctica. Figure taken and modified from *Carter et al.*, [1998a].

1.5.2 Deep waters in the Southwest Pacific Ocean

Deep water from the South Indian and South Atlantic Oceans, together with water produced locally around Antarctica, enter the region near Macquarie Ridge entrained within the Pacific deep western boundary current DWBC which, flows in concert with the ACC around southern Campbell Plateau mainly below 49°S [*Carter and Wilkin*, 1999] but extending up to ~46°S (Figure 1.7). North of ~46°S, the DWBC continues northwards uninterrupted, typically at depths >2000 m with most of the transport at depths >3250 m. Not unexpectedly, for a flow that supplies much of the water filling the Southwest and North Pacific basins, its volume transport is high and variable [*Whitworth III et al.*, 1999].

At Chatham Rise, the DWBC intensifies against the Chatham Rise topography [*Warren*, 1973; *Carter and McCave*, 1994] and deposits a sediment drift on the northern Rise flank [*Carter and McCave*, 1994]. It is this sediment drift that was the target for ODP Site 1123. Because of the water depth, the ocean floor is bathed by lower Circumpolar Deep Water which, on the basis of the salinity and the δ^{13} C signatures, contains a marked North Atlantic Deep Water component (*e.g., Hall et al.*, 2001, the DWBC strikes northwest steered by the subdued topography that steepens markedly along the eastern flank of Hikurangi Plateau. From there, the flow turns north-northeast along the Kermadec Ridge and Trench system and is steered onto the central Pacific [*McCave and Carter*, 1997; *Whitworth III et al.*, 1999].



Figure 1.7: Chart of the New Zealand region and the main elements of the abyssal circulation including the deep western boundary current (DWBC), and the overlying but deep-reaching Antarctic Circumpolar Current (ACC). Figure taken and modified from *Carter et al.*, [1998a].

1.5.3 Oceanography at ODP Site 1123

One of the main components of this study is analysis of foraminifera from a marine sediment core recovered from ODP Site 1123, which is located east of New Zealand (41°47.2'S, 171°29.9'W; 3290 m deep) on the northern flank of a broad, asymmetric submarine high, Chatham Rise, in the Southwest Pacific Ocean (Figure 1.6, 1.7).

Chatham Rise is located below the STF which is geographically locked into a relatively narrow position (~150 km) and limited vertically by the shallow depths of the uppermost

bathymetry (250-350 m) [*Sutton*, 2001] (Figure 1.6). The front is therefore characterised by strong latitudinal (45 to 47°S) temperature and salinity gradients. These gradients correspond to the transition between summer to winter (north to south) surface temperatures and salinities ranging from 15 to 10°C and 34.7 to 34.8 psu respectively [*Heath*, 1985; *Chiswell*, 2003]. However, at ODP 1123, the STF is relatively unconstrained by the deepening rise topography and the associated currents (ECC and SC) that pass eastward along the north and south rise flanks respectively. Accordingly, the STF has more freedom to migrate as represented by the widening STF zone off eastern Chatham Rise (Figure 1.6). Over glacial to interglacial cycles, these fronts migrate (north or south) and reflect the meridional gradient between STW and SAW. For example, during MIS-11 and MIS-5.5, two exceptionally warm interglacial's in the Late Quaternary, southward migration of the STF occurred, reflecting higher SST [*Wilson et al.*, 2005]. Similarly during glacial periods, shifts in the SAF if the STF was geographically 'locked' [*Hayward et al.*, 2008] would result in an increased temperature gradient between the STF and SAF.

As discussed earlier, the STF separates warm, saline, STW in the north with cooler, fresher SAW in the south. Both STW and SAW have distinct nutrient properties, SAW is high in macronutrients and low in micronutrients and chlorophyll whereas STW has low macronutrients but elevated micronutrients [*Bradford-Grieve et al.*, 1999]. The convergence of these two nutrient complimentary surface waters makes Chatham Rise a highly productive environment [*Nodder*, 1997; *Boyd et al.*, 1999]. Studies have shown episodic export of particulate material from the surface with distinct differences north and south of the rise [*Hawes et al.*, 1997; *Nodder,* 1997; *Nodder and Northcote,* 2001] although the region is also controlled by productivity limiting mechanisms, such as light, grazing pressure, silicate limitation as well as micronutrient supply [*Boyd et al.,* 1999; *Boyd et al.,* 2004].

The samples used in this study all come from above the modern regional calcite lysocline (3600-4000 m) [*Berger et al.*, 1976; *Martínez*, 1994]. The application of this study's and extant Mg/Ca – ocean temperature calibrations to planktonic foraminifera from the ODP Site 1123 core, is used to investigate palaeoceanographic and palaeoclimatic change from MIS-29 to 34 [1018-1127 kyr]. The site is close to the northern limit of the modern STF and hence captures the interaction STW and SAW over glacial-interglacial cycles (*e.g., Crundwell et al.*, 2008). In that context, this core provides a record of change in water masses, frontal position and marine productivity [*Hall et al.*, 2001; *Crundwell et al.*, 2008; *Hayward et al.*, 2008].

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Palaeo-records from the Quaternary indicate that during glacial times, there has been a considerable (up to 8°) shift in the STF northwards in open oceanic sites (*e.g.*, *Barrows et al.*, 2000; *Weaver et al.*, 1998). Movement of the STF at Chatham Rise due to forcing from the south during glacial periods has been proposed, [*Weaver et al.*, 1998; *King and Howard*, 2000; *Sikes et al.*, 2002; *Fenner and Di Stefano*, 2004; *Crundwell et al.*, 2008] but is disputed in other studies [*Schaefer et al.*, 2005; *Wilson et al.*, 2005]. It may be that some of the disparity between each side of the debate may be explained by location of the southerly control point in one of the studies [*Schaefer et al.*, 2005; *Crundwell et al.*, 2008].

1.5.4 Application of foraminiferal trace element data from ODP Site 1123 during MIS-31

The main focus of the thesis is the application of the trace element data to Marine Isotope Stage 31. This 'superwarm' interglacial period is of climatic importance for a number of reasons which are summarised below:

- It lies in the Mid-Pleistocene Transition (MPT), 1.2 0.5 Ma, characterised by a shift from low-amplitude 41-kyr obliquity-forced climate cycles typical of the early Pleistocene to high-amplitude 100-kyr cycles, typical of the Late Pleistocene [*Head*, 2005]. These later cycles are indicative of slow ice build-up and subsequent rapid melting, and imply a transition to a strongly non-linear forced climate system [*Head*, 2005]. These changes have also been linked to atmospheric CO₂ [*Medina et al.*, 2005, *Russon et al.*, 2011], and the scouring of continental regolith hypothesis [*Clark et al.*, 1999], although other theories exist (*e.g. Huybers et al.*, 2007; *Tziperman and Gildor*, 2003].
- It has unique orbital parameters where eccentricity, precession and obliquity were high, such that insolation in Southern Hemisphere mid to high latitudes were high.
- The benthic δ¹⁸O record suggests that this period was exceptionally warmer than the present day although much lower in amplitude compared to another earlier 'superwarm interglacial' MIS-11 (Figure 1.8).
- Various proxies suggest sensitivity to the strong precessional forcing in the high and mid latitudes [*Tietler et al.*, 2005; *Kupp et al.*, 2006].

- The local insolation has been modelled in Antarctica, with a suggested 5°C warming resulting in the collapse of the West Antarctic Ice Sheet [*Pollar and DeConto*, 2009]. This is also backed by geological evidence suggesting open water in the Ross Sea during this time [*Naish et al.*, 2009].
- Together this evidence points towards higher SST in the mid to high SH and melting of the WAIS.



Figure 1.8: The LR04 benthic δ^{18} O stack constructed by the graphic correlation of 57 globally distributed benthic δ^{18} O records (*Lisiecki and Raymo*, 2005). MIS-31 is shown in the grey box.

Chapter 2

Materials and Methods

2.1 Fossil and plankton tow material

The core top and plankton tow material used in this work was provided by the New Zealand National Institute of Water and Atmospheric Research (NIWA), the Australian Institute for Marine Sciences (AIMS) and Geological and Nuclear Sciences (GNS). The details of the core tops and plankton tows are discussed individually in each relevant chapter of this thesis.

2.1.1 Recovery of foraminifera from marine sediment cores and preparation of foraminifera for LA-ICP-MS analysis

The core samples used were 1 or 2 cm sediment sections, which were rehydrated for 24 hr. Following this, Calgon® was added and the sample was gently ultrasonicated to disaggregate the mud. The sample was then sieved through a 65 μ m mesh using deionised, distilled water. The remaining particles were then gently sprayed with deionised, distilled water using a spray bottle to remove remaining clay from the fossil material. This was then transferred into a beaker and placed in an oven at 40°C for 24 hr. Once the sample was dry, it was subjected to several rinses in ultra-clean water (>18 M\Omega), followed by ultrasonication in analytical grade methanol for a few seconds, with final rinses in ultra-clean water. These procedures are similar to those followed in *Eggins et al.*, [2003] except that ultrasonication times varied depending on the fragility of samples and/or whether or not they were core top or plankton tow samples (see below and section 2.1.2). These procedures differ to solution chemical cleaning which has been shown to reduce the loss of sample material [*Boyle and Keigwin*, 1985; *Barker et al.*, 2003; *Rosenthal et al.*, 2004; *Yn et al.*,

2005]. The sample was then oven dried at 40°C for 24 hr. Once dry, it was sieved through a series of sediment sieves of varying size fractions (< 65, 65-125, 125-250, 250-355, >355 μ m).

Organic material was removed from the plankton tow samples using a low temperature oxygen plasma asher [*Patterson*, 1978]. The samples were pre-rinsed and oven dried at 40°C prior to ash removal, rinsed in ultraclean water but not ultrasonically cleaned. This is a method used for preparation of cultured foraminifera (J. Wit, pers. comm., 2008) as ultrasonication was previously found to destroy fragile plankton tow tests. Individual foraminifera (n = 15-35) were then picked from a specific size fraction using a clean dry paint brush under a binocular light microscope. The samples were re-cleaned using the procedure described above, and once dried, a selected number of individuals were examined under both a binocular and scanning electron microscope (SEM) for signs of dissolution, breakage and/or contaminants. For SEM imaging, selected individuals were placed onto carbon tape, gold coated and imaged using a JEOL JSM-5300LV SEM.

Cleaned samples selected for analysis were then individually weighed using a Mettler Toledo UMX2 microbalance, and mounted and photographed prior to analysis. After weighing individual foraminifera were mounted onto a thin strip of double sided cellotape, which was placed on one half of a circular wafer of a NIST610 glass standard, and then placed into the laser ablation cell as shown in Figure 2.1.

2.1.2 Basis for the adopted foraminifera cleaning technique

At present, there is no single accepted standard cleaning protocol for ICP-MS solution trace element analysis of foraminifera, with many laboratories following slightly different procedures [*Barker et al.*, 2003; *Yu et al.*, 2007; *Bian and Martin*, 2010]. Cleaning is an important step because the presence of detrital phases, surface coatings (such as clay minerals and iron and manganese oxyhydroxide coatings), barite crystals, calcareous nannofossils and organic material can significantly affect the measured elemental ratios [*Barker et al.*, 2003; *Rollion-Bard et al.*, 2007]. The steps involved in cleaning typically involve chemical reduction and oxidation steps. In solution work, as the whole test is dissolved, these rigorous cleaning regimes ensure that any contaminants on the surface or inside the test are removed. *Hathorne et al.* [2003] found that the Mg/Ca of tests that had not undergone reductive cleaning had higher Mg/Ca ratios than those that had only undergone

an oxidative cleaning step. Other efforts to examine the effect of cleaning on stable isotopes (δ^{13} C and δ^{18} O) revealed that the use of hydrogen peroxide (oxidative cleaning) and ultrasonically cleaned samples produced lower δ^{18} O values compared to control samples [*Serrano et al.*, 2008] either due to elimination of inorganic contaminants or partial dissolution of the test [*Wierzbowski*, 2007; *Serrano et al.*, 2008]. However, it is also likely that the procedure breaks up thinner parts of the test, which are too small to be analysed or become dissolved with further cleaning treatments. The removal of these parts may be the reason that the δ^{18} O appears to decrease as the smaller fragments are more likely to be the thinner ontogenetic parts of the test, whereas secondary or gametogenic calcite is thicker and therefore less likely to be broken. In this study, the ultrasonication power was low (<10 %) so as to prevent breakages of the tests. Where the presence of detrital material was obvious (i.e. after visual inspection under a light microscope), some foraminferal tests were subjected to repeat cleaning.

In this study the same cleaning procedures utilised for previous LA-ICP-MS foraminifera trace element studies were adopted [*Hathorne et al.*, 2003; *Eggins et al.*, 2004], utilising gentle ultrasonication in AR grade methanol to clean tests. This is thought to be gentle and brief enough to prevent significant breakage. There is uncertainty about whether rigorous cleaning, particularly involving reductive steps, is required when preparing foraminifera for LA-ICP-MS trace element analysis [*Haley and Klinkhammer*, 2002]. The ability of the laser to yield trace element depth profiles of the test as it ablates through the chamber wall allows identification (and exclusion) of zones of the test affected by contaminants. This is particularly apparent on the outer and inner surfaces (beginning and end of profiles) of tests. Bulk sampling requires more rigorous cleaning procedures because the whole test is digested and, therefore, any contaminants on the surface or *within* the test will give rise to inaccurate trace element/Ca ratios.

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Figure 2.1: (A) Example of individually mounted foraminifera on the NIST610 glass standard. (B) Photograph of the laser ablation sample cell and the well in the middle of it where the NIST 610 standard is placed. Figure 2.1A was taken from *Marr* [2009].

2.2 LA-ICP-MS analysis of trace elements in foraminiferal calcite

In this study, LA-ICP-MS was used to analyse trace element/Ca ratios in foraminifera as summarised below.

2.2.1 Summary of LA-ICP-MS analysis, data accuracy and standardisation, and an interlaboratory calibration for foraminiferal Mg/Ca palaeothermometry

Foraminifera were analysed at Victoria University of Wellington (VUW) (*Gs. ruber* core top Mg/Ca – temperature calibration) and the Australian National University (ANU) (*N. incompta*, and all down-core samples). An inter-laboratory comparison between the two laboratories is discussed in Section 2.3. The laser ablation unit at VUW is a New Wave deep UV laser (193 nm solid state) and at ANU is a HELEX ArF Excimer laser (193 nm). Both laboratories use the same Agilent ICP-MS allowing the near-simultaneous measurement of a range of trace elements.

The following isotopes were selected for analysis: ²⁴Mg, ²⁷Al, ⁴³Ca, ⁵⁵Mn, ⁸⁸Sr, ⁶⁶Zn and ¹³⁸Ba. Before each analysis the ICP-MS was tuned using the NIST SRM 610 standard in raster mode to optimise sensitivity and signal stability at a low mass range (²⁴Mg to ⁴³Ca). NIST SRM 610 is a synthetically prepared Si-Na-Ca-Al-glass standard reference material spiked with homogeneous amounts of ιa , 60 trace elements at the 500 µg/g level [Reed, 1992] and is commonly used as a reference material in in-situ geochemical studies [NBS, 1970; Rocholl et al., 1997]. The working values compiled by Pearce et al. [1996] for this standard [i.e. Mg/Ca = 9.38, Al/Ca = 195.9, Mn/Ca = 3.86, Zn/Ca = 3.42, Sr/Ca = 2.78, Ba/Ca = 1.51 mmol/mol] were used for this study. The use of a calcite standard has been investigated by de Nooijer et al. [2007] as a fluence of $< 2 \text{ J/cm}^2$ was found to be close to the ablation threshold for the NIST 610 glass standard. However, this method was found to increase the analytical uncertainty in the LA-ICP-MS analyses. Although a matrix matched carbonate standard is theoretically more ideal for in situ foraminiferal trace element analysis, there is currently no suitable standard available. A trial carbonate standard obtained from the University of Utrecht (GJR-carbonate standard) yielded comparable results for Mg/Ca, Al/Ca, Mn/Ca and Sr/Ca ratios (Table 2.2). A two tailed t-test at a 95% confidence interval revealed no significant difference between the analyses performed at

Victoria University of Wellington and the University of Utrecht suggesting that NIST 610 is a suitable standard for analysis of these elements in carbonate material. However, due to the limited availability of this calcite standard, it was not used throughout this study.

		Mg/Ca	Al/Ca	Mn/Ca	Sr/Ca
		(mmol/mol)	(mmol/mol)	(mmol/mol)	(mmol/mol)
		()	()	()	()
VUW	Mean	3.310	0.026	0.199	0.278
	SD	0.033	0.005	0.004	0.017
	%SD	1.0	19.9	2.0	6.0
Utrecht	Mean	3.233	0.029	0.215	0.233
	SD	0.285	0.008	0.010	0.012
	%SD	8.8	28.3	4.8	5.1

 Table 2.1: LA-ICP-MS trace element measurements of the GJR-carbonate standard at VUW compared with data from the University of Utrecht.

Following tuning, a background of 60 s was measured whilst not ablating the sample. This was followed by the measurement of the NIST SRM 610 glass for 60 s ablated using a 25 μ m spot size. Between each standard or sample analysis the ablation cell was allowed to "washout" (purged with He) for 100 s. The NIST SRM 610 standard was measured after every 10-15 analysis of foraminifera to monitor any drift in trace element fractionation produced by the laser and ICP-MS. Typical operating conditions and the range of parameters used during LA-ICP-MS analysis are shown in Tables 2.2 and 2.3. In addition to the analysed elements, ThO⁺/Th⁺ was monitored during tuning so that oxide production was < 2 % to reduce potential polyatomic interferences from oxide species [*Norman et al.*, 1996].

Step	Dwell Time (s)
Background 1 (+ 1 repeat)	120
Washout	100
Standard 1 (NIST 610) (+ 1 repeat)	60
Washout	100
Sample Analysis 1 (10-15 individual spots	
separated by 100 s washouts)	~60-120
Washout	100
Standard 2 (NIST 610)	60
Washout	100
Sample Analysis 2 (10-15 individual spots	
separated by 100 s washouts)	~60-120
Washout	100
Standard 3 (NIST 610) (+ 1 repeat)	60
Background 2 (+ 1 repeat)	120

Table 2.2: Summary of the LA-ICP-MS acquisition protocol during analysis of foraminifera.

Agilent 7500CS	
Forward power	1400-1500 W
Gas flow rate	
Carrier gas (Ar)	0.80-0.90 L/min
Ablation gas (He)	70-90%
New Wave laser ablation system	
Wavelength	193 nm
Energy (2 or 5 Hz)	5 J/cm ²
Trace element analysis of NIST610	
Repetition rate	5 Hz
Spot size	25 μm using a 2 μm/s raster for tuning, 25 μm spot for standardisation
Laser power	60%
Integration time	10 ms
Trace element analysis of foraminifera	
Repetition rate	2 or 5 Hz
Spot size	25 μm
Laser power	50-60%
Integration time	10 ms
Data acquisition	
Protocol	time resolved analysis
Scanning mode	peak hopping

Table 2.3: Typical operating conditions of the LA-ICP-MS during foraminiferal trace element analysis.

2.2.2 Data reduction and screening techniques

Raw data was first screened for outliers, after which the mean background counts were subtracted from the data. The resulting trace element/Ca ratios were then normalised using the measured ratios on the NIST SRM 610 standard relative to the known values for this standard [Craig et al., 2000; Eggins et al., 2003]. Each LA-ICP-MS trace element depth profile was then carefully examined for signs of contamination. A typical depth profile is shown in Figure 2.2A which shows a thin elevated TE/Ca surface veneer, which has also been observed in other laser ablation studies of foraminifera e.g., Sadekov et al. [2008]. This elevated TE/Ca veneer rapidly decreases as the laser ablates towards the inside of the test, where Mg/Ca is relatively homogeneous. The other trace elements Al and Mn, used to infer contamination of the test, remain variable but low ($\leq 1.0 \text{ mmol/mol}$). It is thought that this enriched veneer is of biogenic origin, as it is present in plankton tow samples where it is unlikely to have diagenetic alteration or the addition of surficial contaminant, and was not observed in the NIST 610 standard. Although this could be related to a matrix effect, the calcium carbonate standard (Section 2.2.1) also did not show an elevated TE/Ca enrichment. Furthermore laser ablation work by Hathorne et al., [2008] showed that laser ablation of silicates (e.g. NIST 612 glass) produce microsize particles by hydrodynamic sputtering, while ablation of biogenic carbonates produced them by photomechanical fracturing. The effect of those differences can be minimized using a 193 nm (*i.e.* this work) laser as it produces fewer microsize particles. The elevated TE/Ca veneer is further discussed in Chapter 3, Section 3.5.1.

Additionally, each depth profile was examined such that the enriched surface veneer and internal sediment when the laser penetrates the test wall was excluded from the mean TE/Ca, by selecting and averaging only the data from the middle portion of the test (boxed area, Figure 2.2A). Additionally, the end of each profile can be identified from visual inspection during the analysis or from the sharp reduction of raw Ca counts from the depth profile as these counts decline rapidly once the laser has ablated through each chamber.

A small number of analyses showed high Al/Ca ratios and co-varying high Mg/Ca ratios throughout the trace element depth profile. Figure 2.2B shows a *Gs. ruber* analysis (chamber F) from the core top AIMS3703. Although, like all trace element depth profiles, it has an

elevated TE/Ca surface veneer, in particular, Al/Ca and Mg/Ca have high ratios and covary throughout the test. Duplicate measurements of the same chamber were used in cases where this was observed. Following this screening step, the individual measurements were compared for co-variation of Mg with the elements Mn and Al and those that did co-vary and/or have anomalously high Al/Ca or Mn/Ca values were discarded.



Figure 2.2: (A) Typical laser ablation depth profile of *Gs. ruber* from the AIMS3703 core top. Dashed grey boxed area represents integrated counts which are used to calculate the mean TE/Ca ratios from such profiles. (B) Shows the raw counts per second for ⁴³Ca, ²⁴Mg and ⁸⁸Sr from the same sample. (C) Example of a discarded foraminiferal trace element analysis from the AIMS3703 core top. (D) Shows the raw counts per second for ⁴³Ca, ²⁴Mg and ⁸⁸Sr for the same sample.

2.3 An *inter*-laboratory comparison

Duplicate analyses on a number of individual foraminifera were used to assess the comparability of LA-ICP-MS trace element analyses between the laboratories at VUW and ANU. The same sample of 17 *Gs. ruber* and 18 *G. bulloides* individuals were analysed at each laboratory and their mean trace element ratios compared (Figures 2.3 and 2.4). Both laboratories standardise using the NIST SRM 610 glass standard. The raw data were reduced using the same data reduction process as used at VUW so that the element/Ca ratios should be directly comparable.

The results are plotted as a change in the measured values between ANU and VUW (yaxis) with the measured values from ANU (x-axis) (Figure 2.3 and 2.4, also Table 2.4). The results scatter around zero and indicate that most element/Ca ratios are comparable. For the ratios Al/Ca, Mn/Ca, Zn/Ca and Ba/Ca higher values may indicate presence of a detrital phase. Unsurprisingly, there is some variability even within individual chambers. This is because the analytical technique requires a different site on the chamber for each sample (*i.e.* the laser profile will incorporate varying amounts of the test structure depending on the plane of the test with respect to the laser spot). This is apart from any spatial heterogeneity of the trace elements within the tests. For example some studies have shown intra-test variation of Mg/Ca that cannot be explained by changes in temperature or pH [Raja et al., 2005; Hathorme et al., 2009]. It should also be noted that the values for Zn/Ca and Ba/Ca are close to the detection limit of the techniques used in both laboratories. To test whether the repeated measurements were statistically different between laboratories, independent t-tests were performed. They show no significant difference between the TE/Ca ratios measured at either laboratory (Table 2.4).



Figure 2.3: Graphs showing duplicate LA-ICP-MS trace element analyses of *Gs. ruber* (42.46 mbsf, label #75) carried out at both VUW and ANU. Data are plotted as a change in the measured values between ANU and VUW (y-axis) with the measured values from ANU (x-axis).



Figure 2.4: Data showing duplicate LA-ICP-MS trace element analyses of *G. bulloides* (42.64 mbsf, label #84) carried out at VUW and the ANU. Data are plotted as a change in the measured values between ANU and VUW (Y-axis) with the measured values from ANU (X-axis).

	Independent Samples Test ^a									
	Equality of t-test for Equality of Means									
TE/Ca Pair								95% C.I. Differ	of the ence	
ANU versus VUW	F	Sig.	t	df	Sig. (2- tailed)	Mean Difference	Std. Error Difference	Lower	Upper	
Mg/Ca -Mg/Ca	0.790	0.781	0.696	32	0.491	0.0982	0.141	-0.1891	0.3856	
Al/Ca -Al/Ca ^b	1.956	0.175	-0.643	23	0.526	-0.0928	0.144	-0.3911	0.2055	
Mn/Ca -Mn/Ca	0.931	0.342	-0.105	32	0.917	-0.0041	0.039	-0.0842	0.0759	
Zn/Ca -Zn/Ca ^b	5.767	0.023	-1.556	29	0.131	-0.0061	0.004	-0.0142	0.0019	
Sr/Ca -Sr/Ca ^c	3.954	0.057	-1.650	28	0.110	-0.0456	0.028	-0.1022	0.0110	
Ba/Ca -Ba/Ca ^b	3.407	0.075	1.237	29	0.226	0.0004	0.000	-0.0003	0.0011	

Table 2.4: Statistical summary of inter-laboratory comparison of TE/Ca ratios measured at VUW and ANU.

All samples were separated only by lab, with the null hypothesis that there was no significant difference between the TE/Ca analyses between laboratories.

^a 2-tailed significance level, p. Equal variances assumed. All samples show p>0.05, t-test signifying that there is no statistically significant difference between any of the TE/Ca meaurements performed between ANU and VUW.

^b Samples where df<32 indicate where some negative values were removed. This is due to higher background levels of the TE/Ca.

^c 4 outliers were removed.

In addition to analysing the same foraminifera at the two laboratories, a detailed trace element depth profile was measured from the same fragments of *Orbulina universa* at each of the laboratories. Trace element/Ca variations and absolute values in these fragments measured in the two laboratories are very similar and demonstrate that comparable data was produced using the two different laser ablation systems (Figure 2.5). The figure shows that both the shape of the trace element depth profiles is reproduced in both laboratories. Furthermore, the average absolute trace element/Ca values from both laboratories (Table 2.5) agree within analytical uncertainty.



Figure 2.5: Comparison of laser ablation trace element depth profiles analysed in the same fragments of *Orbulina universa* at VUW and ANU. N.B. Blue line indicates Al/Ca which was not measured at ANU.

	ORB-1							ORB-2								
	VUW			ANU			VUW			ANU						
	Mean	2 S.D.	2	S.E.	Mean	2 S.D.	2	S.E.	Mean	2 S.D.	2	S.E.	Mean	2 S.D.	2	S.E.
Mg/Ca	0.05	277	+	0.07	0.05	1.07	+	0.17	0.28	2.79	+	0.07	0.20	2.04	+	0.16
(mmol/mol)	9.05	2.00	<u> </u>	0.07	0.95	1.07	<u> </u>	0.17	9.20	2.70	<u>+</u>	0.07	9.39	2.04	<u> </u>	0.16
Al/Ca	0.36	2.22	+	0.00					0.21	0.42	+	0.01				
(mmol/mol)	0.50	5.55	<u> </u>	0.09	-	-	-	-	0.21	0.45	<u>+</u>	0.01	-	-	-	-
Mn/Ca	0.07	0.20	+	0.01	0.07	0.04	+	0.00	0.07	0.09	+	0.00	0.06	0.02	+	0.00
(mmol/mol)	0.07	0.20	-	0.01	0.07	0.04	-	0.00	0.07	0.09	-	0.00	0.00	0.02	-	0.00
Zn/Ca	0.05	0.33	+	0.01	0.04	0.03	+	0.00	0.03	0.09	+	0.00	0.04	0.01	+	0.00
(mmol/mol)	0.05	0.55	-	0.01	0.04	0.05	-	0.00	0.05	0.07	-	0.00	0.04	0.01	-	0.00
Sr/Ca	1 27	0.30	+	0.01	1 33	0.10	+	0.01	1 30	0.35	+	0.01	1 34	0.10	+	0.01
(mmol/mol)	1.27	0.50	-	0.01	1.55	0.10	-	0.01	1.50	0.55	-	0.01	1.51	0.10	-	0.01
Ba/Ca	1.07	2 52	+	0.07	1 21	0.46	+	0.04	1 18	2 47	+	0.07	1.09	0.37	+	0.03
(µmol/mol)		2.02	-				_			2	_	0107			_	0.005

Table 2.5: Summan	v of the mean	trace element r	atios for t	he same fragm	ent analysed at	VUW and ANU
				0		

2.4 Other methods for examining trace element ratios in foraminifera

In addition to LA-ICP-MS analysis, a number of individual foraminifera were selected for element mapping using a JEOL JXA-8230 Super Probe. These samples were embedded in epoxy, vacuum sealed to remove air bubbles from inside the tests and then transferred to a hot plate and left at 40°C for 12 hr to set. Each thin section was then lapped and polished to reveal a cross section of the foraminiferal test wall so that each chamber was exposed. Mg, Mn and Al X-ray intensity maps were generated using an accelerating voltage of 15 kV, a beam current of 20 nA, a pixel size of 1 µm and a dwell time of 1000 ms. All available elements were measured by energy dispersive X-ray spectroscopy, and Mg, Mn, Al and Ca were also measured with wave-length dispersive spectrometry. Ca intensities below 10,000 counts per second (cps) were at background level. Using this threshold removes background X-ray levels and helps to delineate and remove effects associated with EMP analysis [*Pena et al.*, 2008]. Element/Ca intensity maps were computed from matrix calculations, which were then calibrated to concentrations using the respective LA-ICP-MS trace element data. The intensity in the middle of a test wall was used in the element/Ca

cps maps with the concentration of what was assumed to be the same part of the wall from the LA-ICP-MS data.

2.5 δ^{18} O and δ^{13} C stable isotope analyses

The minimal destruction of foraminferal tests after LA-ICP-MS analysis leaves behind a significant amount of calcite that can be further analysed for stable oxygen and carbon isotopes to provide paired trace element and stable isotopic data on the same individuals. Samples of *Gs. ruber* (Chapter 3 and 5) and *G. bulloides* (Chapter 5) were re-cleaned (Section 3.4.2), and reacted with 2 drops of 100% H₃PO₄ at 75°C in an automated individual-carbonate reaction (Kiel) device. The device was coupled to a Finnigan MAT252 mass spectrometer at NIWA, Wellington, New Zealand [*Neil et al.*, 2004]. The external reproducibility was estimated by analysing concurrently run carbonate standards (NBS-19). External precision for $\delta^{18}O_c$ and $\delta^{13}C_c$ was 0.04‰ and 0.01‰ respectively. Internal precision for $\delta^{18}O_c$ and $\delta^{13}C_c$ was 0.03‰ and 0.01‰ respectively and are reported relative to Vienna Peedee Belemnite (vPDB).

Chapter 3

Environmental versus biological controls on Mg/Ca variability in *Globigerinoides ruber* (white) from core- top and plankton tow samples in the Southwest Pacific Ocean

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supplementary material.

3.1 Abstract

Laser ablation inductively coupled plasma mass spectrometry was used to analyse the individual chambers from tests of foraminiferal fossil and plankton tow *Globigerinoides ruber* from the Southwest Pacific Ocean, from latitudes 3 to 42°S. The variability of Mg/Ca between chambers of an individual (*intra*) and individuals of the same population (*inter*), is such that when converted to temperature, the extent of *intra*- and *inter*-individual variability appears to exceed that attributable to either calcification or seasonal temperature variability.

The pooled mean chamber Mg/Ca from each core top and plankton tow site demonstrate a significant (p<0.05) positive correlation with temperature. Chamber specific calibrations were derived where: Mg/Ca_{Ch_F-2} = 0.798 exp^{0.070 T}, Mg/Ca_{Ch_F-1} = 0.891 exp^{0.067 T} and Mg/Ca_{Ch_F} = 0.590 exp^{0.072 T}. There was no bias between Mg/Ca ratios from the two morphotypes *Gs. ruber ruber* and *Gs. ruber pyramidalis*. The chamber specific calibrations potentially offset Mg/Ca-based temperature reconstructions if used on bulk (whole) test Mg/Ca or applied to mis-identified chambers. Nevertheless, these calibrations can be used to reliably estimate past sea surface temperatures.

Although there is a general overriding temperature control on Mg/Ca, removal of the effect of temperature at each site reveals a log-normal Mg/Ca distribution. This suggests that Mg/Ca variability at each site is also affected by biological mechanism(s) that may control the distribution of *inter*-individual Mg/Ca. In addition, other trace element/Ca data (Al/Ca and Mn/Ca) from laser ablation trace element depth profiles can be used to identify detrital or diagenetic phases that may bias the trace element/Ca signal.

3.2 Introduction

The ratio of Mg/Ca in planktonic foraminiferal calcite is an important proxy for past sea surface temperatures (SST) [Dekens et al., 2002; Anand and Elderfield, 2003; Barker et al., 2005]. Although there is a strong empirical correlation between calcification temperature and the Mg/Ca ratio as bulk samples (comprising ~5-50 individual tests), planktonic foraminifera exert considerable biological control over the incorporation of Mg (and other trace elements [TE]) into their tests [Elderfield et al., 1996; Zeebe and Sanyal, 2002; Erez, 2003; Eggins et al., 2004]. Furthermore, the TE/Ca ratio measured in foraminiferal tests recovered from deep sea sediments can be complicated by post-depositional digenetic alteration [Dekens et al., 2002; Tachikawa et al., 2008]. Therefore, uncertainties remain over the relative importance of environmental versus biological versus diagenetic factors in determining what controls the Mg/Ca ratio of foraminiferal tests.

The development of microprobe and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) micro-analytical techniques now allow researchers to quantify TE/Ca ratios in individual foraminifer chambers and along profiles through test walls [*Elderfield*, 2002; *Eggins et al.*, 2003; *Hathorne et al.*, 2003; *Reichart et al.*, 2003; *Sadekov et al.*, 2005]. For example, in addition to more traditional estimates of sea surface temperature (SST) (*e.g., Anand and Elderfield*, [2003]), fine scale structural differences such as compositional differences between gametogenic versus ontogenetic calcite can be inferred (*e.g., Kozdon et al.*, [2009]). An additional benefit to using these techniques are the minimal destruction of the test, potentially enabling further paired analyses.

An open question is posed in this study, to what extent does *inter-* and *intra-*individual chamber Mg/Ca variability reflect environmental conditions relative to biological vital effects and what can this variability tell us about the limitations of Mg/Ca for palaeo-ocean temperature reconstruction more generally? To investigate this and other questions, a species of foraminifera commonly used for palaeo-SST reconstruction, *Globigerinoides ruber* [*D'Orbigny*, 1839] white variety, *Gs. ruber* (w) was examined. LA-ICP-MS was used to measure trace element depth profiles from individual chambers of *Gs. ruber* from core top and plankton tows from the South Pacific Ocean spanning a mean annual SST of 14.7 to 28.8°C. The data are presented in terms of a LA-ICP-MS derived SST versus Mg/Ca calibration for *Gs. ruber* for the Southwest Pacific Ocean. Following this, the results are considered in terms of potential environmental controls over Mg/Ca from which it is

argued that individual test and chamber measurements point strongly to biological control over Mg/Ca on an *intra-* and *inter-*individual test basis. These controls are independent of temperature, but the mean Mg/Ca of a foraminiferal population is sensitive to temperature in a manner described by solution-based studies.

3.3 Background

Gs. ruber is a symbiotic-bearing planktonic foraminifera that is abundant in tropical and Subtropical waters occupying a temperature and salinity range between 14-32°C and 22-49 psu respectively [Bé et al., 1977; Bijma et al., 1990b]. The presence of photosynthetic symbionts [Bé et al., 1977] mean it is restricted to the photic zone that is the upper mixed layer of the ocean [Dekens et al., 2002; Anand and Elderfield, 2003; Huang et al., 2008; Regenberg et al., 2009]. Consequently, SST data obtained from Gs. ruber are thought to largely reflect conditions prevailing in the depth range \sim 0-50 m, minimising complications from significant temperature changes associated with migration within the water column during the foraminiferal lifecycle. Gs. ruber has been classified into two end-member morphotypes [Steinke et al., 2005] which previous workers have suggested occupy specific ecological niches based on their significantly different Mg/Ca and oxygen isotope ($\delta^{18}O_c$) values [Kuroyanagi and Kawahata, 2004; Kawahata, 2005; Löwemark et al., 2005; Steinke et al., 2005]. However a separate study [Mohtadi et al., 2009] failed to find geochemical differences between morphotypes whilst Kawahata, [2005] explained the apparent difference as the result of productivity occurring at different times of the year for different morphotypes. Nonetheless, because of its restricted ecological niche in a climatically important part of the water column, it is one of the most widely used planktonic foraminifera for palaeo-ocean thermometry.

3.4 Materials and Methods

3.4.1. Regional Setting and Core Top and Plankton Tow Locations

The study region is situated in the Southwest Pacific Ocean, and includes 10 core top and 3 plankton tow samples spanning 3.4°S to 41.9°S latitude. The tropical sites lie within either the Coral Sea or Timor Sea. The Timor Sea moves warm, low salinity, nutrient poor water

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between the Indonesia archipelago and Australia into the Indian Ocean [Gordon et al., 1997]. The site AIMS1631 lies seaward of the north flowing Sepik River that drains largely volcanic and igneous terrain into the Coral Sea [Brunskill, 2004]. Currents from the Coral Sea bring warm nutrient-poor waters down the east coast of Australia to the cool waters of the Tasman Sea. This flow forms a counter-clockwise gyro which includes the East Australian Current (EAC), the largest ocean current off the Australian coast [Ridgway and Godfrey, 1997; Ridgway and Hill, 2009]. Mid-latitude sites are located in subtropical higher salinity waters, which flow south along the Tasman Front (TF) separated at Chatham Rise (CR).



Figure 3.1: Chart showing the annual sea surface temperatures for the Southwest Pacific Ocean [Locarnini et al., 2006] and locations of core top (black dots) and MOCNESS tow (black triangles) samples. Also shown are the East Australian Current (EAC), South Equatorial Current (SEC), Tasman Front (TF) and the Chatham Rise (CR). Major surface water masses shown are Subtropical Water (STW) and Subantarctic Water (SAW). Samples were selected to represent a latitudinal gradient with sea surface temperatures ranging from 14 to 29 °C. Isotherms are in °C. Source: Ocean Data Viewer [Schlitzer, 2002].

The Subtropical Front forms the boundary between this Subtropical water (STW) and cold, low salinity and macro-nutrient-rich Subantarctic Surface Water (SAW) from the within the Subantarctic Front of the Antarctic Circumpolar Current [*Uddstrom and Oien*, 1999; *Morris et al.*, 2001; *Neil et al.*, 2004; *McCare et al.*, 2008] (Figure 3.1).

The core top samples were selected from archives managed by the National Institute of Water & Atmospheric Research (NIWA), New Zealand and the Australian Institute of Marine Sciences (AIMS). These sites ranged in depth from 3290 mbsl to 430 mbsl and the mean and seasonal range of SSTs and Sea Surface Salinity (SSS) for each site were taken from the World Ocean Atlas 2005 (WOA05) [*Antonov et al.*, 2006; *Locarnini et al.*, 2006] (Table 3.1). In addition, foraminifera from 3 plankton tow samples were also analysed. They were collected from water depths of 10-50 m (U2322 net 7), 50-100 m (U2322 net 6) and 50-100 m (U2315) using a Multiple Opening-Closing Net and Environmental Sensing System (MOCNESS) [*Wiebe et al.*, 1985] during March and April, 2001 (voyage TAN0103, NIWA). During deployment of the MOCNESS, separate downcast measurements of temperature and salinity data were measured with a conductivity/temperature/depth (CTD) probe. The temperature and salinity data from the CTD agree well with estimates obtained from WOA05.

An important aspect of the suite of samples used in this study is that almost all of the sites are above the present day, regional foraminiferal lysocline (3600-4000 m) with the exception of ODP Site 1123, which is the deepest site at 3290 m [Berger et al., 1976; Martínez, 1994]. Other data suggest the modern planktonic foraminifera lysocline in this region is ~3250 m [Feely et al., 2004]. However, previous studies assessing ratios of benthic to planktonic foraminifera, fragmentation indices, test ultra-structure [Crundwell et al., 2008] and the preservation of associated calcareous nannofossils [Fenner and Di Stefano, 2004] suggest this site has not been adversely affected by dissolution. In addition, a study measuring Mg/Ca ratios in the benthic foraminifera Uvigerina spp. at ODP Site 1123, compared the Mg/Ca ratio of that species with the shell weights of the planktonic species Globigerina bulloides (G. bulloides) from the same record [Elderfield et al., 2010].

They found that where Mg/Ca was high in the *Uvigerina* spp. record, the corresponding shell weights of *G. bulloides* were low. They also did not find any discernible relationship between Mg/Ca and either Al/Ca or Mn/Ca that may signal a diagenetic overprint. Using these two approaches they concluded that dissolution was unlikely to influence Mg/Ca measured in their study.

Table 3.1: Core top and MOCNESS tow sample locations, seafloor depths, SST (annual and range) and calibrated ¹⁴C ages of core tops

Sample	Latitude	Longitude	Depth	Mean Annual SST ^a (0-50m)	S.D. SST ^a (0-50m)	Annual Range SST ^a (0-50m)	SSS ^b	Age
	(South)	(East)	(metres)	(°C)	(°C)	(°C)	(psu)	(k.a.) ^c
AIMS1361	3.37	144.335	1,100	28.8	0.8	27.8-29.6 (1.8)	34.5	
AIMS3703	11.153	125.023	504	28.4	1.6	26.3-30.2 (3.9)	34.3	<100 years (Gregg Brunskill, pers. comm.)
AIMS1631	11.158	145.79	1,468	26.8	1.7	24.8-29.2 (4.4)	35.0	
AIMS2078	18.212	147.597	880	26.4	1.5	24.6-28.9 (4.3)	35.0	2160 ± 50 based on nearby piston cores [<i>Dunbar et al.</i> , 2000]
FR1/97/GC12	23.577	153.793	991	24.7	1.6	22.4-27.4 (5.0)	35.4	8955 \pm 25 (NIWA, unpublished data)
P81	34.02	173.51	2,036	18.1	2.3	15.6-21.2 (5.6)	35.6	$5715\pm40^{\rm e}$
P71	33.855	174.693	1,919	18.8	1.9	16.3-21.9 (5.6)	35.6	5715 ± 40
Z7003	36.693	176.238	430	18.1	2.4	15.8-21.2 (5.4)	35.5	5932±55
U2322 net 7 ^d	41.601	178.05	50-10	18.8	-	18.0-18.6 (0.6)	35.6	Plankton tow - April 2001
U2322 net 6 ^d U2315 ^d	41.601 38.509	178.05 179.018	100-50 100-50	18.3 18.7	-	18.6 (0) 17.1-20.2 (3.1)	35.6 35.6	Plankton tow - April 2001 Plankton tow - April 2001
TAN0706 C4	29.353	180.972	2,258	20.7	2.1	18.1-24.0 (5.9)	35.7	
ODP Site 1123	41.942	188.501	3,290	14.7	1.9	12.1-17.6 (5.5)	35.1	

^a Annual sea surface temperatures (SST), seasonality, and standard deviations (SD) were derived from the World Ocean Atlas 2005 [*Locarnini et al.*, 2006] except for plankton tow samples that used CTD data to infer actual SST and SSS.

^b Annual sea surface salinities (SSS), were derived from the World Ocean Atlas 2005 [Antonov et al., 2006].

^c Ages were calculated using either radiometric dating within the same core or in cores located close by.

Errors are in radiocarbon years.

^d Plankton tow temperature data derived from CTD.

^eAssumes similar sedimentation rate to P71

3.4.2. Sample Preparation

Foraminiferal samples were dry sieved so that the size fraction 250-355 μ m remained. Previous experiments on *Gs. ruber* have shown that an increase in size corresponds to an increase in Mg/Ca ratios [*Elderfield et al.*, 2002] although not all studies are in agreement [*Ni et al.*, 2007]. In the plankton tow material there were few specimens >250 μ m in size, therefore individuals were selected from the >150 μ m size fraction. At ODP Site 1123, the morphology of most of the specimens was smaller and more compact than archetypal Subtropical specimens that have large tests and large, well developed, supplementary apertures. In these specimens, the majority had very small supplementary apertures consistent with specimens living at the cold limit of their biogeographic range (M. Crundwell, pers. comm., 2009). Following sieving, each individual foraminifer was carefully picked under a binocular microscope resulting in a random sample of 12-30 individuals from each sample set. In order to test for morphotype differences, where possible, the two major morphotypes *Gs. ruber ruber and Gs. ruber pyramidalis* were identified prior to LA-ICP-MS analysis using the descriptions from *Steinke et al.*, [2005].

Arbitrary values of 0.1 mmol/mol have been used by previous workers to reject planktic foraminiferal TE analyses with suspected high Al/Ca, Fe/Ca and Mn/Ca ratios from samples analysed in solution (*e.g., Boyle et al.,* 1983). This is based on the assumption that high Al/Ca and Mn/Ca are indicators of contaminants such as clay minerals and surface coatings that also contain Mg, consequently contributing to the Mg/Ca that would otherwise be attributed to primary foraminiferal calcite. To ensure detrital contamination was minimised [*Rollion-Bard*, 2005], three methodologies were employed to identify such specimens:

- (i) Specimens were visually inspected and those with obvious adhering sediment were either re-cleaned or discarded (*e.g.*, red/brown coloured tests were avoided);
- (ii) All data were analysed for the degree of covariance of Mg/Ca with Al/Ca and Mn/Ca. A few outliers were discarded. The remaining data did not show a statistically significant correlation ($r^2 < 0.5$).
- (iii) Terrigenous clay mineral assemblage data was examined for the Southwest Pacific Ocean and did not suggest major contamination of Mg from the sediments [*Glashy*, 1979]. For example, a foraminiferal analysis yielding an Al/Ca of 0.2 mmol/mol from a mixture of 25% kaolinite (Al₂Si₂O₅(OH)₄), 15% illite (K_{0.40} Na_{0.40} Fe_{0.24} Mg_{0.34} Al_{1.50} (Al_{0.57} Si_{3.43} O₁₀) (OH)₂) and 60% smectite (Na_{0.165}Ca_{0.165}Al_{1.2}Mg_{0.8}Si₄O₁₀ (OH)₂ nH₂O) would add 0.06 mmol/mol Mg/Ca to a foraminiferal Mg/Ca ratio of 1.35 mmol/mol.

In addition, the laser ablation technique itself yields data that can resolve the contaminants by enabling the analyst to exclude data from certain regions of the test (*e.g.*, *Creech et al.*, 2010) and therefore avoiding the contributions from those deposits - these were the main source of concern for those analysing foraminifera by solution in the work of [*Boyle*, 1981; 1983] and from other techniques with secondary high Mg-carbonate overgrowths [*Hoogakker et al.*, 2009]. The use of the above methodologies allows some confidence that detrital contamination was minimised by the elimination of individual samples. However, samples which were eliminated were done so without using an arbitrary "contaminant" cut-off level.

Following selection of clean foraminifera, each sample was transferred to a clean glass vial. Each core top sample was initially given 3 rinses in ultra-clean water (>18 M Ω), followed by 2 rinses in analytical grade methanol, where the first rinse was additionally treated by gentle ultra-sonication (at 10% power) for < 5 s. Clearly, the better preserved the specimens or the thicker the tests, the more they will stand up to the rigours of ultra-sonication. Ultra-sonication for longer than 5 s often resulted in partial or complete destruction of tests, particularly those obtained from the plankton tows. Broken tests were discarded from further analyses.

Finally, each sample was rinsed three times with ultra-clean water. Following cleaning, each sample was transferred to an oven and allowed to dry for 24 hrs at 40 °C. These preparation procedures prior to laser ablation are similar to those used in other studies [*Eggins et al.*, 2003; *Reichart et al.*, 2003; *Bergami et al.*, 2008; *Sadekov et al.*, 2008; *Hathorne et al.*, 2009]. Cleaned individual foraminifera were also weighed using a Mettler-Toledo UMX2 microbalance, mounted and photographed prior to LA-ICP-MS analysis.

Organic material was removed from the plankton tow samples using a low temperature oxygen plasma asher. The samples were cleaned using the same procedure as the core top samples but excluding the ultrasonic cleaning step. Other studies have used oxidative cleaning to remove organic material (*e.g.*, buffered hydrogen peroxide or sodium hypochlorite). However, sample loss can be minimised by avoiding the use of these chemicals [*Boyle and Keigwin*, 1985; *Barker et al.*, 2003; *Rosenthal et al.*, 2004; *Yu et al.*, 2005].

Following cleaning, a selected number of samples were also examined with a scanning electron microscope (SEM) for any signs of dissolution and/or contaminants prior to and post LA-ICP-MS. These individuals were placed onto sticky carbon tape; gold coated and imaged using a JEOL JSM-5300LV SEM.

3.4.3 Trace elemental analysis of Gs. ruber in the Southwest Pacific Ocean

Prior to laser ablation analyses, each foraminifera was carefully mounted onto a NIST610 glass standard using very weak adhesive tape and a clean paint brush. The outside to the inside (*c.f. Sadekov et al.*, 2008) of the 3 chambers in the final whorl per individual were

analysed for the isotopes ²⁴Mg, ²⁷Al, ⁵⁵Mn, ⁶⁶Zn, ⁸⁸Sr and ¹³⁸Ba relative to ⁴³Ca, using a New Wave deep UV (193 nm) solid state laser ablation system coupled to an Agilent 7500CS ICP–MS. *Gs. ruber* chamber formation can be either sinistral or dextral and coiling direction can be identified by examining the dorsal view of the test. Here chamber 'F-2' represents the antepenultimate chamber; 'F-1' is the penultimate chamber prior to the ultimate (final) chamber 'F'. Measurements were standardised using known elemental compositions of the NIST610 standard [*Pearce et al.*, 1996]. The resulting data were processed using a MATLAB script which allowed for initial screening of outliers, background correction, and Cacorrected internal standardisation.

Background and NIST610 measurements were made for 60 seconds at the start and end of each run. For the NIST610 a laser spot size of 35 μ m and repetition rate of 5 Hz was used. For foraminiferal measurements a laser spot size of 25 μ m and repetition rate of 2 or 5 Hz was used. The washout time between standards and samples was 100 seconds. For individual chambers the measurement profile took a maximum of 120 seconds to penetrate from the outer to inner chamber wall. The LA-ICP-MS depth profiles were used to distinguish between contaminant phases and only include the ontogenetic calcite for calculation of TE/Ca ratios (*e.g.*, Figure 3.2). The end of each profile was identified either visually when the laser had ablated through the test well, or from the sharp reduction of raw Ca counts from the laser ablation profile which decline rapidly once the laser has ablated through each chamber. The complete ablation of a chamber wall is sometimes observed in conjunction with elevated Al/Ca and Mn/Ca, suggesting the presence of phases containing these metals on the inside of the tests. Using the laser ablation profiles, it is possible to avoid both surface veneers and internal trapped sediment by selecting the middle portion of the test, thus, removing the influence of these contaminants.

Duplicate measurements on sub-samples of individual tests were taken to ensure reproducibility of individual chamber analyses. From these measurements the two standard deviation (2 S.D.) and the median of the 2 S.D. respectively were: 0.72 and 0.25 mmol/mol for Mg/Ca; 0.79 and 0.04 mmol/mol for Al/Ca; 0.03 and 0.01 mmol/mol for Mn/Ca; 0.03 and 0.01 for Sr/Ca; 0.09 and 0.03 mmol/mol for Zn/Ca and 4 and 0.83 μ mol/mol for Ba/Ca.


Figure 3.2: Selected LA-ICP-MS profiles of *Gs. ruber* from particular sites in the Southwest Pacific Ocean (A) Subtropical site core top P71 (low Mg/Ca), and (B) high Mg/Ca, (C) Tropical site AIMS3703 showing low Mg/Ca and (D) high Mg/Ca (E) plankton tow U2325 and (F) contaminated sample from AIMS3703. Note how high Al/Ca co-varies with Mg/Ca.

3.5 Results

3.5.1. Elemental profiles through tests of Gs. ruber

The wall structure of a typical *Gs. ruber* is illustrated by Scanning Electron Micrograph (Figure 3.3) which shows an outer calcite layer representing ~ 90 % of the total wall thickness separated by an inner laminar calcite layer representing the remaining ~ 10 % of the wall thickness by the primary organic membrane (POM). These images are consistent

with previous work showing that *Gs. ruber* does not produce a typical gametogenic calcite crust, *i.e.* thickening and change in crystal structure affecting the mass, thickness and dissolution rate of the test [*Hamilton et al.*, 2008; *Williams*, 2008]. Furthermore, thin sections of *Gs. ruber* show chamber specific outer calcite layers that generally follow the model of lamellar wall construction as described in *Reiss* [1958]. However, these distinct layers do not follow the general globular shape of the chamber but instead follow the shape of the interpore ridges (Figure 3.3).

The SEM images also show pores that are \sim 3-6 µm in diameter at the inner wall, expanding in a funnel-like form to \sim 10 µm in diameter at the outer surface. Pores are typically spaced \sim 10-20 µm apart, regardless of chamber. Consequently, as this study's ablation profiles were measured with a spot size of 25 µm, each one will typically encompass one or two pores, providing a pathway by which surface material can "appear" in the middle of the profile. It is expected that, because of these funnel shaped pores, the TE/Ca ablation profile from the outer to the inner test will reflect, in part, the ratio between the calcite and potentially any adhering contaminants.

With the exception of Sr/Ca, laser ablation profiles from the outer to inner test walls show a thin (<1-2 µm) TE/Ca-enriched (by several orders of magnitude) outer surface veneer compared to the innermost (ontogenetic) calcite. This enriched layer was present in every chamber analysed, regardless of location, (i.e. independent of temperature and depth) and was also present in plankton tow samples (Figure 3.2E) although it is not distinguishable in the SEM images. Apart from the enriched outer veneer, there appears to be relatively uniform Mg/Ca and Sr/Ca along the inner profile, that is, there is no compositional difference between the inner and outer calcite layers identified in SEM images. Individuals within a core-top or plankton tow population with high Mg/Ca values maintain such values throughout the thickness of their tests and vice versa for individuals where Mg/Ca ratios were lower. In a number of individuals there were observed changes between low and high Mg/Ca ratios in chambers F-2 and F-1 that seemed to have analogues in the SEM images (Figure 3.2). However, the relatively "smoothed" nature of the profiles (caused in part by ablation of an uneven surface, resulting in material being incorporated from various different depths in the profile for each ablation event) meant that the potential presence of sub-micron thick Mg-rich bands inside the tests is difficult to resolve. Improvements to this resolution may involve ablating the test from the smooth inside to the rougher outside [Sadekov et al., 2009], but this greatly increases preparation time and introduces difficulties with identification of specific chambers as they must be individually dismembered from the

test. These high and low Mg/Ca bands are not apparent with Sr/Ca, that is, there is no significant difference in composition between the outer calcite layers from the inner laminar layers.



In contrast, for samples that were not obviously contaminated, and where there is no strong co-variation between Mg/Ca and Al/Ca (*e.g.*, Figure 3.2E) the ratios Al/Ca and Mn/Ca are more variable, typically low, with a minima occurring about 30% of the way through the test wall and elevated (by a factor of 1 to 1.5) along the inner 50% of the profile. Note the logarithmic scale enhances that apparent variability for elements occurring in very low concentrations.

Based on this pattern of variability observed in the TE depth profiles, the mid-portion of each test was selected to determine an average Mg/Ca value for each chamber as shown in

Figure 3.2, specifically excluding enhanced values in the outer veneer and inner chamber wall which are particularly vulnerable to surface contamination and/or dissolution (*e.g., Pena et al.*, [2008]). A t-test rejects the null hypothesis (at a confidence interval of 95%) that there is a significant difference in Mg/Ca between the two morphotypes of *Gs. ruber* where the same chambers were compared. Therefore all data reported are data based on all *Gs. ruber*.

3.5.2. The distribution of Mg/Ca within a population

Having obtained Mg/Ca values for each chamber of each individual and calculated pooled chamber means (*i.e.* the pooled chamber of mean all F-2, all F-1 or all F per site) the results are compared against WOA05-derived SST for each sample location (Figure 3.4; Table 3.2).

For each site, the pooled chamber mean Mg/Ca ratio from each site is positively correlated with temperature. The chambers F-2 or F-1 show a statistically significant difference in the Mg/Ca value when compared to the ultimate chamber F, (paired t-test [2-tailed], $p \le 0.05$), with the exception of site FR1/97/GC12 where p = 0.058 (F-2 versus F) and p = 0.110 (F-1 versus F).

Having considered these differences, chamber specific equations were derived, fitted to an exponential relationship, as shown in Figure 3.4. In considering each equation it is observed that the exponential coefficient 'A' for each chamber is similar (0.067 to 0.072) and within the confidence interval of each chamber (*i.e.* standard error = \pm 0.005 to 0.007). However, the pre-exponential coefficient 'B' shows a considerable difference between the two earlier chambers F-2 and F-1 (0.798 and 0.891) with the ultimate chamber F (0.590). The standard error of the pre-exponential coefficients for chambers F-2 and F-1 (\pm 0.091 and \pm 0.133) are outside the confidence interval for chamber F (\pm 0.091). Therefore, although the gradient for the ultimate chamber F is comparable to the chamber F-2 and F-1, it is offset to lower Mg/Ca between 0.4 – 2.0 mmol/mol (Figure 3.4). This would potentially indicate that the ultimate chamber is calcifying in colder temperatures compared to chambers F-2 and F-1.

Site		F-2 Mg/Ca	F-1 Mg/Ca	F Mg/Ca
		(mmol/mol)	(mmol/mol)	(mmol/mol)
AIMS1361	Mean	5.33	5.15	4.17
n=7	Minimum	4.44	4.09	3.02
	Maximum	6.11	6.06	5.89
	S.D.	0.63	0.72	0.88
AIMS3703	Mean	5.97	6.18	5.02
n=13	Minimum	3.21	4.15	2.90
	Maximum	8.74	8.83	7.88
	S.D.	1.47	1.46	1.28
AIMS2078	Mean	5.64	5.76	3.64
n=10	Minimum	4.34	4.17	2.33
	Maximum	7.06	7.60	4.65
	S.D.	1.01	1.02	0.69
AIMS1631	Mean	4.69	4.82	4.12
n=4	Minimum	4.15	3.66	3.91
	Maximum	5.13	5.98	4.62
	S.D.	0.40	0.97	0.34
FR1/97/GC12	Mean	4.83	5.29	4.05
n=12	Minimum	3.73	2.31	2.40
	Maximum	5.86	6.81	6.78
	S.D.	0.64	1.20	1.23
TAN0706 C4	Mean	3.71	3.84	2.77
n=26	Minimum	2.39	2.20	1.66
	Maximum	6.59	7.11	4.48
	S.D.	1.20	1.22	0.81
U2322net7 (PT)	Mean	2.91	2.99	2.00
n=8	Minimum	1.78	2.21	1.30
	Maximum	4.01	3.42	2.69
	S.D.	0.67	0.39	0.55
U2322net6 (PT)	Mean	2.89	3.38	2.77
n=7	Minimum	2.16	2.34	1.80
	Maximum	3.93	4.60	4.24
	S.D.	0.58	0.83	0.79
P71	Mean	3.26	3.08	2.46
n=7	Minimum	2.11	2.19	1.53
	Maximum	4.37	4.21	3.29
	S.D.	0.75	0.54	0.40
U2315 (PT)	Mean	3.10	3.73	2.29
n=13	Minimum	2.09	2.80	0.91
	Maximum	5.91	6.08	3.25
	S.D.	0.99	0.92	0.70
Z7003	Mean	2.92	2.98	2.32
n=16	Minimum	1.98	0.84	1.37
	Maximum	5.27	4.49	4.17
	S.D.	0.76	0.94	0.86
P81	Mean	2.88	2.87	2.18
n=18	Minimum	1.41	1.40	1.12
	Maximum	4.77	4.62	4.53
	S.D.	0.91	0.84	0.94
ODP1123	Mean	1.90	2.01	1.53
n=13	Minimum	1.41	1.42	1.06
	Maximum	2.94	3.03	2.62
	S.D.	0.53	0.46	0.43

For comparison, the *Gs. ruber* Mg/Ca versus SST calibration derived by *Sadekov et al.*, [2008] for sites in the Indian Ocean is shown on Figure 3.4. This study's "F" calibration (*i.e.* Mg/Ca_{Ch-F} = 0.590 [\pm 0.091] exp (0.072 [\pm 0.007] * T) is comparable to that of *Sadekov et al.* [2008] (*i.e.* Mg/Ca = 0.520 [\pm 0.08] exp (0.076 [\pm 0.002] * T) which was derived using a

similar LA-ICP-MS technique to measure Mg/Ca on the same ultimate chamber (Table 3.3). In addition, *Anand et al.*, [2003] summarised a number of Mg/Ca versus temperature calibrations for planktonic foraminifers determined using solution-based analysis, including several specifically for *Gs. ruber* (w). Their study yielded a widely-used generic (combining data from 10 planktonic species recovered from N. Atlantic sediment traps) Mg/Ca versus temperature relationship of Mg/Ca = 0.38 [± 0.02] exp (0.09[± 0.003] * SST), identical to the *Gs. ruber* (w) (250-350 µm) core top calibration of *Dekens et al.*, [2002]. A similar relationship in *Gs. ruber* (w) (250-350 µm) from sediment traps, revealed a relationship of Mg/Ca = 0.34 [± 0.08] exp (0.102 [± 0.01] * T). Therefore, published solution-based Mg/Ca versus temperature relationships for *Gs. ruber* (w) for tests <350 µm in size have yielded a smaller pre-exponential coefficient and a larger exponential co-efficient although the significance of this, if any, remains to be explored.



Figure 3.4: Mg/Ca for each chamber plotted against mean annual SST from each sampling site. The green crosses represent chamber F-2, red circles F-1 and blue squares F. The exponential regression for each chamber and for the mean test values (*i.e.* the mean of chambers F-2, F-1 and F) are fitted against the mean Mg/Ca: mean annual temperature (WOA05, 0-50 m), where the green line represents the exponential fit for chamber F-2, the red line F-1, the blue line F and the black line the mean. Also shown are the calibrations of *Anand et al.*, [2003], grey line and *Sadekov et al.*, [2008], black dashed line. The equations for each of these calibrations are summarised in Table 3.3.

Table 3.3: Summary of this study's Mg/Ca chamber specific calibrations and selected existing calibrations for Gs. ruber (white).

		Mg/Ca	= B e xp ^{AT}							
Reference	Source	Slope (A)	y-intercept (B)	r^2	n	Errors on A and B	Instrument	Ana lys is Type	Temperature Source	SST range (°C)
This study, pooled F-2 chamber	Core top and plankton tow	0.070	0.798	0.94	4-26	A = ± 0.005 B = ± 0.091	LA-ICP-MS	in-situ, 25 μm spot size	Annual SST World Ocean Atlas 2005	12.1-29.6
This study, pooled F-1 chamber	Ocean (250 -350 μm ^ª).	0.067	0.891	0.89	4-26	$A = \pm 0.007$ $B = \pm 0.133$	LA-ICP-MS	in-situ, 25 µm spot size	Annual SST World Ocean Atlas 2005	12.1-29.6
This study, pooled F chamber		0.072	0.590	0.90	4-26	$A = \pm 0.007$ $B = \pm 0.091$	LA-ICP-MS	in-situ, 25 µm spot size	Annual SST World Ocean Atlas 2005	12.1-29.6
Anand et al., [2003]	Sediment trap. Sargasso sea, North Atlantic Ocean (250 - 350 μm).	0.102	0.340	0.91	5-15	$A = \pm 0.01$ $B = \pm 0.08$	ICP-AES	bulk solution	Calculated isotopic temperatures (d ¹⁸ O)	22-28
Anand et al., [2003]	Ten planktonic species, sediment trap (250 - 500 μm). Sargasso sea, North Atlantic Ocean.	0.090	0.380	0.93	5-15	A = ± 0.003 B = ± 0.02	ICP-AES	bulk solution	Calculated isotopic temperatures (δ^{18} O)	22-29
Dekens et al ., [2002]	Core top, Atlantic and Pacific Ocean.	0.090	0.380	0.70	40-60	A = ± 0.015 B = ± 0.05	ICP-MS	bulk solution	AnnualSST	21.2-29.5
Sadekov et al., [2008]	Core top and plankton pumped samples. Eastern Indian Ocean (>250 μm).	0.076	0.520	0.99	20-35	A = ± 0.002 B = ± 0.08	LA-ICP - MS	in-situ, 30 μm spot size	Annual SST World Ocean Atlas 2001	18.5-29.2

ICP -MS, inductively coupled plasma mass spectrometry.

DP Site 1123

^a With the exception of plankton tow samples and those from O

3.5.3. A log-normal model for the distribution of Mg/Ca measurements

There are currently a limited number of micro-analytical studies that have analysed Mg/Ca from individual chambers. *Sadekov et al.*, [2005] produced element maps that show high and low Mg/Ca bands in individual chambers from several planktonic foraminiferal species, describing individual measurements across chambers by comparing the arithmetic and harmonic mean. These authors found that the few high Mg/Ca ratios skew the data away from the more uniform low Mg/Ca. Similarly *Anand et al.*, [2005] and *Sadekov, et al.*, [2005] fitted individual chamber measurements that gave Gaussian averages smaller than the arithmetic means. This skew was also interpreted to reflect *intra*-individual Mg/Ca variation *i.e.* the presence of occasional high Mg/Ca ratios from within individual chambers. This study contributes to these studies by examining the distribution of Mg/Ca walues that exceed those expected from a Gaussian distribution, *i.e.* the distribution is positively skewed.

From these observations, it is hypothesised that the Mg/Ca distribution at any of this study's sites are log-normal; *i.e.* the distribution of log(Mg/Ca) values at any temperature is Gaussian. These log-normal distributions are found regardless of which chamber is examined. To demonstrate this, firstly, the distributions of Mg/Ca for each chamber, at different temperatures, were normalised by dividing them by their mean temperatures, (the latter being obtained by simple regression, chamber by chamber, of Mg/Ca versus temperature). This method of normalising was used so that log values normalised to 1 can be converted to zero, allowing the data for each chamber to be pooled. Further, maximum likelihood estimates of the parameters of the best fitting log-normal distribution for each of the three chambers were also obtained. Specifically, these are the mean and standard deviations of the logarithms of the pooled data. The results are illustrated in Figure 3.5 and also show that the log-normal model fits the data distinctly better than a Gaussian model.

Secondly, the temperatures were put into seven bins, where the temperatures are within a range of 0.5°C. For each bin, the normalised Mg/Ca data for the three chambers were pooled and their distribution plotted, along with the best-fitting log-normal (Figure 3.6). It is inferred that the log-normal distribution models the data better than the normal distribution at any temperature.

However, the seven standard deviations (S.D.) of the logs of pooled data in each temperature bin are dissimilar, ranging from 0.19 to 0.32 (rms 0.27). The hypothesis that the seven temperature sets have a common variance of their logs is rejected by a Levene or Bartlett test of homogeneity of variance. But their variability is apparently not due to temperature: the slope of a regression of the S.D. on temperature is not significantly different from zero (95 % C.I).



Figure 3.5: Mg/Ca data for each chamber (F-2 = crosses, F-1 = circles, F = squares), normalised by the mean value for their temperature and pooled. Also shown are the overall best fitting log-normal and Gaussian distributions, obtained by pooling the data from the three chambers. Inset in Figure 3.5 shows histogram of log-normalised Mg/Ca from pooled chambers (F-2 = black, F-1 = dark grey, F = light grey shaded bars).



Figure 3.6: Mg/Ca data binned by temperature (legend) and pooled from the three chambers. Also shown is the overall best fitting log-normal distribution (as Figure 3.5).

3.6 Discussion

3.6.1 Impacts of dissolution

All of the sites except ODP Site 1123 are located well above the regional lysocline (~3250 m) [*Feely et al.*, 2004]. Smaller test sizes and kummerform chambers were observed at ODP Site 1123, indicators of environmental stress [*Schmidt et al.*, 2006]. In addition, this site has highly variable frontal systems that have been demonstrated to result in decreased foraminiferal test size [*Hecht*, 1974]. *Gs. ruber* at this latitude are at the cold limit of their temperature tolerance [*Bé*, 1977; *Bijma et al.*, 1990b] therefore environmental stress is likely to result in decreased growth rates [*Bijma et al.*, 1990b; *Caron et al.*, 1990] and may influence Mg/Ca incorporation [*Elderfield et al.*, 1996]. However, the supporting evidence from SEM images [*Williams et al.*, 2007], the benthic to planktic ratios and fragmentation indices from *Crundwell et al.*, [2008], plus the presence of the typical enriched surface veneer found in samples from other locations suggest that at least the outer surface of Mg-rich calcite had not been subject to dissolution.

3.6.2 LA-ICP-MS trace element depth profiles

The test profiles reveal an elevated TE-surface veneer (except Sr/Ca) on all the profiles that were measured. Such TE-rich veneers were also reported in previous LA-ICP-MS studies [*Sadekov et al.*, 2008] although their origin is not clear. *Eggins et al.*, [2003] suggested these are of biogenic origin, formed during the lifetime of the foraminifera, whilst *Hathorne et al.*, [2003] proposed these are of post-depositional diagenetic origin. An open question is whether this high Mg/Ca veneer is different to that substituted into the calcite lattice. For example, TE located at grain boundaries and/or dislocations may be higher than the TE in the calcite lattice [*Weiner and Dove*, 2003]. The data support a biogenic origin, based on the presence of such a veneer on individuals recovered from plankton tow samples where there is no possibility for diagenetic alteration or the addition of surficial contaminant phases on the seafloor, as is the case for core-top samples. The exclusion of these elevated surface veneers offers one explanation for the differences between the chamber specific calibrations and those from bulk solution-derived Mg/Ca methods (see section 3.6.4).

3.6.3 An LA-ICP-MS-derived Mg/Ca versus SST calibration for Gs. ruber in the Southwest Pacific Ocean

The data support the notion that LA-ICP-MS is a robust method for determining Mg/Ca ratios in *Gs. ruber* for palaeoceanographic studies with the previously noted benefits of rapidity, test preservation (measurements are minimally destructive) and the ability to measure other elements that are useful quality checks for measuring primary foraminiferal Mg/Ca ratios.

Regardless of the wide scatter of Mg/Ca within individual populations, the mean Mg/Ca value for each population shows a positive correlation with SST. On this basis three empirical calibrations between Mg/Ca (mmol/mol) and SST (°C) were generated for the three final chambers of *Gs. ruber*. The Mg/Ca versus SST relationship for chambers F-2 and F-1 is essentially identical, however, although chamber F has a similar gradient (exponential coefficient "A"), the mean Mg/Ca in chamber F is 4 to 35 % depleted in Mg/Ca, thereby resulting in apparently higher Mg/Ca derived temperatures (pre-exponential "B") (Table 3.3). Examination of Mg/Ca from the final chamber of *Gs. ruber* in the Indian Ocean measured using a similar LA-ICP-MS technique shows very comparable A and B values, and therefore similar Mg/Ca versus SST calibrations [*Sadekov et al.*, 2008]. Interestingly, their study did not find a systematic relationship between a chamber's mean Mg/Ca value and its position within the test whorl, *i.e.* the Mg/Ca value for F was not measurably less than that derived for preceding chambers F-1 or F-2. In contrast to the *Sadekov et al.*, [2008] study, *Anand and Elderfield* [2003] used *Gs. ruber* from sediment traps to derive their calibration which lies in between the F-2/1 and F chamber specific calibrations from this study's work (Figure 3.4). This suggests in general terms that Mg/Ca from the laser ablation depth profiles are characteristic of the bulk test composition, although other variables such as cleaning techniques [*Martin and Lea*, 2002; *Barker et al.*, 2003], preservation state [*Dekens et al.*, 2002] and regional and/or site specific oceanography [*Barker et al.*, 2005] may also contribute to these differences. Constraining the relative importance of analytical versus environmental influences on foraminiferal Mg/Ca can perhaps best be resolved with paired laser ablation – solution Mg/Ca measurements.

For the purposes of determining mean Mg/Ca in a sample, it is sufficient to measure one chamber per individual. Whilst the reason(s) for the offset between chambers F-2 and F-1 with F remain unclear (and are discussed in section 4.4), it would appear either calibration is valid for palaeoceanographic purposes. However, it is important that each chamber is identified prior to analysis and that the same chamber is consistently ablated, otherwise, the single chamber calibrations will not yield meaningful palaeo-temperature estimates. Regardless, for *Gs. ruber*, calibrations are not interchangeable between LA-ICP-MS and solution methods of measuring Mg/Ca.

3.6.4 Intra-individual mean Mg/Ca variability

Intra-individual mean Mg/Ca compositional measurements show the ultimate chamber "F" is consistently depleted in Mg relative to the mean value in chambers "F-2 and F-1", the latter two chambers having no statistical compositional difference. If considering the construction of lamellar walls [*Bé and Lott*, 1964; *Bé and Hemleben*, 1970; *Hansen*, 1999], found in this species, then the lower Mg/Ca associated with the formation of chamber F should also be visible as a low Mg/Ca zone in the LA-profiles through F-2 and F-1 chambers. However, there is no evidence of such a zone, implying calcification associated with chamber F is limited to that chamber. In addition, *Gs. ruber* does not precipitate a gametogenic calcite crust of any

significance, [*Caron et al.*, 1990], if it produces one at all [*Hamilton et al.*, 2008]. Although these crusts are also considerably lower in Mg/Ca compared to ontogenetic calcite in other planktonic species [*Eggins et al.*, 2003; *Klinkhammer et al.*, 2004; *Anand and Elderfield*, 2005; *Lombard et al.*, 2010] it is unlikely that the lower Mg/Ca in chamber F is what is considered to be a 'typical' gametogenic crust.

Therefore, potential reasons for this offset include: (1) the mean Mg/Ca in the chamber F represents a systematically lower calcification temperature than for previous chambers, by an amount equivalent to \sim 2.3 to 4.4 °C, (2) lower Mg/Ca is the product of a biologically mediated "vital" effect that does not directly relate to lower calcification temperature, or (3) some combination of the two.

With respect to (1), the variability between chambers where Mg/Ca ratios between F-2 and F-1 are similar could be interpreted as both chambers calcifying at the same water temperature, and hence water depth. By contrast, the relatively lower Mg/Ca from chamber F may represent calcification in cooler, deeper water during the terminal stage of its ontogeny. The interpretation that the F chamber is formed deeper in the water column than F-1 and F-2 is consistent with known life-cycle of various spinose taxa, as discussed by *Bijma et al.* [1990a] and references therein. However, the occurrence of a relatively Mg depleted "F" in the shallow plankton tows would tend to count against this as the primary reason for the offset.

With respect to (2), internal or genetic controls that are not strongly correlated with the surrounding environment are known to produce variations in skeletal Mg content, the physical basis of which is not well understood [*Williams*, 2008; *Wang et al.*, 2009]. These "vital" effects could in turn affect the biologically induced mineralisation (bio-mineralisation) of Mg between different chambers. *Anand and Elderfield* [2005] attributed lower Mg/Ca in the ultimate chamber of *G. bulloides* from North Atlantic core tops to such a bio-mineralization effect. Similarly, culture experiments on tests of *Globigerinoides sacculifer* kept at a constant temperature and salinity in the laboratory also show a statistically significant depletion in Mg in the final gametogenic chamber clearly unrelated to environmental conditions [*Dueñas-Bobórquez et al.*, 2010].

Considering these, in (3) the symbiotic algae of Gs. ruber may, indirectly modulate the calcification process as suggested in other symbiont-bearing species where lower Mg/Ca of the

ultimate chamber may be due to loss of symbiotic activity [Eggins et al., 2003]. Furthermore, symbionts may also alter the calcification rate toward the end of this species' life cycle, in turn influencing the elemental composition of this ultimate chamber [Lohmann, 1995; Nürnberg et al., 1996]. For example in selected globigerinid planktonic foraminifer, Brummer et al., [1987] described the terminal stage of ontogeny with the disappearance (lysis and digestion) of symbionts and regulation of the calcium budget (resorption, calcification) prior to gamete release. However, in *Globigerinoides sacculifer* the precipitation of the ultimate chamber occurs prior to the expulsion or consumption of algal symbionts [Hemleben et al., 1989]. Moreover, the non-symbiont bearing species G. bulloides was recently demonstrated to have reduced Mg/Ca in the final chamber [Anand and Elderfield, 2005; Marr et al., 2011] suggesting that symbionts do not regulate the calcification process, but instead both Gs. ruber and G. bulloides share a similar biological mechanism. Thus, these studies suggest that biological internal regulation plays a more prominent role in the Mg variability of tests [Bentov and Erez, 2006] and the mechanism(s) which account for low Mg/Ca in the final chamber of G. bulloides [Anand and Elderfield, 2005; Marr et al., 2011] and Gs. sacculifer [Sadekov et al., 2008; Dueñas-Bohórquez et al., 2010] may also be applicable to Gs ruber.

3.6.5 Inter-individual Mg/Ca variability

A wide range of Mg/Ca values between individual foraminifers from each sample site was found that *prima facie* can be described by a log-normal distribution. An open question is whether or not this is the result of seasonal temperature and productivity variability at the site, or the product of biologically mediated "vital" effects unrelated to temperature. When considering morphotypes, although a significant difference in Mg/Ca was not observed it is entirely possible one species had its production peak at a different depth and month to the other which when translated to Mg/Ca would appear to record no offset. However, several lines of evidence point towards the "vital" effect explanation. First, if it is assumed that Mg/Ca is temperature related, there is a much wider range of values than expected from environmental conditions, particularly if productivity is largely confined to one season (hence narrower range of temperature). Using the chamber specific equations to convert each Mg/Ca from chambers F-2 and F to temperature (*i.e.* Figure 3.4), shows the range of values estimated for each site is much greater than can be explained by the modern seasonal range of SST

(Figure 3.7). Secondly, although some of this variability may be explained by the age of the core top samples and bioturbation effects, *i.e.* the mean and seasonal SSTs may have differed (slightly) from today, the spread of Mg/Ca in plankton tow samples follows a similarly wide variability (see Figure 3.7). In terms of bioturbation, One would expect that these samples would reflect a narrower range of Mg/Ca as the calcification temperature is more or less known for each site (assuming that each chamber calcifies within a few hours) [*Bé et al.*, 1979], however this is not the case in this study. Similar observations from individually pooled chambers from cultured foraminifera kept at constant temperatures also suggest that there is a wide variability in Mg/Ca (~2.3 mmol/mol @ 25 °C in *G. bulloides*) [*Lea*, 1999]. Thirdly, the observation that the spread between individuals can be described by a common distribution irrespective of site points to a vital effect. Thus, the data suggest that *inter*-individual variability is most likely caused by a biological vital effect, placing a limit on detailed Mg/Ca SST reconstructions, especially where only a small number of individuals are available from a sample.



Figure 3.7: Mg/Ca for individual chambers F-2 and F converted to SST using this study's chamber specific equations (see Figure 3.4). Also shown is the seasonal range of SST (WOA05) (black dashed lines) and the mean SST calculated for chambers F-2 (black line) and F (grey line). The boxed samples are plankton tows (PT).

3.7 Summary and Conclusions

In this study LA-ICP-MS was employed to examine the *intra-* and *inter*-chamber distribution of Mg/Ca within individual tests of *Gs. ruber*. The LA-ICP-MS profiles showed that this technique can be used to identify areas of secondary calcite crusts, and/or surface contamination and thus, isolate them from ontogenetic calcite by careful screening of profiles. These profiles show a lack of any surface layer on either of the chambers F-2 or F-1 that may typify gametogenetic calcite crusts (*i.e.* low Mg/Ca). Therefore it was inferred that *Gs. ruber* does not produce a gametogenic layer over previously precipitated chambers that may bias the Mg/Ca signal.

However, the ultimate chamber F of *Gs. ruber* is systematically (4- 35 %) lower in Mg/Ca compared to chambers F-1 and F-2. The variability of Mg/Ca ratios found between these chambers, could in part, be explained by the ecology of the species. On account of these systematic changes a number of chamber-specific empirical calibrations that reliably estimate SST were derived. These calibrations are comparable to extant calibrations based on LA-ICP-MS and demonstrate that chamber-specific calibrations are an alternative to bulk Mg/Ca analyses of foraminifera. These single chamber calibrations provide a time efficient method, requiring minimal cleaning, fast analysis time and leave material for use in other analyses.

The *inter*-individual variability of TE/Ca of *Gs. ruber* within populations suggest the temperatures (Mg/Ca) recorded from individual foraminifera, including plankton tow samples are often outside the seasonal ranges of the sample sites. Removal of the temperature effect from each site, by dividing by the mean temperature value of each site and normalising the data to a single value reveals a log-normal distribution. The log-normal distribution describes well the variability of Mg/Ca values but the spread parameter of this distribution, being the standard deviation of log(Mg/Ca) values, is not universal. This variation with temperature is at most weak, suggesting that it is due to some other, unknown, possible vital effect. Micro-analytical techniques in other foraminifera may shed more light on this observation.

3.8 Supplementary Material

Chapter 3 is published in the journal *Paleoceanography*. This supplementary material describes additional research related to that paper, but beyond its scope and the journal's length limitations. Material reported here includes presentation and discussion of: (1) trace element (TE)/Ca ratios (other than Mg/Ca) and δ^{18} O data for *Gs. ruber*; (2) size and weight measurements for *Gs. ruber*.

3.8.1 Trace element analysis of Ba, Zn and Sr in Gs. ruber tests

Introduction

Ba/Ca and Zn/Ca ratios are thought to be indicators of ocean nutrient and palaeoproductivity [*Lea*, 1999a; *Yu et al.*, 2005]. Ba and Si* (see *Sarmiento et al.*, 2004) are strongly correlated in the modern ocean, which has led to the suggestion that Ba in foraminifera could be used as a tracer of circulation and chemistry of past oceans [*Lea and Boyle*, 2003]. Further work from laboratory experiments on living planktonic foraminifers (*Globigerinoides sacculifer* and *Orbulina universa*) showed that Ba in tests can provide an accurate record of seawater barium, although others have suggested its application to reconstructing past ocean alkalinity may be limited because Ba export to the deep ocean is primarily through marine barite formed in decaying organic matter [*Katz et al.*, 2010]. Moreover, in benthic foraminifers, Δ Ba: Δ Alk relationships may not differ regionally [*McManus et al.*, 1999] and/or may not be constant over time due to decoupled Ba and Alk biogeochemical cycles [*Rubin et al.*, 2003].

Therefore, these 'nutrient tracers' from *Gs. ruber* were compared between different core-top sites to see if the foraminifera preserve a trace element fingerprint of the chemistry of the water masses they lived in. Similarly, zinc is a nutrient element required for phytoplankton and, especially, diatom growth [*Lynch-Stieglitz*, 2003], which results in a strong correlation between oceanic zinc and silicon concentrations.

In both inorganic and biogenically crystallized calcite there is a positive linear correlation between Sr/Ca and Mg/Ca [*Mucci and Morse*, 1983; *Carpenter and Lohmann*, 1992]. However the incorporation of Sr into foraminiferal calcitic tests appears to be species-specific [*Mortyn et al.*,

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2005] and is potentially related to different controls on bio-mineralisation [*Kisakürek et al.*, 2008]. Sr/Ca in *Gs. ruber* shows a dependence on the average growth rate, whereas temperature and salinity have an indirect effect on shell Sr/Ca through the biological control of foraminiferal growth rates [*Kisakürek et al.*, 2008]. As such, *intra* and *inter*-individual Sr/Ca measurements from *Gs. ruber* may yield more insights into the mechanisms of Sr incorporation into this species of foraminifera, and the relationships that exist between Sr/Ca and temperature, salinity and test size.

Methods

The method of analysis of trace element data reported in this Supplementary Material for *Gs. ruber* is the same as reported in Chapter 3. In addition to ²⁴Mg, ²⁷Al, ⁵⁵Mn, the elemental abundance of ⁶⁶Zn, ⁸⁸Sr and ¹³⁸Ba relative to ⁴³Ca were determined by LA-ICP-MS.

Results and discussion

Ba/Ca ratios

When the mean site values are considered, the Ba/Ca ratios from the higher latitude tropical sites (AIMS1361, AIMS3703, AIMS1631, AIMS2078 and FR1/97/GC12) range in value from 1.16 to 2.66 µmol/mol which is lower than mean seawater Ba/Ca measurements taken from the almost constant surface layer in the Pacific Ocean of 3.5 µmol/mol (*c.f. Kunioka et al.*, [2006]). At the subtropical sites (TAN706, P71, P81, Z7003) the range is more variable (1.20 to 5.69 µmol/mol). The plankton tow samples consist of the lowest levels of Ba/Ca and do not differ greatly between one another or different sites (0.92 to 1.12 µmol/mol). This may suggest lower Ba/Ca in the water column, and/or reflect conditions at the time of the plankton tow collection. ODP Site 1123 shares higher levels of Ba/Ca (5.29 µmol/mol) when compared to the tropical sites (Table 3.4). The reasons for these site differences are not clear but may relate to areas of high productivity [*von Breymann et al.*, 1992], upwelling [*Kunioka et al.*, 2006] or reflect different calcification depths. Previous work in a frontal system of the Crozet–Kerguelen Basin in the Southern Ocean has shown that hydrodynamic effects control the dissolved Ba more than biogeochemical processes [*Jacquet et al.*, 2005] and due to increased barite solubility with depth, deeper sites reflect palaeoproductivity better than shallow sites [*von Breymann et al.*, 2005]

1992]. However, the mean range of Ba/Ca for *Gs. ruber* would seem to suggest that Ba/Ca recorded in this species may have potential for recording surface Ba/Ca, although this requires local seawater measurements to confirm.

Sample	Ba/Ca	Ba/Ca	Zn/Ca	Zn/Ca
	(µmol/mol)	S.D. (µmol/mol)	(µmol/mol)	S.D. (µmol/mol)
AIMS1361	1.56	0.76	8.00	3.94
AIMS3703	2.01	1.06	24.28	23.25
AIMS1631	1.16	0.30	22.55	8.80
AIMS2078	1.89	0.68	45.97	151.01
FR1/97/GC12	2.66	1.67	8.39	26.23
TAN0706 C4	1.20	1.38	30.29	17.65
P71	2.96	3.20	30.78	16.90
P81	5.69	3.11	94.39	74.09
Z7003	1.32	0.70	11.46	14.20
U2322 NET7	1.01	0.42	188.54	185.72
U2322 NET6	0.92	0.23	105.69	113.42
U2315	1.12	0.42	145.77	133.11
ODP1123	5.29	2.56	47.33	26.81

Table 3.4: Mean Ba/Ca and Zn/Ca and standard deviation (S.D.) of for each site (sites in bold are plankton tows).

Zn/Ca ratios

Mean Zn/Ca ratios from all the core top sites are low (32 μ mol/mol) compared to the plankton tows that exhibit considerably higher values (106-189 μ mol/mol) (Table 3.4). This

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might reflect a number of factors including Zn contamination during MOCNESS sampling, high zinc in the surface waters where the MOCNESS samples were taken, or difficulty in removing Zn-rich organic material from the captured living foraminifera. Zn/Ca data for *G. bulloides* from a core-top site near the MOCNESS plankton tow sites also have elevated Zn/Ca ratios (J. Marr, pers. comm., 2009) and potentially indicates that the elevated zinc may be a feature of the surface ocean at this site. Moreover, dissolved Zn in sub-surface waters close to Site U2322, off the east coast of New Zealand, are also elevated in Zn and Fe, with sub-surface Zn concentrations at of *ca.* 1 nmol/L, compared to surface concentrations of 70 to 300 pmol/L (M. Ellwood, unpubl. data). Given these observations and that this region is subject to upwelling [*Chiswell*, 2003], a nutrient-related origin for the high Zn/Ca in *Gs. ruber* from the plankton tow sites is tentatively favoured.

Sr/Ca ratios

Mean Sr/Ca ratios are higher in *Gs. ruber* from the plankton tow samples compared to the core top samples with average Sr/Ca ratios between all sites varying from 1.24 to 1.56 mmol/mol. Unlike Mg/Ca ratios which vary from chamber-to-chamber in *Gs. ruber* individuals, Sr/Ca ratios vary very little (Table 3.5). This implies that Sr/Ca is not affected by the same mechanisms that influence Mg/Ca chamber variability. This is also apparent in the repeat measurements where the 2 S.D. was extremely low (\pm 0.04 mmol/mol). However paired t-tests reveal a statistically significant difference between Sr/Ca between some chambers at 6 sites (Table 3.6).

It has been previously demonstrated that Sr-rich parts of the test *G. tumida* are preferentially dissolved with increasing water depth [*Brown and Elderfield*, 1996]. There appears to be no difference in mean Sr/Ca and depth (Table 3.5). The laser ablation profiles in this study have relatively homogeneous Sr throughout the test suggesting that high and low Sr banding (as found with Mg in *G. tumida* and other species) [*Sadekov et al.*, 2005; *Bentov et al.*, 2009] and Sr in *Globigerinoides sacculifer* [*Brown and Elderfield*, 1996] are not present in *Gs. ruber*. More detailed analytical studies using NanoSIMS in other planktonic species have shown stronger correlations of Mg and Sr that correspond to high organic layers within the test [*Kunioka et al.*, 2006].

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Other studies [*Lea et al.*, 1999] have linked Sr uptake with calcification rate, which was associated with higher temperature, salinity and pH. It is unclear to what degree these associations are linked to the carbonate ion concentration $[CO_3^{2^-}]$, a driver of calcification rate and growth mechanisms [*Lorens*, 1981; *Paquette and Reeder*, 1990]. Moreover, there is no relationship between Sr/Ca and temperature suggesting that a large temperature dependence on Sr partitioning [*Stoll et al.*, 1999] is not apparent in *Gs. ruber* from this study. These results are also consistent with those of *Kisakürek et al.* [2008] and *Cleroux et al.* [2008] who found no clear temperature dependence on measured Sr/Ca in cultured and fossil *Gs. ruber*.

		Chamber							
Site		F-2 Sr/Ca	F-1 Sr/Ca	F Sr/Ca					
		(mmol/mol)	(mmol/mol)	(mmol/mol)					
AIMS 1361	Mean	1.45	1.42	1.40					
n=7	Minimum	1.37	1.36	1.28					
Depth = 1100 m	Maximum	1.58	1.49	1.48					
	S .D.	0.07	0.05	0.06					
AIMS 3703	Mean	1.49	1.48	1.54					
n=13	Minimum	1.41	1.40	1.41					
Depth = 504 m	Maximum	1.58	1.55	1.72					
beptil sorili	S.D.	0.05	0.04	0.10					
AIMS 2078	Mean	1.53	1.55	1.51					
n=10	Minimum	1.42	1.38	1.33					
Depth = 880 m	Maximum	1.64	1.69	1.67					
	S.D.	0.08	0.12	0.12					
AIMS 1631	Mean	1.45	1.51	1.39					
n=4	Minimum	1.39	1.42	1.30					
Depth = 1468 m	Maximum	1.49	1.64	1.46					
	S .D.	0.04	0.10	0.06					
FR1/97/GC12	Mean	1.45	1.51	1.53					
n=12	Minimum	1 36	1 36	1.37					
Depth = $991m$	Maximum	1.50	1.30	1.57					
beptil = 55 mil	S D	0.07	0.11	0.09					
TAN0706 C4	Mean	1.38	1.36	1.39					
n=26	Minimum	1.24	1.26	1 30					
Depth = 2258 m	Maximum	1.52	1.49	1.54					
Deptil - 2200 III	S.D.	0.07	0.06	0.06					
U2322net7 (PT)	Mean	1.55	1.53	1.54					
n=8	Minimum	1.44	1.39	1.43					
Denth – 50 m	Maximum	1.57	1.55	1.63					
Deptil = 50 m	C D	0.07	0.00	0.10					
112222not6 (DT)	S.D. Moan	0.07	1.50	1.52					
0232211et0 (F1)	Minimum	1.49	1.30	1.55					
n=7	Maximum	1.45	1.44	1.43					
Depth = 100 m		1.57	1.50	1.03					
D 7 1	J.D. Moan	0.04	1.47	1.48					
r / I n - 7	Minimum	1.40	1.47	1.40					
n – 7 Denth – 1919 m	Maximum	1.30	1.54	1.33					
Deptil = 1919 III	S D	0.11	0.11	0.14					
U2315 (PT)	Mean	1.53	1.57	1 38					
n=13	Minimum	1.55	1.57	1.30					
Depth = 100 m	Maximum	1.60	1.45	1.54					
beptil 100 m	S D	0.04	0.11	0.06					
77003	Mean	1.42	1.40	1.46					
n=16	Minimum	1.31	1.18	1.32					
Depth = 430 m	Maximum	1.54	1.56	1.59					
	S.D.	0.06	0.08	0.08					
P81	Mean	1.24	1.24	1.26					
n=18	Minimum	0.98	1.02	1.01					
Depth = 2036 m	Maximum	1.42	1.47	1.49					
	S.D.	0.15	0.15	0.16					
ODP1123	Mean	1.42	1.45	1.47					
n=13	Minimum	1.35	1.33	1.35					
Depth = 3290 m	Maximum	1.53	1.76	1.53					
	S.D.	0,06	0,11	0.05					

Table 3.6: Significant differences in Sr/Ca between individual chambers analysed in Gs. ruber at different sites

				Paired Samples	Fest ^a				
				Paired Differen	ces		t	df	t-test (p)
					95% C.I. of the	e Difference	_		Sig. (2-tailed)
Site	Chamber Pair (Sr/Ca)	Mean	Std. Deviation	Std. Error Mean	Lower	Upper	-		
AIMS1361	F-2 - F	0.052	0.041	0.015	0.014	0.090	3.387	6	0.015
AIMS1631	F-1-F	0.113	0.079	0.035	0.016	0.211	3.229	4	0.032
AIMS3703	F-2 - F	-0.055	0.084	0.023	-0.106	-0.005	-2.373	12	0.035
FR1/97/GC12	F-2 - F-1	-0.067	0.103	0.030	-0.132	-0.001	-2.232	11	0.047
FR1/97/GC12	F-2 - F	-0.086	0.106	0.031	-0.153	-0.018	-2.792	11	0.018
ODP Site 1123	F-2 - F	-0.049	0.068	0.019	-0.090	-0.008	-2.603	12	0.023
Z7003	F-2 - F	-0.041	0.073	0.018	-0.079	-0.002	-2.243	15	0.040

^a 2-tailed significance level, p. Only values that are statistically (p<0.05) are shown. This means that there is a significant difference (at the 95% level) between Sr/Ca and the specified chambers.

3.8.2 Oxygen Isotopes

Introduction

An alternative method to calibrate the Mg/Ca - ocean temperature relationship is the use of calcification temperatures calculated from the δ^{18} O composition of planktonic foraminifera, which allows for the varying depth habitat of each species to be incorporated into the temperature calibration [*Elderfield and Ganssen*, 2000; *Anand and Elderfield*, 2003; *McConnell and Thunell*, 2005].

Methods

Paired oxygen isotope ratios from test calcite ($\delta^{18}O_c$) were measured on material selected where Mg/Ca ratios varied *i.e.* individual *Gs. ruber* were pooled together according to whether Mg/Ca was high, low or average. Prior to analysis for $\delta^{18}O_c$ samples were cleaned (Section 4.2.), and reacted with 2 drops of 100% H₃PO₄ at 75°C in an automated individual-carbonate reaction (Kiel) device. The device was coupled to a Finnigan-MAT 252 mass spectrometer at the National Institute of Water and Atmospheric Research, Wellington, New Zealand [*Neil et al.*, 2004]. The internal and external precision of the $\delta^{18}O_c$ measurements is ±0.03‰ and ±0.04‰, respectively, as determined by analysis of carbonate standards (NBS-19). The $\delta^{18}O_c$ values are

reported relative to Vienna Peedee Belemnite (vPDB) where $\delta^{18}O_c$ has a value of -2.20‰ for NBS19 calcite.

To derive a temperature, the δ^{18} O - temperature equation of *Bemis et al.* [1998] for *Gs. ruber* was applied:

T (°C) = 14.9 – 4.80 × (
$$\delta_{c} - \delta_{w}$$
) [Eq. 3.1]

The $\delta^{18}O_c$ is the measured $\delta^{18}O$ of *Gs. ruber*, and $\delta^{18}O_{sw}$ the oxygen isotope composition of ambient seawater. The Global Seawater Oxygen-18 Database (http://data.giss.nasa.gov/O18data) lacks $\delta^{18}O_{sw}$ data from the Southwest Pacific Ocean. Hence, $\delta^{18}O_{sw}$ was calculated using the relationship between $\delta^{18}O_{sw}$ and salinity (SSS) determined by *Savin et al.* [1985] where:

$$\delta^{18}O_{sw} = [0.687 \times \text{site salinity}] - 23.74$$
 [Eq. 3.2]

Results and discussion

Mg/Ca and stable oxygen isotope data for *Gs. ruber* tests ($\delta^{18}O_{o}$) are reported in Table 3.7, which includes a comparison with actual measurement of $\delta^{18}O_{sw}$ from north of Chatham Rise, (0.57‰, H. Neil, unpubl. data) and from the global seawater oxygen-18 database [*Schmidt et al.*, 1999] and the estimate of $\delta^{18}O_{sw}$ using the equation from *Savin et al.* [1985]. This independent $\delta^{18}O_{sw}$ derivation and the measured $\delta^{18}O_{c}$ can be substituted into the equation of *Epstein, et al.* [1953] so that the Mg/Ca derived ocean temperatures could be compared to those from the $\delta^{18}O_{c}$:

$$T = 16.5 - 4.3 \left(\delta^{18}O_{c} - [\delta^{18}O_{sw} - 0.27] \right) + 0.14 \left(\delta^{18}O_{c} - [\delta^{18}O_{sw} - 0.27] \right)^{2}$$
[Eq. 3.3]

The relative isotopic abundance of ¹⁸O in $\delta^{18}O_c$ increases with decreasing temperature [*Urey*, 1947; *Kim and O'Neil*, 1997]. Shallower dwelling species such as *Gs. ruber* (w) generally have a more negative $\delta^{18}O_c$ ratio compared to deeper dwelling species living and calcifying at colder temperatures. This is evident in the warmest subtropical sites where $\delta^{18}O_c$ is more negative (-2.49 to -2.86 ‰), compared to the colder sites that become increasingly more positive (0.53 to 0.76 ‰ at ODP Site 1123) (Table 3.7). The conversion of $\delta^{18}O_c$ to calcification temperatures is comparable to those estimated from Mg/Ca although there are some large differences at some sites (AIMS3703, Z7003 and ODP Site 1123). In addition, the variability of Mg/Ca at a given site is not comparable to that of $\delta^{18}O_c$, which instead show comparable measurements (with the exception of P71). These differences suggest that Mg/Ca variations between individuals are controlled by other processes such as seasonal changes in salinity and/or carbonate ion concentration (*e.g.*, *Wit et al.*, 2010) when compared to those that govern $\delta^{18}O_c$.

Table 3	3. 7:	Gs.	ruber	$\delta^{18}O_c$	with	calculated	and	measured	$\delta^{18}O_{sw}$	compared	to	annual	SST	(WOA05)	and	Mg/Ca	derived	SSTs
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Sample		Latitude	SST ^a	δ ¹⁸ Ο _c	δ ¹⁸ Ο _{sw}	δ ¹⁸ Ο _{sw} b	SST _(Mg/Ca) ^c	SST _(180c) d	Pooled Mg/Ca	Salinity
	n	(°S)	(°C)	(‰)	(‰)	(‰)	(°C)	(°C)	(mmol/mol)	(‰)
AIMS1361/1/R	3	3.37	28.8	-2.49	-0.69 (Ashi et al ., 1994)	-0.31	30.3	26.5	6.35	34.5
AIMS1361/2/R	2	3.37	28.8	-2.55	-0.69 (Ashi et al ., 1994)	-0.31	26.8	26.8	4.97	34.5
AIMS1361/3/R	3	3.37	28.8	-2.73	-0.69 (Ashi et al ., 1994)	-0.31	25.4	27.7	4.51	34.5
AIMS3703/22/R	2	11.153	28.4	-2.83	0.07 (Craig and Gordon , 1973)	-0.38	30.7	27.9	6.52	34.4
AIMS3703/23/R	3	11.153	28.4	-2.85	0.07 (Craig and Gordon , 1973)	-0.38	22.0	28.0	3.55	34.4
AIMS3703/24/R	3	11.153	28.4	-2.71	0.07 (Craig and Gordon , 1973)	-0.38	20.2	27.3	3.12	34.4
AIMS3703/25/R	3	11.153	28.4	-2.86	0.07 (Craig and Gordon , 1973)	-0.38	15.6	28.0	2.27	34.4
TAN0706/15/R	2	29.355	20.7	-0.77		0.52	25.8	22.3	4.64	35.7
TAN0706/16/R	3	29.355	20.7	-1.32		0.52	23.5	24.9	3.94	35.7
TAN0706/17/R	3	29.355	20.7	-0.95		0.52	18.5	23.1	2.78	35.7
P71/4/R	2	33.855	18.8	-1.83	0.54 (H. Neil, pers. comm)	0.45	29.1	27.0	5.84	35.6
P71/5a/R	3	33.855	18.8	-0.71	0.54 (H. Neil, pers. comm)	0.45	21.0	21.7	3.31	35.6
P71/7/R	2	33.855	18.8	1.11	0.54 (H. Neil, pers. comm)	0.45	17.0	13.7	2.50	35.6
Z7003/18/R	2	36.69	18.1	-0.32	0.54 (H. Neil, pers. comm)	0.38	29.7	19.6	6.11	35.5
Z7003/19/R	2	36.69	18.1	-0.24	0.54 (H. Neil, pers. comm)	0.38	21.7	19.2	3.48	35.5
Z7003/20/R	3	36.69	18.1	-0.56	0.54 (H. Neil, pers. comm)	0.38	21.7	20.7	3.47	35.5
Z7003/21/R	2	36.69	18.1	-0.19	0.54 (H. Neil, pers. comm)	0.38	17.8	19.0	2.65	35.5
U2315/11/R	4	38.509	18.7	-0.95	0.54 (H. Neil, pers. comm)	0.45	25.2	22.8	4.43	35.6
U2315/12/R	4	38.509	18.7	-1.02	0.54 (H. Neil, pers. comm)	0.45	19.9	23.1	3.07	35.6
U2315/13/R	3	38.509	18.7	-0.90	0.54 (H. Neil, pers. comm)	0.45	17.8	22.5	2.64	35.6
ODP1123/8/R	6	41.786	14.7	0.59	0.54 (H. Neil, pers. comm)	0.86	15.6	17.7	2.26	36.2
ODP1123/9/R	5	41.786	14.7	0.53	0.54 (H. Neil, pers. comm)	0.86	11.7	17.9	1.72	36.2
ODP1123/10/R	6	41.786	14.7	0.76	0.54 (H. Neil, pers. comm)	0.86	9.9	16.9	1.52	36.2

 $a^{18}O_w$ derived using the equation from Savin et al., (1975) where $\delta^{18}O_w = 0.687 * salinity (%) - 23.74 and converting to PDB by subtracting 0.27 %$

^b Annual SST from the World Ocean Atlas (2005), Locarnini et al., (2006).

^c SST derived using this studies derivation where SST = ln (Mg/Ca / 0.761) / 0.07 ^d SST derived using the equation from Epstein et al., (1953) where T = 16.5 - 4.3(δ^{18} O_c - δ^{18} O_w) + 0.14 (δ^{18} O_c - δ^{18} O_w)²

3.8.3 Weight and size determinations

Introduction

There is a current debate as to the factors that control foraminiferal test weight, such as marine carbonate ion concentration $[CO_3^2]$ [Lohmann, 1995; Barker and Elderfield, 2002; Moy et al., 2009] or optimal growth conditions [de Villiers, 2004]. To examine these relationships more carefully Beer et al. [2010] studied Gs. ruber and G. bulloides from plankton net samples and found statistically significant inverse correlations with $[CO_3^2]$, temperature and salinity but were unable to conclusively decide what parameter primarily controls test weight. Culture studies offer the best way to examine these relationships, and have shown that size-normalised weights (SNW) and growth rates increase with increasing $[CO_3^2]$ [Bijma et al., 1992; Kisakürek et al., 2008].

However post-depositional effects can also change foraminferal test weights upon burial, and transect studies have shown a decrease in Mg/Ca with increasing water depth, particularly at deep sites (>3500 m) below the lysocline [*Dekens et al.*, 2002] implying that bottom water $[CO_3^{2^2}]$ has more influence over test weights than surface water $[CO_3^{2^2}]$. This is supported by microprobe element maps linking this lower Mg/Ca to the selective removal of high Mg bands within tests [*Febrenbacher et al.*, 2006]. Therefore test weights may also be useful indicators of dissolution. *Gs. ruber* Mg/Ca ratios were compared with test weight, depth and surface $[CO_3^{2^2}]$ from each site. Surface $[CO_3^{2^2}]$ was chosen as bottom water $[CO_3^{2^2}]$ data is limited for this region.

Methods

High precision size and weight measurement data were determined for all the *Gs. ruber* specimens. First, the mean weights of all tests from each sample were normalised by the mean size to minimise any size effect (equation 3.4). The normalised mean weight was then compared to temperature (calculated from Mg/Ca in chamber F-2 [Mg/Ca_{ChF-2}]), $[CO_3^{2-}]$ from the surface waters obtained from GEOSECS [*Key et al.*, 2004] and salinity from the World Ocean Atlas [*Antonov et al.*, 2006].

Normalised weight (per site) = {mean weight (μg) / mean width (μm)} x 100 [Eq. 3.4]

Results and discussion

The majority of *Gs. ruber* weights in this study are similar to those found in the South Pacific [*de Villiers*, 2005] although the distribution at each site is highly variable. There is no obvious relationship between normalised weight and surface $[CO_3^{2-}]$ contrary to results from plankton tow *Gs. ruber* samples from a limited surface $[CO_3^{2-}]$ range (260-300 µmol/kg) [*Beer et al.*, 2010] (Figure 3.8). There is a weak relationship between Mg/Ca_{ChF-2} as a proxy for temperature and normalised weight and no relationship with salinity.



Figure 3.8: Relationship between SNW and (A) surface water $[CO_3^{2-}]$, (B) temperature (Mg/Ca_{ChF-2}) and (C) salinity. The legend represents mean core top values (black diamonds), plankton tows (PT), green circles and the site where *Gs. ruber* is at its environmental tolerance limit for temperature (ODP Site 1123).

3.8.4 Summary and Conclusions

- Given the above results, there is some further work required to examine relationships between other TE/Ca in foraminifera with other sedimentary and water column measurements.
- The δ¹⁸O measured in Gs. ruber suggests it is not sensitive to biological or 'vital effects' compared to Mg/Ca
- Weight and size measurements appear to be correlated with temperature and not [CO₃²].

Chapter 4

Evaluating complexities in the application of the Mg/Ca palaeo-ocean thermometer to the planktonic foraminifer *Neogloboquadrina incompta* from the Southwest Pacific Ocean

4.1 Abstract

Mg/Ca and Sr/Ca ratios are presented for the planktonic foraminifera *Neogloboquadrina incompta* (*N. incompta*) from core-top, dredge and plankton tow material from the Southwest Pacific Ocean. The ultra-structure (reticulate or crystalline) of each foraminifera test was determined using a scanning electron microscope, after trace element analysis by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) to examine the variability in Mg/Ca and Sr/Ca between these two different ultra-structures.

For Sr/Ca there was no difference the two ultra-structures studied, nor within individual chambers. *N. incompta* demonstrate far greater Mg/Ca heterogeneity both in individual chambers and between chambers. Comparison of the mean Mg/Ca ratios of both reticulate and crystalline *N. incompta* to mean ocean temperatures did not reveal a significant relationship. This lack of correlation between Mg/Ca ratios of *N. incompta* with ocean temperature may suggest that this species does not dwell at the same depths at each core top site and instead may reflect migration within the water column that is not uni-directional, or some other unidentified controls on Mg incorporation into *N. incompta* that require further study.

The LA-ICP-MS trace element data reveal differences in Mg/Ca between outer calcite crusts in crystalline forms that have an outer layer with very low Mg/Ca compared to the inner ontogenetic calcite. In reticulate or non-crystalline forms, this layer is either absent, or is only a thin layer with low Mg/Ca ratios. These individuals may represent intermediates of crystalline forms, but this is not obvious with SEM imaging. The majority of reticulate tests without an outer layer with low Mg/Ca have high and low Mg/Ca bands in the inner ontogenetic calcite layer(s), which are interpreted as reflecting organic layers of ontogenetic calcite. The ablated gametogenic calcite in crystalline forms of *N. incompta* have similar Mg/Ca ratios regardless of the location from which the foraminifera were taken, indicating a possible temperature or vital effect that controls incorporation of Mg. The data also suggest that the ontogenetic calcite in crystalline tests is precipitated in warmer or shallower parts of the water column compared to the low Mg/Ca outer calcite layer. Neither reticulate nor crystalline forms of *N. incompta* from sediments of the Southwest Pacific Ocean appear to be reliable palaeo-ocean thermometers.

4.2 Introduction

This chapter presents results of a study designed to investigate the utility of the planktonic foraminifera *Neogloboquadrina incompta (N. incompta)* for Mg/Ca palaeo-ocean thermometry in the temperate Southern Ocean. Both temperature and non-temperature related controls on the uptake of Mg/Ca are considered. This species is of particular interest because it is one of the few that occurs in abundance throughout glacial-interglacial cycles in New Zealand waters [*Kennett and Vella*, 1975; *Crundwell et al.*, 2008]. More generally, members of the genus *Neogloboquadrina* tolerate low temperatures in sub-polar and polar regions highlighting their palaeo-oceanographic importance, given most Mg/Ca – ocean temperature calibrations for planktonic foraminifera are for water temperatures >15°C [*Pak et al.*, 2004; *Barker et al.*, 2005].

Several solution-derived Mg/Ca - ocean temperature calibrations exist for the genus Neogloboquadrina i.e., Neogloboquadrina pachyderma (N. pachyderma) [Nürnberg, 1995] Neogloboquadrina dutertrei (N. dutertrei) and N. incompta [Von Langen et al., 2005]. Other researchers have also utilised these species in generic Mg/Ca - ocean temperature calibrations for planktonic foraminifers (e.g., Barker et al., 2005; Table 4.1), suggesting Neogloboquadrind Mg/Ca variability with respect to calcification temperature is similar to that found in other planktonic foraminifera. Moreover, most of these calibrations are based on cultured foraminifera and none have been developed from the Pacific Ocean.

However, further studies have highlighted the relatively poor correlation between Mg/Ca ratios and ocean temperatures for this genus for the Southern Ocean, which may partly reflect large Mg/Ca heterogeneities within the test of this genus [*Nürnberg*, 1995; *Bergami et al.*, 2008].

Reference	Sample Type	Location	$Mg/Ca = B \exp (A \times T)$		
			Α	В	
Nürnberg [1995]	N. pachyderma, core-top	Norwegian Sea	0.099	0.549	
Nürnberg [1995]	N. pachyderma, core-top	South Atlantic	0.083	0.406	
Von Langen et al. [2005]	cultured N. incompta	Southern California Bight	0.101	0.510	

Table 4.1: N. incompta and N. pachyderma Mg/Ca - temperature calibrations adapted from Von Langen et al. [2005].

For example, at high southern latitudes growth of the juvenile phase of *N. pachyderma* may occur in sea ice brine channels which have higher Mg concentrations and temperatures than ambient seawater [*Spindler*, 1996; *Hendry et al.*, 2009]. While this cannot be a reason for lack of correlation between ocean temperature and Mg/Ca at lower latitudes it highlights potential additional complexity in terms of test growth beyond that identified with shallow dwelling tropical species such as *Globigerinoides ruber e.g.*, *Sadekov et al.*, [2008]. Unlike *Gs. ruber*, the life cycle of *N. incompta* is thought to be characterised by migration through a depth range up to 100 m during its life [*Schiebel et al.*, 2001]. *Bé* [1977] places undifferentiated *N. pachyderma* (*i.e.* both *N. incompta* and *pachyderma*) in his "polar water" grouping. A particular point of difference between *Gs. ruber* and *N. incompta* is the precipitation of gametogenic calcite (absent in *Gs. ruber*), as part of the reproductive cycle of *N. incompta* as discussed further below.

Neogloboquadrina incompta [Cifelli, 1961] is non-spinose, asymbiotic planktonic foraminifera. This classification was proposed to formally recognise a form previously regarded as the dextral coiling variant of *N. pachyderma*. *N. pachyderma* is one of the few species of planktonic foraminifera that thrive in cold waters (<8°C), therefore it is widely used in palaeo-oceanographic reconstructions involving foraminiferal assemblages [Reynolds and Thunell, 1986]. Earlier workers described *N. pachyderma* as *Globorotalia (Turbototalia) pachyderma* [Ehrenberg, 1861; Ehrenberg, 1873]. Later it was re-classified by *Cifelli* [1961] to *Globigerina incompta* and the synonym *Neogloboquadrina pachyderma* based upon scanning electron microscope (SEM) studies of surface features. Subsequent authors considered *N. incompta* to be a coiling variant of *N. pachyderma*, due to their morphological similarities but opposite coiling directions. Hence, they

were referred to as *N. pachyderma* (dextral) and (sinistral) [*Bandy*, 1972]. The relative abundance of these variants were considered at first to reflect different properties of the mixed layer (temperature), where the left coiling (sinistral) form was more abundant in colder waters or during glacial periods in down-core records and the right coiling variant (dextral) was more abundant in warmer waters or during interglacial periods [*Kennett*, 1968; *Dieckmann et al.*, 1991]. Sub-unit ribosomal RNA genotyping evidence has since confirmed that the different coiling types are, in fact, genetically distinct [*Darling et al.*, 2006]. Based on this evidence, the dextrally-coiled populations of *N. pachyderma* are now classified as *N. incompta* with the sinistral form remaining as *N. pachyderma*.

Part of the reproductive process of some species of planktonic foraminifera, including *N. incompta*, involves the production of a gametogenic calcite layer that is precipitated over all previous chambers at the time of reproduction and subsequent death. In *Globigerinoides sacculifer* this layer represented an average of 28% by weight [*Bé*, 1980] and in *Orbulina universa* ranged from 4-20% of the final shell mass in cultured tests [*Hamilton et al.*, 2008] although comparable data have not been published for *N. incompta*. The formation of these 'crusts', often referred to as 'encrusted' tests or gametogenic calcite, may be related to changes in temperature, illumination, depth, water chemistry or some combination thereof [*Bé and Ericson*, 1963; *Orr*, 1967; *Srinivasan and Kennett*, 1974; *Bé et al.*, 1977; *Bé*, 1980]. For example, some species of foraminifera, prior to gametogenesis, descend deeper in the water column where they precipitate a gametogenic calcite crust [*Duplessy et al.*, 1981], hence the suggestion that the production of this crust may be stimulated by changes in temperature and/or depth. The amount of light in the photic zone also decreases with increasing depth, although this will primarily affect calcification of symbiont-bearing foraminifera, as opposed to those that are symbiont barren [*Bé et al.*, 1983; *Lohmann*, 1995] such as this species.

The addition of gametogenic calcite precipitated under temperature conditions different to those found at the ocean surface, and also under different biophysiological conditions (*e.g.*, *Barker et al.*, 2005; *Nürnberg et al.*, 1996) is likely to result in a complex relationship between bulk Mg/Ca and SST. For example, stable oxygen isotope compositions (δ^{18} O₂) of the different ultra-structures of *N. pachyderma*, that is the arrangement of growth layers of the test wall, as observed by SEM, show that large euhedral crystals dominate gametogenic crusts, and an enrichment in δ^{18} O_c in tests that were classified as 'encrusted' as opposed to non-encrusted is observed [Kohfield et al., 1996; Sautter, 1998]. Further evidence from Kozdon et al., [2009] and Rohling and Cooke, [2003] suggested that the addition of a gametogenic calcite crust in some individuals results in oxygen isotope compositions increasing by 1.5‰, equivalent to calcification at 6.5°C lower temperatures, in response to changing calcification depths, implying bulk analysis of $\delta^{18}O_c$ could be biased to lower temperatures depending on the proportion of the total test mass that consists of gametogenic calcite.

4.3 Regional Setting of this Study

Nine recent marine sediment samples from the Southwest Pacific Ocean (22 to 53°S) comprising piston core-top and dredged samples were obtained from the Australian Institute of Marine Sciences (AIMS), National Institute of Water and Atmospheric Research (NIWA), New Zealand, and GNS Science, New Zealand. In addition to these sediment samples, three plankton tows taken from east of New Zealand by NIWA were also used in this study (Table 4.2).

The region over which the samples were taken is variably influenced by atmospheric and oceanic links from both Antarctica and the equatorial Pacific [*Carter et al.*, 2008]. Relatively warm, saline, micro-nutrient rich, macro-nutrient poor waters from the north converge around the south of Chatham Rise with colder, macro-nutrient rich, micro-nutrient poor waters brought northwards from the Subantarctic Front (Figure 4.1). In the Southwest Pacific Ocean, sediments show that both *N. pachyderma* and *N. incompta* occupy the same water mass and are two of the few species that occur in abundance throughout glacial-interglacial cycles in New Zealand waters [*Kennett*, 1968; *Crundwell et al.*, 2008].

Calcification temperatures calculated from $\delta^{18}O_c$ were not used in this study, due to reasons implied in previous work where crystalline parts of tests were shown to be enriched in $\delta^{18}O_c$ compared to ontogenic calcite [*Kozdon et al.*, 2009] and the lack of local $\delta^{18}O_{sw}$ measurements. Instead mean annual temperatures for each site were calculated for sub-surface ocean depths (0-100 m) obtained from the World Ocean Atlas (WOA05) [*Locarnini et al.*, 2006]. This depth range was chosen based on previous work linking *N. incompta* abundance to the depth of greatest food availability (*e.g.*, *Fairbanks et al.*, 1980; *Ortiz et al.*, 1995; *Darling et al.*, 2006). This depth is usually within a warm, well stratified near surface layer [Reynolds and Thunell, 1986; Sautter and Sancetta, 1992].

Sediment trap data from east of New Zealand, established the greatest flux of *N. incompta* occurred during the early austral summer (December) in traps north of Chatham Rise (Subtropical waters), whereas traps located south of the rise (Subantarctic waters) peaked during the late austral summer (March) [*King and Howard*, 2001]. The peak flux in foraminiferal production was related to moderate thermal stratification with food availability as secondary factor. It is therefore assumed that the majority of *N. incompta* in sediments calcified during spring or summer.

Chart ID	Sample	n	Latitude	Longitude	Depth	Annual SST ^a (0-10m) WOA05	Annual SSTª (0-100m) WOA05	Salinity ^a (0-100m)	Ageb
(Figure 5.1)	Ĩ		(South)	(East)	(metres)	(°C)	(°C)	(psu)	(yr)
1	274/61/DR05C1	2	22.133	156.743	1,600	24.7	23.8	35.49	
2	FR1/97/GC09	6	23.885	152.636	166	24.4	23.5	35.48	
3	Z7003	31	36.693	176.238	430	17.5	16.9	35.46	4650 ± 35
								35.65	
4	U2315 net 5	2	38.509	179.018	100-50m day	20.3	20.3		plankton tow
5	S938	12	40.330	179.990	3003	15.7	14.9	35.34	843±35
								35.61	
6	U2322 net 6	4	41.601	178.050	100-50m day	18.8	18.3		plankton tow
7	ODP Site 1123	18	41.942	188.501	3,290	14.2	13.5	35.11	
8	R623	19	43.200	186.000	1128	13.2	12.7	35.01	6519±35
								34.37	
9	U2309 net5	4	46.678	178.506	150-100m night	11.2	7.9		plankton tow
10	F111	11	48.950	174.980	704	11.3	10.3	34.29	6755±36
11	D178	15	51.720	167.830	629	10.3	10.3	34.46	4835±3
								34.33	
									Holocene <i>c.f.</i>
12	B32	22	53.630	169.870	799	9.2	9.1		2005]

Table 4.2: Details of core-top and plankton tow samples from the Southwest Pacific Ocean.

^a Annual sea surface temperature (SST) and salinity were derived from the World Ocean Atlas 2005 [*Antomv et al.*, 2006; *Locarnini et al.*, 2006], except for plankton tow samples where temperature and salinity measured from CTD were used. ^b Ages were calculated using radiometric (¹⁴C) dating within the same core. Ages for Z7003, S938, R623, F111 and D178 are from C. Prior (unpublished data). Data in bold refers to plankton tow samples. Samples 274/61/DR05C1, FR1/97,GC09, Z7003, S938, R623, F111, D178, B32 and all plankton tow samples were provided by the National Institute of Water and Atmospheric Research (NIWA). The ODP Site 1123 sample was provided by Geological and Nuclear Sciences (GNS), NZ. In the table 'n' refers to the number of samples analysed.


Figure 4.1: (A) Location chart of the core-top (black circles) and plankton tow (white circles) samples from the Southwest Pacific Ocean including annual SST [*Locarmini et al.*, 2006]. The inset (B) shows the surface ocean currents of New Zealand and surrounding regions. Blue arrows indicate the cold, fresher Subantarctic Front (SAF) within the Antarctic Circumpolar Current (ACC), whilst the purple arrows show warmer, saltier subtropical water that is brought to the west of New Zealand from the East Australian Current (EAC) and the Tasman Front (TF), which branches into the East (EAUC) and West Auckland Current (WAUC). The Subtropical Front (STF) forms part of the South Pacific subtropical gyre that moves warm water in a counter-clockwise direction down the east coast of Australia. West of New Zealand, the westerly winds force warm water via the Westland Current (WC) and Southland Current. Some of the former flow moves through Cook Strait as the D'Urville Current (DC). The Southland Current reaches the south of New Zealand and is diverted by Chatham Rise to the east. Figure taken and modified after *Carter et al.*, [1998a].

4.4 Methods

4.4.1 Sample Preparation

Approximately 10-35 *N. incompta* and *Neogloboquadrina pachy-dutertrei* (P-D intergrades) were randomly picked from samples. P-D intergrades were chosen as they have been shown to occupy similar ecological niches to *N. incompta* [Ebrenberg, 1861; Sautter, 1998; Von Langen et al., 2005], implying there is no need to separate them for palaeo-oceanographic studies. Size was limited to the 150-350 µm range because individuals >350 µm are more likely to be *N. dutertrei* [Sautter, 1998]. Each sample was cleaned according to the method outlined in Bolton et al. [2011] with the exception of plankton tows which were cleaned following the procedure in Barker et al., [2003]. The cleaning method for the plankton tows was modified (compared to Chapter 3) due to the presence of much larger amounts of organic material on the tests compared to *Gs. ruber* plankton material. Large amounts of organic material can contaminate Mg/Ca measurements [e.g. Hastings et al., 1996; Barker et al., 2003]. Following the cleaning procedures, individual foraminifera were weighed. All individuals were then mounted onto a glass plate using gum tragacanth and a dry brush.

4.4.2 Trace element analysis by LA-ICP-MS

The *in situ* LA-ICP-MS technique was used so that potential differences within and between individual chambers of each foraminiferal test could be examined. The individual chambers F-3 (representing the oldest, thickest visible chamber) and the ultimate or final chamber F were analysed from each individual.

Each test was ablated from the outside to the inside with a pulsed ArF Excimer laser ($\lambda = 193$ nm) using a laser beam spot size of 25 µm. During ablation, the isotopes ²⁴Mg, ²⁷Al, ⁴³Ca, ⁵⁵Mn ⁸⁸Sr and Ba¹³⁸ were measured using an Agilent 7500CS ICP–MS at The Australian National University (ANU) that was coupled to the laser ablation system.

Each analysis took a maximum of 120 s to ablate through the chamber walls. Measurements were standardised using interspersed analyses of the glass standard NIST SRM 610, with reference to its known elemental composition [*Pearce et al.*, 1996]. The resulting raw data were processed using MATLAB-developed software which allowed for initial screening of outliers, background correction (washout of 60 s, followed by counts with laser off for 60 s), and Ca-

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corrected internal standardisation. Duplicate measurements on sub-samples of individual tests were made to check reproducibility of individual chamber analyses. From these measurements the two standard deviation (2 S.D.) for each element/Ca ratio were: 0.35 mmol/mol for Mg/Ca; 0.27 mmol/mol for Al/Ca; 0.008 mmol/mol for Mn/Ca; 0.08 mmol/mol for Sr/Ca; and 0.004 mmol/mol for Ba/Ca. Following analysis, data were screened for clay contamination using the methods described in *Bolton et al.* [2011]. Approximately 18% of analyses with high Al/Ca and Mn/Ca were eliminated on the basis of this screening.

4.4.3 Electron Microscopy

Following LA-ICP-MS trace element analysis each test was imaged by a JEOL JSM-5300LV scanning electron microscope (SEM) under both secondary electron imaging and backscatter electron imaging. These images were used to determine test ultra-structure and identify morphotypes.

To further investigate the distribution of Mg, Mn and Al within the test wall, three individuals were also analysed in cross-section by electron microprobe imaging (EMP). These samples were embedded in epoxy resin, vacuum sealed to evacuate air bubbles from the inside of the tests, and then transferred to a hot plate at 40°C for 12 hr to set. Each epoxy mount was thin sectioned, then lapped and polished to reveal cross sections of the test wall. Mg, Mn and Al/Ca X-ray raw intensity maps were generated on a JEOL JXA-8230 Super Probe using an accelerating voltage of 15 kV, a beam current of 20 nA, a pixel size of 1 µm and dwell time of 1000 ms. All available elements (Mg, Mn, Al and Ca) were measured by energy dispersive Xray spectrometers, and these elements were also measured with wavelength dispersive spectrometers. Ca intensities below 10,000 cps were at background level, Al >100 and Mg or Mn > 70 were used to exclude 'hotspots' to maximise the range. Using this threshold removes background X-ray levels that helps to delineate and remove "edge effects" associated with EMP analysis that are produced as a result of the excitation volume of Mg being larger than Ca in calcite that can produce artificially high Mg/Ca values [Pena et al., 2008; Sadekov et al., 2005]. Element/Ca intensity maps were computed from matrix calculations, which were then converted from cps/cps to mmol/mol ratios by calibration with LA-ICP-MS trace element data from the central part of the wall profile from the same chamber. This intensity measured

in the middle of a test wall was used in the element/Ca cps maps with the concentration of what was assumed to be the same part of the test wall from the LA-ICP-MS data.

4.5 Results

4.5.1 Morphological variation in N. incompta

SEM images of the outer surface of tests confirm two types of ultra-structure - reticulate and crystalline *c.f. Bandy* [1972] - were present in the samples (Figure 4.2). Some individuals appeared to have an intermediate structure, particularly some plankton tow individuals and were subsequently classed as crystalline if pore pits were not visible. Both ultra-structures are present at all sites, except those from the two most northerly sites which were solely reticulate. SEM microscope cross-sections of *N. incompta* in Figure 4.2 show two easily distinguishable layers of calcite *i.e.*, inner ontogenetic calcite and the outer 'gametogenic crust'. This is further illustrated in Figure 4.2F, where sub-micron scale internal banding within the ontogenetic layer can also be distinguished, whereas the crystalline structure is more apparent in SEM images of the outer surface.

Specimens consisting of less than 4, or more than 5, chambers visible in umbilical view were extremely rare and the distinction between specimens with 4.5 to 5 chambers and those with 4 was considered arbitrary, consistent with *Kennett* [1968]. Other morphological differences observed for *N. incompta* include forms that were more quadrate, with an apertural lip (although this was often obscured in some crystalline forms) (see Figure 4.3). Another distinct form observed was more lobular, with increasing chamber sizes, often with a larger ultimate chamber in the final whorl (Figure 4.3). This latter form is commonly referred to as a normal form. A kummerform individual on the other hand refers to a specimen in which the final chamber is smaller than the previously secreted chambers but similar in shape [*Bijma and Hemleben*, 1994]. For further analyses, these two ultra-structures (reticulate and crystalline) were separated in order to examine the potential *inter*-individual variability.



Figure 4.2: (A) Illustration adapted from *Sadekov et al.* [2005] and *Reiss* [1958] showing a cross-section of an *N. incompta* test and chamber wall construction. F-3, F-2, F-1 and F refer to position of the chamber in the final whorl, where F is the final or ultimate chamber. (B) Cross-section of an *N. incompta* test showing lamellar wall features. ICL = inner calcite layer; POM = primary organic membrane; OCL = outer calcite layer; GAMC = gametogenic calcite. *N.B.* As whole tests were broken, it was not possible to differentiate between specific chambers. (C) Example of reticulate ultra-structure on the surface of *N. incompta* (site F111). (D) Example of crystalline ultra-structure on the surface of *N. incompta* (site B32). (E) Crystalline fragment showing what is two distinct layers of calcite, an inner and outer calcite layer (Site S938). (F) A crystalline fragment with some visible layers present, possibly from an older chamber (Site S938). Secondary electron imaging mode was used for images C, D and E and backscatter electron imaging mode was used for image F.



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Figure 4.3: Morphotypes and ultra-structures of N. incompta from this study. (A) P-D intergrade reticulate morphotype from plankton tow TAN0103 U2309 net 5. Note this morphotype is quadrate with a larger final chamber (F) and apertural rim. This is less calcified than crystalline surfaces in images D-E. Chamber formation is shown for reference where f is the ultimate chamber and F-1, is the penultimate chamber etc. (B) N. incompta reticulate morphotype from core top B32. Note this morphotype has another half chamber in between chambers F-3 and F and is more lobate (C) N. incompta collected by plankton tow sample U2315 showing reticulate surface with calcite ridges surrounding individual pore pits. This surface varies between individuals but in all cases pore pit remain visible. (D) N. incompta crystalline morphotype from core top B32. Note the quadrate and more compact form with all chambers having similar sizes. (E) N. incompta crystalline form from core top B32. This morphotype is quadrate with a larger final chamber, and less than 4.5 chambers in the final whorl. (F) Textural detail of a crystalline surface in individual from core top B32, chamber F-3, where euhedral crystals are visible. (G) N. incompta from plankton tow TAN0103 U2309 net 5. This is a reticulate form showing less calcification than crystalline form. (H) Test section of chamber F-1 in crystalline N. incompta from core top B32 showing thicker outer wall and thin septum. Note the presence of nanno-fossil material on the inner wall. (I) Test section of chamber F in crystalline N. incompta from core top ODP Site 1123 showing calcite rhombohedrons. (J) Crystalline lobulate PD-intergrade from core top B32. (K) Crystalline N. incompta from tropical site 271/61/DR05C1. (L) Reticulate PD-intergrade from core top D178, with a kummerform ultimate chamber.

4.5.2 Weight variation between reticulate and crystalline forms of N. incompta

Mean weights from each site were normalised using the mean width of individual *N. incompta* measurements as per Chapter 3, section 3.8.3. The deepest sites (ODP Site 1123 and S938) share similar mean weights with samples from shallower sites and did not correlate with depth suggesting that carbonate ion concentration and associated partial dissolution is not significantly altering the test weights. The difference in size-normalised weight between the two ultra-structures within the same sites, show that crystalline forms were slightly heavier than the reticulate forms except at site D178 (Figure 4.4). These differences in weight were not statistically significant (t-test, p > 0.05).



Figure 4.4: (A) Reticulate and crystalline mean test weight from each site. (B) Reticulate and crystalline mean test weight versus depth.

4.5.3 Trace element depth profiles of N. incompta test

Previous laser ablation studies of foraminifera have identified an elevated TE/Ca veneer on the surface of tests in other planktonic species [*Eggins et al.*, 2003; *Sadekov et al.*, 2009; *Bolton et al.*, 2011]. This TE-enriched veneer is also present on *N. incompta* tests, including plankton tow samples and irrespective of test ultra-structure type (Figure 4.5). In Figure 4.5 these elevated TE/Ca veneers were subsequently excluded from the selected profile (dotted box) for calculating the average TE/Ca composition of chambers. Monitoring the TE/Ca depth profiles to screen for potentially contaminated samples (as indicated by co-varying Mg and Al or Mn) was also combined by detecting the rapid decrease in the raw counts of Ca when the inner wall of the test had been breached by the laser. Following screening, the remaining mean Al/Ca and Mn/Ca at all sites was low (≤ 0.28 and ≤ 0.0281 mmol/mol, respectively),

suggesting that samples were not contaminated by clay minerals or diagenetic coatings such as Fe-Mn oxyhydroxides [*Boyle*, 1983].



Figure 4.5: (A) LA-ICP-MS depth profile for crystalline *N. incompta* (chamber F). (B) Shows the raw counts per second (CPS) during the laser ablation profiles for Ca, Mg and Sr.

Three typical laser ablation TE/Ca depth profiles in Figure 4.6 show differences in Mg/Ca between reticulate and crystalline tests measured in both (F and F-3) chambers. The crystalline test (Figure 4.6A), exhibits a lower Mg/Ca immediately after the elevated TE/Ca surface veneer and increases in Mg/Ca towards the inner profile of the test. These changes between low and high Mg/Ca are highly variable between individuals and are apparent from the variable length of the low Mg/Ca region from each individual depth profile. In some individuals, there were low and high 'bands' of Mg/Ca such as those observed in the reticulate sample shown in Figure 4.6B. Some reticulate individuals also show relatively homogeneous Mg/Ca throughout the entire depth profiles (Figure 4.6C), although the initial low Mg/Ca could be related to the ablation of surface features such as pore pits. It was also observed that ablation time was longer in crystalline tests compared to the reticulate tests. This suggests that the crystalline test structure were either thicker or of denser structure to the reticulate tests.

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In contrast, where Mg/Ca is lower in the crystalline tests (Table 4.3), Sr/Ca does not exhibit this pattern and remains relatively homogeneous throughout the entire depth profile (not shown). Both reticulate and crystalline tests of *N. incompta* share similar Sr/Ca with the highest value from one plankton tow (Table 4.4). However, these high values were not coupled with high ratios of other trace elements (Supplementary Table 4.5). It is noteworthy that t-tests did not reveal any statistically significant differences (P = 0.05) in Sr/Ca reticulate and crystalline tests from chambers F-3 or F.



Figure 4.6: (A) Mg/Ca for chambers F and F-3 in a crystalline sample. (B) Mg/Ca for chambers F and F-3 in a reticulate sample. (C) Mg/Ca for chambers F and F-3 in a reticulate sample. Note no log scale.

4.5.4 Intra-test Mg/Ca variability

Initial analysis of chambers F-4 to F in individual reticulate *N. incompta* from a single core-top (R623) did not reveal any discernable inter-specific differences in Mg/Ca ratios, in contrast to those observed earlier in *Gs. ruber* and other planktonic foraminifera [Marr et al., 2011] (Figure





Figure 4.7: Mg/Ca from individual chambers of N. incompta from core top site R623.

Additionally, those smaller individuals identified as kummerform (where the ultimate chamber F was smaller or the same size as the penultimate chamber), do not show any significant difference in Mg/Ca (Figure 4.8). Some studies have suggested that kummerform chambers are grown in abnormal conditions [*Bijma et al.*, 1990b] but because this was not clearly evident from the Mg/Ca ratios measured in this study kummerform chambers were pooled with analyses of the normal morphotypes of *N. incompta* from each site.



Figure 4.8: (A) Comparison of Mg/Ca ratios in the final (F) chamber of in kummerform and normal-forms of reticulate and (B) in crystalline *N. incompta*.

For all sites, the pooled mean Mg/Ca for both F-3 and F in reticulate forms is higher when compared to inner part of the calcite from the crystalline tests (as determined by the LA-ICP-MS where the Mg/Ca ratios are higher) except at site S938 (Table 4.4). However, in many cases this difference was marginal, with the largest difference being at site F111 (0.48 mmol/mol). Reticulate forms show variability between individual chambers in some of the sites, whereas other chambers share similar Mg/Ca ratios. The variability in the Mg/Ca ratios of the ontogenetic calcite is similar but not as clear as that observed in *Gs. ruber*. While the surface dwelling planktonic foraminifera *Gs. ruber* was found to have a significantly lower Mg/Ca in the final chamber (F) as compared to its other visible chambers, this characteristic is not apparent in *N. incompta.* There is a general decrease in Mg/Ca with increasing latitude with divergence from this trend at 38°S, 43°S (just north of the Subtropical Front [STF]) and 49°S (close to the northern boundary of the Subantarctic front [SAF]).

Table 4.3: Summary of Mg/Ca ratios for *N. incompta* chambers F-3 and F at all study sites. Samples are ordered from high to low SST. PT = plankton tow.

				Crystalline					
		Reticulate Chamber		Ontog	enetic	Gametogenic			
				Chan	Chamber		nber		
Site		F-3 Mg/Ca	F Mg/Ca	F-3 Mg/Ca	F Mg/Ca	F-3 Mg/Ca	F Mg/Ca		
271/61/DR05C1	Mean			1.92	3.69	0.72	0.72		
	Minimum			1.92	2.46	0.72	0.72		
	Maximum			1.92	4.93	·	0.72		
	5.D. n			1	1.75	1	1		
FR09/GC12	Mean	1 16	2.48		1 48				
THOS/ GCT2	Minimum	0.81	2.01		1.48				
	Maximum	1.42	2.95		1.48				
	S.D.	0.31	0.67						
	n	3	2		1				
Z7003	Mean	1.76	1.74		1.7		1.14		
	Minimum	0.74	1		1.2		0.69		
	Maximum	2.72	3.09		2.5		1.97		
	S.D.	0.58	0.64		0.6		0.56		
	n	12	21		4		5		
U2315	Mean	1.59	4.06						
	Minimum	1.47	2.88						
	Maximum	1.71	5.25						
	S.D.	0.17	1.67						
	n	2	2						
5938	Mean	1.26	1.3	1.37	1.28	0.91	1.01		
	Minimum	0.69	0.74	1.33	1.17	0.91	0.82		
	Maximum	1.68	1.92	1.4	1.3/	0.91	1.3/		
	S.D.	0.37	0.43	0.05	0.08	0	0.24		
112222 mat C	n Maan	0	8	2	4	2	4		
02522 net 6	Minimum	2.4	1.81						
	Maximum	2.00	1.44						
	SD	0.73	2.49						
	5.D. n	0.75	0.40						
ODP1123	Mean	1 16	1 32	1	1.05	1 17	0 00		
0011125	Minimum	0.92	1.32	0.82	0.5	0.54	0.55		
	Maximum	1.4	1.35	1.18	1.36	2	1.25		
	S.D.	0.34	0.05	0.25	0.29	0.61	0.27		
	n	2	2	2	9	5	8		
R623	Mean	1.56	1.61	1.16	1.53	0.86	1.01		
	Minimum	0.86	0.91	0.7	1.24	0.51	0.56		
	Maximum	2.02	2.58	1.48	2.05	1.57	1.79		
	S.D.	0.32	0.51	0.25	0.26	0.28	0.33		
	n	14	21	8	11	12	15		
U2309 net 5	Mean	1.6	1.64						
	Minimum	1.33	1.36						
	Maximum	1.74	2.21						
	S.D.	0.19	0.39						
	n	4	4						
F111	Mean	2.35	2.04	1.87	1.91	1.57	1.21		
	Minimum	2.06	1.42	1.32	1.5	0.72	0.98		
	Maximum	2.84	3.1	2.42	2.46	2.42	1.5		
	S.D.	0.34	0.72	0.78	0.5	1.21	0.26		
0170	n Maar	4	6	2	3	2	3		
אווט	Minimum	1./9	1.3/		1.31	0.6	0.96		
	Maximum	1.5	1.04		0./6	0.6	0./6		
	Maximum S D	2.59	0.0.1		0.51	0.0	0.0		
	э. <u></u> . n	5	4		0.51 A	•	2		
B32	Mean	173	1 58	166	1 46	0.9	07		
2.52	Minimum	0.72	0.95	1.00	1.25	0.29	0.33		
	Maximum	2.86	2.81	1.79	1,81	1.93	1.02		
	S.D.	0.65	0.52	0.22	0.26	0.61	0.29		
	n	10	13	3	4	6	5		

^a refers to the number of individual chamber analyses

blank spaces indicate 1 or 0 tests were analysed

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Table 4.4: Individual Sr/Ca in chambers F-3 and F from reticulate and crystalline tests of N. incompta

		Reti	culate	Crystalline			
Site		F Sr/Ca	F-3 Sr/Ca	F Sr/Ca	F-3 Sr/Ca		
		(mmol/mol)	(mmol/mol)	(mmol/mol)	(mmol/mol)		
271/61/DR05C1	Mean			1.64	1.57		
	Minimum			1.64	1.57		
	Maximum			1.64	1.57		
	S.D.						
FD00/CC10	n Maan	1.25	1.20	1	1		
FR09/GC12	Minimum	1.35	1.39	1.3/	1.48		
	Maximum	1.24	1.55	1.37	1.40		
	SD	0.12	0.05	1.37	1.40		
	n.	5	5	1	1		
Z7003	Mean	1.45	1.41	1.43	1.38		
	Minimum	1.26	1.28	1.34	1.50		
	Maximum	1.73	1.62	1.54	0.05		
	S.D.	0.09	0.09	0.08			
	n			7	6		
U2315	Mean	1.55	1.40				
	Minimum	1.53	1.37				
	Maximum	1.58	1.42				
	S.D.	0.04	0.03				
6020	n Maan	2	2	1 5 4	1.51		
2938	Minimum	1.56	1.51	1.54	1.51		
	Maximum	1.38	1.39	1.49	1.49		
	SD	0.10	0.10	0.05	0.04		
	n.	8	8	4	3		
U2322 net 6	Mean	1.33	1.37		5		
	Minimum	1.29	1.31				
	Maximum	1.40	1.43				
	S.D.	0.05	0.05				
	n	4	4				
ODP 1123	Mean	1.40	1.47	1.44	1.40		
	Minimum	1.30	1.36	1.28	1.30		
	Maximum	1.47	1.54	1.52	1.63		
	S.D.	0.09	0.09	0.07	0.09		
Brook.	n	3	3	14	13		
R623	Mean	1.44	1.45	1.47	1.48		
	Maximum	1.24	1.26	1.33	1.35		
	SD	1.01	0.15	1.01	1.55		
	5.D. n	22	20	16	12		
U2309 net5	Mean	1.47	1.38	10	12		
	Minimum	1.42	1.35				
	Maximum	1.50	1.44				
	S.D.	0.04	0.04				
	n	4	4				
F111	Mean	1.47	1.41	1.48	1.45		
	Minimum	1.37	1.29	1.45	1.39		
	Maximum	1.53	1.46	1.53	1.50		
	S.D.	0.06	0.07	0.03	0.08		
D470	n	6	5	4	2		
0178	Minim	1.56	1.54	1.63	1.65		
	Maximum	1.40	1.40	1.50	1.55		
	Maximum S D	0.07	1.01	0.00	0.12		
	з. . . n	0.07	6	0.09	2		
B32	Mean	140	1 40	148	1 4 5		
552	Minimum	1.23	1.23	1.38	1.35		
	Maximum	1.48	1.48	1.64	1.57		
	S.D.	0.07	0.07	0.09	0.09		
	n	14	12	6	6		

4.5.5 Mg/Ca – ocean temperature calibration for N. incompta from the Southwest Pacific Ocean?

A calibration was derived for reticulate forms using the mean Mg/Ca ratio of all chambers (*i.e.* the pooled average of chamber F and the pooled average of chamber F-3 from all individuals per site) and compared to the calibration of *Von Langen et al.* [2005]. Each site was calibrated against seasonal SST at which known *N. incompta* populations are highest across the surface to 100 m depth [*King and Howard*, 2001]. For plankton tow samples, calcification temperatures were obtained from conductivity-temperature-density (CTD) measurements collected at the same time of the tow.

In order to compare the data from the reticulate forms with those that were crystalline, the mean Mg/Ca of the inner most 'ontogenetic' calcite and the outer, assumed 'gametogenic' crust were calculated separately for the crystalline forms. This allows assessment of whether there is a chemical difference between these two layers of calcite.

The Mg/Ca ratios in reticulate forms exhibit a positive significant ($r^2=0.38$, p=0.044) relationship with ocean temperature in the final chamber F. However, in the older chamber F-3 there is no significant relationship between Mg/Ca and temperature. This is the same for the Mg/Ca ratios in chambers F and F-3 in the ontogenetic and gametogenic calcite of crystalline forms (Figure 4.9, Table 4.5).



$Mg/Ca = B \exp AT$												
Reference		Source	Slope (A)	y- intercept (B)	r ²	р	n	errors on A and B	Instrument	Analysis Type	Temperature Source	SST Range (°C)
This study, pooled F chamber, reticulate forms		Core top and plankton tow samples, Southwest Pacific Ocean (150-350 µm)	0.032	1.102	0.38	p=0.044	87	$A = \pm 0.014$ $B = \pm 0.227$	LA-ICP-MS	in-situ, 25μm spot	Annual SST World Ocean Atlas 2005	7.9 - 23.5
This study, pooled F-3 chamber, reticulate forms			-0.014	1.975	-0.026	p=0.409	67	$A = \pm 0.016$ $B = \pm 0.471$	LA-ICP-MS	in-situ, 25µm spot	Annual SST World Ocean Atlas 2005	7.9 - 23.5
This study, pooled F chamber, crystalline forms, ontogenic calcite)		0.271	1.223	-0.004	p=0.358	41	$A = \pm 0.014$ $B = \pm 0.349$	LA-ICP-MS	in-situ, 25µm spot	Annual SST World Ocean Atlas 2005	7.9 - 23.5
This study, pooled F chamber, crystalline forms, secondary calcite	}		0	0.974	-0.167	p=0.993	45	$A = \pm 0.015$ $B = \pm 0.207$	LA-ICP-MS	in-situ, 25µm spot	Annual SST World Ocean Atlas 2005	7.9 - 23.5
This study, pooled F-3 chamber, crystalline forms, ontogenic calcite			0.004	1.365	-0.196	p=0.904	20	$A = \pm 0.029$ $B = \pm 0.599$	LA-ICP-MS	in-situ, 25µm spot	Annual SST World Ocean Atlas 2005	7.9 - 23.5
This study, pooled F-3 chamber, crystalline forms, secondary calcite			-0.014	1.162	-0.119	p=0.633	33	$A = \pm 0.027$ $B = \pm 0.467$	LA-ICP-MS	in-situ, 25µm spot	Annual SST World Ocean Atlas 2005	7.9 - 23.5
Nürnberg [1995]		Core-top N. pachyderma from the Norwegian Sea	0.099	0.549	0.583				Electron-microprobe	in-situ	Hydrographic atlas	
Nürnberg [1995]		Core top N. <i>pachyderma</i> from the South Atlantic	0.083	0.406	0.892				Electron-microprobe	in-situ	Hydrographic atlas	
Von Langen et al. [2005]		Cultured <i>N. incompta</i> , Southern California Bight	0.101	0.51	0.9	p<0.001		$A = \pm 0.02$ B =-0.15,+0.23	ICP-MS	solution		10.2 (range)

Table 4.5: Summary of Mg/Ca chamber specific calibrations and existing calibrations for N. incompta and N. pachyderma

4.5.6 Electron Microprobe Element maps of Mg, Al and Mn/Ca ratios in N. incompta tests

Mg, Al and Mn/Ca element ratios maps are presented in Figure 4.10 and are shown as counts per second in order to illustrate the relative intensities of the different elements measured [*Pena et al.*, 2008]. These samples were selected from ODP Site 1123 after laser ablation trace element analysis, and had varying concentrations of trace elements including one sample with relatively high Al/Ca (7.6 mmol/mol, ODP1123_3) and Mn/Ca (0.17 mmol/mol, ODP1123_3) (Table 4.6).

			Average TE/Ca (LA-ICP-MS)					
Sample Number	Shell ultra-structure	Depth	Mg/Ca	Al/Ca	Mn/Ca			
		(mbsf)	(mmol/mol)	(mmol/mol)	(mmol/mol)			
ODP1123_2	crystalline	3290	0.80	0.35	0.03			
ODP1123_3	crystalline	3290	1.98	7.63	0.17			
ODP1123_5	crystalline	3290	1.19	0.08	0.01			

Table 4.6: N. incompta samples from ODP Site 1123 selected for trace element mapping post LA-ICP-MS

These element maps do not show any clear differences in Mg/Ca between the ontogenetic calcite and gametogenic crusts in the selected samples. Sample ODP1123_3 with high Al/Ca ratios had higher Al/Ca ratios showed the highest Al/Ca were concentrated around pores. ODP1123_2 and ODP1123_5 also show similar, but smaller spots of high Al/Ca although these do not appear to have influenced the Mg/Ca ratios during laser ablation.





Figure 4.10: (A, B and C) Electron microprobe elemental maps of three *N. incompta* individuals (ODP1123_numbers 2, 3 and 5; Table 4.6) on exposed cross sections of foraminifera tests. Images 1 and 2 on all figures show the SEM images the cross-section of *N. incompta* tests with the highlighted area where the element maps were made. Images 3 to 6 on all figures show intensity values are expressed as counts per second (cps) of Ca, Mg, Al and Mn as shown in the colour bars. Images 7 to 9 all figures show the Mg/Ca, Al/Ca and Mn/Ca expressed as cps converted to mmol/mol (see section 4.3.3).

4.6 Discussion

4.6.1 Mg/Ca variability within test walls of N. incompta

Of the crystalline forms, the innermost ontogenetic calcite (ICL) is characterised by a moderately higher Mg/Ca layer whereas the outer calcite layer (OCL) or gametogenic crust in many samples is usually has a lower Mg/Ca. The ratio of high to low Mg/Ca between these layers is variable but it appears, in general, that the lower Mg/Ca is often denser than the inner, higher Mg/Ca layer(s). Mean Mg/Ca between ICL in reticulate and crystalline forms varies from 16 to 63% lower (compared to reticulate) in chamber F-3 and 6 to 80% lower in chamber F. Other micro-analytical studies have established in many planktonic species that the OCL typically has lower Mg/Ca ratios (by up to a factor of 3) than the ICL of the test [*Duplessy et al.*,

1981; Klinkhammer et al., 2004; Anand and Elderfield, 2005; Schmidt et al., 2006; Hamilton et al., 2008; Lombard et al., 2010], which is consistent with the findings of this study. Element maps of N. dutertrei and N. incompta specimens have previously shown only limited Mg/Ca variation across chamber walls, with two distinct layers [Sadekov et al., 2005]. In that study, the ICL was characterized by a moderately high Mg/Ca ($4 \pm 1 \text{ mmol/mol}$), compared to the equally thick or thicker OCL that has significantly lower Mg/Ca ($1.5 \pm 1 \text{ mmol/mol}$). Similar variations were found in N. dutertrei and occasionally in N. pachyderma analysed by LA-ICP-MS [Eggins et al., 2003; Bergami et al., 2008]. N. pachyderma, in particular, showed a considerable range of Mg/Ca that extended well beyond plausible calcification temperatures [Eggins et al., 2003]. These authors suggested that this may be due to variation in calcification kinetics, or other factors not related to temperature, such as salinity. However, salinity was not considered to be a significant factor in controlling the chemistry of N. pachyderma from the Southern Ocean [Nürnberg, 1995]. Although the salinity range from this study's sample sites is considerably larger than that of Nürnberg, [1995], the results suggest no significant relationship with salinity.

Furthermore, the Mg/Ca data presented in this study are consistent with all ICL forming in warmer or shallower depths than the OCL, which is typically precipitated in deeper water in other Neogloquadrinid species [Orr, 1967; Erez and Honjo, 1981; Lohmann, 1995; Sadekov et al., 2008]. This is a characteristic observed in other planktonic foraminifera, including N. pachyderma, which is thought to add a final, often thick outer ("gametogenic") crust in deeper colder waters immediately prior to gametogenesis, and ensuing death [Brown and Elderfield, 1996; Elderfield and Ganssen, 2000; Jha and Elderfield, 2000; Hathorne et al., 2003]. Based on these observations, it is reasonable to propose that reticulate forms are pre-gametogenic variants of the same species. The $\delta^{18}O_c$ of reticulate and crystalline ultra-structures of N. *incompta* in a study by *Kozdon et al.*, [2009] found distinctly more negative $\delta^{18}O_c$ in reticulate forms, indicating a least some of the test in crystalline forms is precipitated at greater (colder) depths than reticulate forms from the same location. Alternatively, the difference between OCL and ICL may be the result of a biological mechanism that results in a different chemical composition between these layers [Bé, 1980; Hemleben et al., 1989]. The magnitude of these effects will depend on factors such as the temperature gradient in the water column, the amount of calcite secreted at these various depths, and any additional effects from dissolution (c.f. Duplessy, et al. 1981).

For all sites, the mean Mg/Ca in reticulate forms is higher when compared to crystalline forms, suggesting that these tests grow in warmer water or during warmer seasons when compared to the crystalline forms. This is consistent with the results of a study using *N. pachyderma* from the Southern Ocean, which recognised two different morphotypes [*Bergami et al.*, 2008]. One morphotype is described as having a "*thin and lobate walled test*" (assumed to be equivalent to "reticulate" forms described in this study), which had much higher Mg/Ca ratios compared to the morphotype with "*subspheric and heavily encrusted tests*", assumed here to be crystalline forms.

The Mg/Ca of the OCL between each site does not vary greatly and may indicate a particular temperature where this layer is secreted. Assuming that Mg/Ca variability is the result of differences in calcification temperature, applying the generic planktic species calibration of *Elderfield and Ganssen* [2000] and that from *Von Langen et al.*, [2005] reveals a temperature range for the OCL (all chambers) that varies from -9.4 to 15.47°C and -5.5 to 15.4°C respectively. There are a number of possible explanations for these large ranges:

- The current calibrations do not include individuals collected from colder sampling sites, thus the regressions used to calculate temperatures are based on the extrapolation of current data;
- (2) The range reported in this study are from all sites, and the maximum range found within an individual site is much smaller *e.g.*, Table 4.2;
- (3) That temperature is not the primary reason for these observed ranges in Mg/Ca. Instead, there may be a specific biological mechanism that favours the precipitation of a chemically (in terms of Mg) uniform calcite.

4.6.2 Comparison with other calibrations

The Mg/Ca – ocean temperature calibrations derived in this study do not show a significant relationship with temperature. The best correlation is for the final chamber in reticulate forms ($r^2=0.33$) although this is still not statistically significant (p=0.09) in contrast to the results of *Von Langen et al.* [2005] who show a strong ($r^2=0.90$) positive correlation between Mg/Ca and temperature that is similar to trends reported for other planktonic species. The *Von Langen et al.* [2005] calibration was based on *N. incompta*, PD-intergrades and *N. dutertrei* cultured under

known temperature conditions. The main disadvantage of culturing lies in the controlled environment that cannot fully replicate the complexities captured in samples recovered from the sea floor, in terms of factors including but not exclusive to nutrient availability, ontogenic migration through the water column and diagenesis. *Hilbret* [1997] suggested that *N. incompta* is more likely to be showing variable ontogenic cycles where conditions in the water column do not depend strictly on depth but also other factors such as nutrient availability (see also *Hemleben et al.*, 1989), depth of the thermocline, the deep chlorophyll maximum and upwelling conditions [*Fairbanks et al.*, 1980; *Ravelo et al.*, 1990; *Brock et al.*, 1992; *Ravelo and Fairbanks*, 1992]. The above conditions cannot be replicated in under culture but these different factors may explain the lack of correlation between Mg/Ca and ocean temperatures in this *N. incompta* from the Southwest Pacific Ocean.

Apart from these factors, the samples in the Von Langen et al., [2005] study were based on individuals that had been collected at shallower depths (0-50 m) although previous plankton tows had noted that specimens were considerably more encrusted in deeper tows (300 m). It could be that those shallower specimens did not undergo gametogenesis, as this process is rarely observed in cultured specimens [Bé, 1980].

The implications for palaeoceanographic studies would be that calibrations from cultured conditions are less representative of the actual ocean conditions than those from core-tops. As pointed out in earlier studies, when measured by solution, a prerequisite for palaeoceanographic applications is the demonstration that the temperature sensitivity of foraminiferal calcite is retained from the initial chamber formation through to the development of gametogenic calcite crusts, with the additional effects of dissolution, to residence at the sea bed [*Elderfield and Ganssen*, 2000]. Although, this does not explain why *N. incompta* measured from the Southwest Pacific do not display a significant positive Mg:temperature relationship, other studies have also found inconsistencies in *Neogloboquadrinids*. For example, covariance of magnesium concentrations and water temperature in *N. pachyderma* from both northern and southern high latitudes showed similar regression lines and inclination, however the relationship was much weaker in the southern high latitudes (Southern Ocean) [*Nürnberg*, 1995]. In the latter study, the author speculates that the hemispheric discrepancies must be associated, in addition to temperature effects, to differences in plankton biosynthesis and metabolism. Additionally, *Bergami et al.*, [2008] could not find a clear relationship between the

distribution of dextral coiling specimens of *N. pachyderma* and water temperature. This leads towards the conclusion that perhaps this species is not a good (geochemical) palaeothermometer.

4.6.3 Vital Effects

In this study, the low Mg/Ca ratios in crystalline forms were less variable compared to that considered to be ontogenetic calcite. *Kennett*, [1968] found no temperature dependence in gametogenic calcite in the same species. This would mean, however, that because this study's sites span both Subtropical and Subantarctic sites, for each site the depth at which gametogenesis occurred would be different. A different possibility is that the composition of gametogenic calcite is entirely determined by a biological mechanism which is unrelated to seawater temperature (or depth). As the thickness of the gametogenic crust varies between individuals, it may be related to the calcium budget of the individual at the time of gametogenesis such that the Ca^{2+} or alkalinity (carbon pool) volume of cytoplasm inside a sphere, increases the calcite saturation state in the microenvironment prior to gametogenesis [*Hemleben and Spindler*, 1983; *Hamilton et al.*, 2008].

4.6.4 Palaeoceanographic implications

The two different ultra-structures of *N. incompta* clearly have variable intra and inter-test Mg/Ca values and this will bias temperature values derived from fossil samples, if one form is more dominant than the other. For example, it has been shown that crystalline forms have lower Mg/Ca ratios (if gametogenic calcite is considered) compared to the reticulate forms (Table 4.3). Given that most studies use bulk Mg/Ca ratios, it is important to discriminate between reticulate and crystalline ultra-structures before analysis. This may explain some large variations found in temperature and salinity from down-core records [*Came et al.*, 2007; *Benway et al.*, 2010], particularly if the production of gametogenic forms is stimulated by specific environmental conditions. In other studies, dissolution appears to discriminate between different calcite structures so that crystalline tests can appear to be well preserved on the outer surface when in fact the inner calcite has been preferentially dissolved [*Barker et al.*, 2005; *Johnstone et al.*, 2010]. This could also bias the inferred temperature signal to much lower

temperatures, however the presence of high and low Mg in this study does not suggest a dissolution effect.

The application of LA-ICP-MS this study has shown varying layers of Mg/Ca within *N. incompta* that may be related to the presence of gametogenic and various ontogenetic layers of calcite of varying thickness. The Mg/Ca profile increases towards the inner (ontogenetic) calcite, and the signal appears to be mixed, probably because the test surface is lobate but also due to varying organic layers of ontogenetic calcite. In addition, the crystalline tests required more laser power and it was noted that once the entire crystalline layer has been fully ablated, the thinner primary calcite layer requires less laser power to ablate. These settings need to be considered in future analyses in order to resolve the two calcite types more confidently. In addition, the non-destructive nature of LA-ICP-MS allows SEM images to be taken of each individual, allowing accurate analyses of test ultra-structure.

4.6 Conclusions

An electron microscopy and LA-ICP-MS trace element study of modern *N. incompta* from a range of ocean temperatures (9 to 24°C) has shown that:

- (a) Only a weak positive relationship exists between ocean temperature and Mg/Ca ratios in reticulate forms of *N. incompta* from the Southwest Pacific Ocean, although this was not statistically significant. What was tentatively identified to be ontogenetic calcite in crystalline forms of *N. incompta* also shows a general increase of Mg/Ca with increasing ocean temperature, but again this relationship is not statistically significant.
- (b) Gametogenic calcite in crystalline forms of *N. incompta* is lower in Mg/Ca compared to the ontogenetic calcite.
- (c) In crystalline forms of *N. incompta*, based on the laser ablation depth profiles, the gametogenic calcite crust (rather than the ontogenetic calcite) typically appears to be either thicker or denser. The similarity of Mg/Ca in the outer crusts of all chambers suggests that this crust was deposited at the same temperature or is controlled biologically.

- (d) The presence of inter-gradational surface ultra-microstructures between reticulate and crystalline forms suggests that they are the same phenotypic variant.
- (e) There does not appear to be a difference in weight between the two ultra-structures.

In summary, it can be concluded that Mg/Ca ratios from *N. incompta* in the studied specimens from core-top sediments and plankton tows from the Southwest Pacific Ocean do not appear to suggest this species will be a reliable archive of past ocean temperatures in this region.

Chapter 5

Southwest Pacific Ocean response to Marine Isotope Stage 31 as recorded at ODP Site 1123

5.1 Abstract

Marine Isotope Stage (MIS) 31 occurred from 1.081-1.061 Ma and coincided with one of the phases of highest mid- to high latitude insolation and warm temperatures of the past 5 Ma. A high-resolution foraminiferal trace element and stable isotope chemistry record from Ocean Drilling Program Site (ODP) 1123, offshore of eastern New Zealand, was produced here to investigate the palaeoceanographic and palaeoclimatic history of the Southwest Pacific Ocean during the 'super-warm' MIS-31.

Mg/Ca ratios measured by laser ablation inductively coupled plasma mass spectrometry on planktonic foraminifera reveal distinct shifts during glacial-interglacial (G-IG) cycles encompassing MIS 34–29 (1.14 to 1.00 Ma). During interglacials, the planktonic species *Globigerinoides ruber* (*Gs. ruber*) and *Globigerina bulloides* (*G. bulloides*) record elevated sea surface temperatures (SSTs) that reached 19°C in MIS31 - *ca.* 4°C warmer than the present interglacial. Coolest climatic conditions occurred during MIS-30 when SSTs fell to *ca.* 10°C.

Paired Mg/Ca and δ^{18} O data reveal significant changes in ice volume over the sampling period, with increases in SSTs recorded by the planktonic foraminifera leading the seawater stable isotope record by up to 10 kyr suggesting a significant influence from changes in Northern Hemisphere ice sheet volume during MIS-31. Other trace element data (Mn, Ba and Zn) in the planktonic foraminifera reveal somewhat systematic changes on G-IG cycles. In particular, Mn/Ca appears to co-vary with SSTs and increases in Ba and Zn/Ca ratios proceed the peak MIS-31 interglacial that may reflect enhanced southward transport of micro-nutrient rich Subtropical Surface Waters and/or increased productivity. The fact that the patchy distribution of *Gs. ruber* increases during interglacial periods and signals a southward shift or strengthening foraminifera Mn, Ba and Zn/Ca ratios as reflecting meridional changes in the surface water masses.

Size-normalised weights (SNW) of *G. bulloides* tests show systematic variations over G-IG cycles. For much of the record, SNW anti-correlate with SST in a manner similar to the modern relationship between SNW and SST in the Southwest Pacific Ocean. However, in the warm period marked by high SST during and immediately prior to MIS-31 during the Southern

Hemisphere insolation maxima, SNW correlate with SST suggesting a fundamental change in surface ocean carbonate ion chemistry occurred that is unique to this warm event.

5.2 Introduction

Reconstructed records of past climatic conditions can provide important constraints on the potential environmental responses to projected changes in the Earth's climate system [*Berger and Loutre*, 2002; *Skinner*, 2010]. Global wind- and the thermohaline-driven circulation system is the primary means by which heat is transported globally. Two key parameters that can be used to define past climate are ocean temperatures and other oceanographic changes, such as the reorganisation of major ocean currents, water masses and the position of ocean fronts between these.

MIS-31 occurred from 1.081 – 1.061 Ma [*Lisiecki and Raymo*, 2005] during the Mid-Pleistocene Transition (MPT) that took place from *ca.* 0.5 to 1.2 Ma [*Head and Gibbard*, 2005]. The MPT represents a period from the 41-kyr world of the late Pleiocene/early Pleistocene to the emergence of the 100-kyr world of the late Pleistocene, in the absence of any change in the orbital forcing [*Clark et al.*, 2006]. Several indirect and direct lines of evidence suggest that MIS-31 was one of the warmest periods during the Quaternary within the MPT. As well as being a particularly long and warm interglacial, it was also characterised by an orbital configuration unique in the last 5 Ma [*Scherer et al.*, 2008]. The orbital configuration at this time consisted of high obliquity and precession combined with a January perihelion early in the interglacial. Combined, these caused extreme southern mid-high latitude insolation (Figure 5.1). Additionally, the stable oxygen isotope compositions of benthic foraminiferal calcite $(\delta^{18}O_c)$ at this time reflect the dominant 40 kyr periodicity that represents Earth's obliquity (tilt) *e.g. Raymo and Nisancioglu* [2003], *Liu and Herbert* [2004] and, *Kupp* [2006].

There are two recently proposed explanations to explain this periodicity: (1) The ice sheets responded to obliquity (tilt), which determined the duration of the high latitude summer at the expense of mid- and low-latitude summer insolation, and its effect was synchronous in the northern and southern hemispheres (*e.g. Huybers*, 2006). In this scenario, ice sheets expand and contract with a 40 kyr period. (2) Alternatively, the ice sheets are more sensitive to precession which affects the intensity at all latitudes by altering the Earth-Sun distance during each season

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and are out-of-phase between the hemispheres [*Raymo et al.*, 2006; *Scherer et al.*, 2008]. In this model, ice sheets expand and contract with a ~19 to 23 kyr period. The effect of ice growth in one hemisphere on sea level may thus be cancelled by melting in the other hemisphere, so the weaker 40 kyr obliquity period is recorded by globally integrated proxies such as foraminiferal stable oxygen isotopes ($\delta^{18}O_c$).



Figure 5.1: (A) Orbital parameters during MIS 34-29. For units of precession ε is the eccentricity of the Earth's orbit and ω is the Earth's angular velocity. (B) Mean daily insolation at perihelion for latitudes 80°S, 42°S and 65°N [Laskar, 2004]. Extreme high southern latitude insolation is evident at ca. 1082 Kyr. *Pollard et al.* [2009] used the insolation at 80°S to model West Antarctic Ice Sheet (WAIS) variations in the same time period as this study. Insolation at 65°N represents the summer insolation records for the Northern Hemisphere (NH) used in the *Raymo* and *Haybers* [2008] models of global ice volume change. The peak NH insolation maximum also coincides with the Jaramillo palaeomagnetic reversal at 1.07 Ma. The insolation at 42°S represents that received at the latitude of this study's site (ODP Site 1123). The shaded gray bars (top of figure) indicate the MIS age boundaries as defined in the *Lisiecki and Raymo* [2005] global benthic stack (LR04).

During MIS-31 ice-rafted debris is abundant in sediment cores from ODP Sites 1090 and 1165 suggesting that Antarctic ice sheets generated icebergs capable of at least reaching the subpolar South Atlantic [*Becquey and Gersonde*, 2002; *Kupp*, 2006]. Furthermore, a 5 Myr simulation from the early Pliocene to present, suggests the East Antarctica Ice Sheet (EAIS) was relatively stable with nearly all of the ice-volume variability being due to the West Antarctic Ice Sheet (WAIS) [*Pollard and DeConto*, 2009]. During MIS-31, their model simulates a partial retreat to collapse of the WAIS, which is consistent with geological evidence from a coastal Antarctic sediment core (AND-1B) [*Naish et al.*, 2007]. This sediment core from the Ross Sea sector of the Southern Ocean suggests that MIS-31 was indeed characterised by a prolonged retreat or collapse of the Ross Ice Shelf and likely led to a substantial reduction in the volume of the WAIS and a contribution to sea level rise of 3 to 6 m [*Bamber et al.*, 2009; *Villa et al.*, 2010]. The *Pollard and DeConto* [2009] model suggests that retreat/collapse of the WAIS occurred when nearby ocean temperatures warmed by ~5°C.

Given the substantial changes in the Antarctic cryosphere and climate predicted from models and inferred from sedimentary evidence during MIS-31, this study uses the geochemistry (trace element and stable isotope data) and shell weights of planktonic foraminifera to investigate the palaeoceanographic and palaeoclimatic history of the Southwest Pacific Ocean at this time. The foraminifera were sampled from a high resolution sediment core from ODP Site 1123, located at southern mid-latitude, east of New Zealand and directly downstream of the Antarctic Circumpolar Current (ACC) and directly above the Pacific Deep Western Boundary Current (DWBC) (Figure 5.2). This site also lies close to the northern limit of the modern Subtropical Front (STF) and hence captures the interaction between Subtropical Water (STW) from the north and Subantarctic Water (SAW) from the south.

5.3 Materials and Methods

5.3.1 Regional Setting of ODP Site 1123

ODP Site 1123 (41°47.2' S, 171°29.9 W) is located at 3290 m depth on the northeastern flank of Chatham Rise, east of New Zealand [*Carter et al.*, 1998b]. The site is immediately north of the STF that separates warm, saline macro-nutrient poor and micro-nutrient rich STW in part

carried by the South Pacific Subtropical Gyre (SPSG) from cold, low salinity and macronutrient rich, micro-nutrient poor SAW within the Subantarctic Front (SAF) of the ACC [*Heath*, 1985; *Boyd et al.*, 1999; *Uddstrom and Oien*, 1999; *Morris et al.*, 2001; *Murphy et al.*, 2001; *Neil et al.*, 2004; *McCave et al.*, 2008]. This site also lies beneath the Pacific DWBC, which flows northwards east of New Zealand (Figure 5.2). Modern SSTs at this site have a seasonal range from 12.3 to 17.6°C (0-50 m), with a mean annual value of 14.6°C [*Schlitzer*, 2002; *Locarnini et al.*, 2006]. Salinity ranges from 35 to 35.2 psu with an annual average of 35.1 psu [*Antonov et al.*, 2006].



Figure 5.2: (A) Chart of the surface ocean currents of offshore New Zealand and surrounding regions. Blue arrows indicate the transport of Subantarctic and circumpolar surface waters mainly within the Subantarctic Front (SAF) of the Antarctic Circumpolar Current (ACC), while the purple arrows show warmer, saltier Subtropical Water (STW) carried to New Zealand via the South Pacific Subtropical Gyre (SPSG) that is locally represented by the Tasman Front (TF). That frontal flow branches mainly into the East Auckland Current (EAUC) with some water also contributing to an ephemeral West Auckland Current (WAUC). The eastern surface flow continues as the East Cape Current (ECC) that contributes to the Subtropical Front (STF). West of New Zealand the westerly zonal winds force the Westland Current (WC) and its offshoot the D'Urville Current (DC) into Cook Strait whereas to the east of the South Island, the Southland Current (SC) moves mainly Subantarctic surface water northward where some continues north to central New Zealand, and the remainder is diverted east along Chatham Rise and help form the southern boundary of the STF. (B) Chart of the New Zealand region and the main elements of the abyssal circulation system including the Pacific Deep Western Boundary Current (DWBC), and the overlying but deep-reaching Antarctic Circumpolar Current (ACC). Both charts taken and modified from *Carter et al.*, [1998a].

5.3.2 Age Model

Stable oxygen isotopes ($\delta^{18}O_e$) of the benthic foraminifera species *Uvigerina* spp. were used to complement the first isotope-based age model of *Hall et al.* [2001], which was tuned to an ice-volume model using boreal summer (July) insolation values at 65 °N [*Imbrie and Imbrie*, 1980]. An average of 10-15 samples of *Uvigerina* spp. from the 250 to 355 µm size fraction were pooled and analysed from 5 cm sections of the ODP Site 1123 'C' core. In some sections, there were too few individuals available for analysis and, although smaller individuals were present, these were not analysed due to potential size specific isotopic fractionation effects [*Schumacher et al.*, 2010]. In addition, other workers using this core (*e.g. Crundwell et al.*, 2008) use a similar age model that is modified and supported by the ODP 1123 palaeomagnetostratigraphy [*Carter et al.*, 1998b], ages of interbedded tephra [*Alloway et al.*, 1995; *Carter et al.*, 2004a] and microfossil biostratigraphy [*Carter and Wilkin*, 1999].

This original age model was initially based on shipboard palaeomagnetic and micro faunal data but further work on palaeomagnetic U-channel samples revealed that the palaeomagnetic reversal at the base of the Jaramillo subchron (C1r.1n) in core 'C' of ODP 1123 (1123C) was 41.68 meters below sea level (G. Wilson, personal communication). This is an important age control dated at 1.072 Ma and coincides with the NH insolation peak during MIS-31. Based on this new information a modified age model was derived from this study's benthic oxygen isotope data, the new U-channel palaeomagnetic data and correlation to the stacked benthic oxygen isotope stratigraphy model of *Lisieki and Raymo* [2005] (LR04) using Analyseries v.2.0.3. Previous age models were also adjusted so that other proxy data could be incorporated into this study (see Supplementary Material 5.8.1). The LR04 age model is a global Pliocene-Pleistocene stack that contains benthic δ^{18} O data from 57 globally distributed sites and has an average standard error of only 0.06%. The LR04 age model is designed to minimize changes in global sedimentation rates such that the uncertainty including all sources of error is estimated 4 kyr from 1–0 Ma.



Figure 5.3: Age model of ODP Site 1123, which was derived by correlating this study's benthic oxygen isotope record (*Unigerina* spp.; black filled diamonds and black curve), to the global stacked benthic oxygen isotope record of *Lisiecki and Raymo* [2005] (LR04; grey curve). The U-channel palaeomagnetic susceptibility data were used to tie the base of the Jaramillo subchron (C1r.1n) at 41.68 mbsf to 1.072 Ma (red solid line). The red stars indicate the age tie-points used to align the benthic δ^{18} O sections (see Supplementary Table 5.1.). MIS boundaries, taken from *Lisiecki and Raymo*, [2005], are shown at the bottom of the figure.

5.3.3 Foraminifera

This study utilises 110 sediment samples from ODP Site 1123, core 'C', from 39.9 to 43.34 mbsf totalling a 3.44 m section of the core (see Supplementary Material for further details). Samples of \sim 1 cm intervals, were collected at \sim 5 cm intervals (an average resolution of 1.9 kyr) and record the glacial to interglacial MIS-34 to MIS-29 (\sim 1140 to 1000 kyr). The materials from this study were collected by hydropiston coring [*Carter et al.*, 1998b].

Two planktonic foraminiferal species were studied. *Globigerinoides ruber* white (*Gs. ruber*) which is a subtropical to tropical species [*Anand and Elderfield*, 2003] and records surface water temperatures (0-50 m) equivalent to a spring/summer signal of 13.0 to 17.6°C at ODP Site 1123. At mid-latitudes *Gs. ruber* becomes less dominant within the foraminiferal assemblage, particularly during glacial periods [*Crundwell et al.*, 2008], therefore *Globigerina bulloides* (*G. bulloides*) was also studied as is it common throughout the record. *G. bulloides* is a non-symbiotic species and typically a transitional species. High abundances of this species are often associated with enhanced nutrient supply and a spring/summer flux as determined by sediment traps [*King and Howard*, 2001; *Nürnberg and Groeneveld*, 2006; *Crundwell et al.*, 2008]. Although this species lives in the surface mixed layer, its ontogeny means it migrates within it and hence records a wider temperature range than *Gs. ruber* at water depths of ~50-150 m [*Hemleben et al.*, 1989]. Moreover, recent work on *G. bulloides* from core-tops in the Southwest Pacific calibrated the Mg/Ca ratios of this species to calcification depths of 75 to 150 m equivalent to spring/summer temperatures of ~11.7 to 13.5°C at ODP Site 1123 [*Marr et al.*, 2011].

5.3.4 Sample preparation

From ODP Site 1123 core 'C', approximately 10-35 individual foraminifera (Gs. ruber, G. bulloides, and Uvigerina spp.) were selected and cleaned according to the methods outlined in Bolton et al., [2011]. Specimens of Gs. ruber and G. bulloides were randomly picked from the 250-355 μ m size fractions. Both Gs. ruber and G. bulloides are not considered to produce gametogenic calcite of any significance [Caron et al., 1990; Hamilton et al., 2008], therefore prior to geochemical analysis, the mean shell weights of ca. 10-15 individuals from each sample were measured with an ultra-microbalance. The shell or test area has been previously used to normalise weights [Elderfield et al., 2002], whereas other studies have used the mean diameter of G. bulloides as opposed to the height as it is less sensitive to variations in shape of the highly variable final chamber [Malmgren and Kennett, 1978]. Given test diameter is highly correlated with test area [Beer et al., 2010]; each mean weight in this study was used to calculate size-normalised weight (SNW) as follows [Equation 1]:

$$SNW = \{\text{mean weight } (\mu g) / \text{mean diameter } (\mu m)\} * 100 \qquad [Eqn. 5.1]$$

In addition, during the picking of *Gs. ruber*, its morphotype was noted where possible. High spired and normal forms were assigned the morphotype of *Gs. ruber* senso stricto (s.s) and smaller forms similar to those described as type b "platys" in *Numberger et al.* [2009] were defined as *Gs. ruber* sensu lato (s.l.) [*e.g. Wang*, 2000]. Following geochemical analysis, photographs of all samples were taken to scale using an Olympus DP70 camera attached to a

binocular light microscope. Although morphotypes of *G. bulloides* exist, they are not as morphologically distinguishable as *Gs. ruber* (K. Darling, pers. comm., 2010) and were not identified separately in this study.

5.3.5 Trace element analysis

The ratios of Mg, Al, Mn, Zn, Sr and Ba to Ca were analysed by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) on *Gs. ruber* and *G. bulloides* as described in Chapter 3. To estimate ocean temperatures, the Mg/Ca ratio of the oldest chamber (F-2) (Mg/Ca_{chF-2}) was analysed and converted to temperature using locally derived, chamber-specific core-top calibrations from the Southwest Pacific [*Bolton et al.*, 2011; *Marr et al.*, 2011] where:

For Gs. ruber.

$$\frac{Mg}{Ca_{chF-2}} = 0.798 \times \exp^{0.070 \times SST}$$

(Eqn. 5.2)

For G. bulloides:

$$\frac{Mg}{Ca_{chF-2}} = 0.983 \times \exp^{0.067 \times SST}$$
(Eqn. 5.3)

5.3.6 Stable oxygen and carbon isotope analyses

LA-ICP-MS is a non-destructive method and allows samples to be subsequently analysed for other geochemical proxies such as stable oxygen and carbon isotope ratios (δ^{18} O and δ^{13} C). Following trace element analysis, the same specimens of *Gs. ruber* and *G. bulloides*, as well as the *Uvigerina* spp., were pooled and analysed for δ^{18} O and δ^{13} C. The methods for stable isotope analysis are outlined in Chapter 3, Section 3.8.2. Analyses were performed using a Finnigan stable isotope mass spectrometer at Stanford University, California.
5.3.7 Estimation of the $\delta^{18}O_{sw}$ 'salinity proxy' from G. bulloides

Over geological timescales, the $\delta^{18}O_{sw}$ reflects two components. The major component of the planktonic foraminifera signal over periods greater than a few thousands years [*Charles et al.*, 1996] are changes in continental ice volume. The second component is the $\delta^{18}O_{sw}$ of the regional water mass (and/or local salinity). The two equations that were applied for *Gs. ruber* and *G. bulloides* are based on culturing experiments on the symbiotic foraminifera *Orbulina universa* (*O. universa*) and *G. bulloides* [*Bemis et al.*, 1998] where:

For O. universa/Gs. ruber.

$$\delta^{18}O_{sw} = [T (^{\circ}C) - 14.9 + 4.8 * \delta^{18}O_{c}]/4.8 + 0.27$$
 [Eqn. 5.4]

For G. bulloides:

$$\delta^{18}O_{sw} = [T (^{\circ}C) - 16.5 + 4.8 * \delta^{18}O_{c}]/4.8 + 0.27$$
 [Eqn. 5.5]

Only *G. bulloides* is considered in the discussion due to the intermittent record of *Gs. ruber*. However, because both species calcify in the mixed layer, their $\delta^{18}O_{sw}$ should be similar. A factor of 0.27‰ was used to convert $\delta^{18}O_c$ of calcite measured and reported on the vPee Dee Belemite (vPDB) scale to water on the standard mean ocean water scale (SMOW).

For comparison, the global sea-level curve of *Raymo et al.*, [2006] was converted into $\delta^{18}O_{sw}$ (‰) using the assumption that a relative sea level drop of -130 m corresponded to a global mean $\delta^{18}O_{sw}$ enrichment of 1.1‰ [*Yokoyama et al.*, 2000]. Independent constraints on ice volume-sea level changes before the Late Pleistocene using shallow-marine continental margins have indicated that the sea level $\delta^{18}O$ calibration may have been the same over the last 2.6 Ma *e.g.* [*Pekar and DeConto*, 2006; *Pollard and DeConto*, 2009]. The component of $\delta^{18}O_{sw}$ that is due to changes in regional hydrology over MIS-34 -29 was then calculated by subtracting the influence of continental ice volume [*Yokoyama et al.*, 2000; *Raymo et al.*, 2006] and subtracting the modern surface $\delta^{18}O_{sw}$ value based on a local measurement close the ODP Site 1123 (H.

Neil, pers. comm., 2009) to produce an ice-volume-free residual, $\Delta \delta^{18}O_{IVF-SW}$ [Schmidt et al., 2004]. Removing the influence of ice volume [Waelbroeck et al., 2002] and subtracting the modern surface $\delta^{18}O_{sw}$ value of 0.40% for G. bulloides yields $\Delta \delta^{18}O_{IVF-sw}$. Positive values indicate increased surface salinity due to the excess removal of H₂¹⁶O during evaporation [Schmidt et al., 2004].

There are a number of limitations surrounding the estimation of $\delta^{18}O_{sw}$ and the ice-volume-free residual, which are discussed in more detail in the Supplementary Material (Section 5.8.2).

5.4 Results

5.4.1 Morphotypes of Gs. ruber

Two main morphotypes of *Gs. ruber* were classified; although there are some inter-gradational forms also present. Morphotypes of *Gs. ruber* have previously been used to indicate habitat preferences, where the normal form (*senso stricto*) occupies the upper water column, and the smaller form commonly referred to as *sensu lato* (s.l.) preferring slightly deeper waters (*e.g. Steinke et al.*, 2003; *Löwemark et al.*, 2005). However, throughout the glacial to interglacial cycles of MIS-34 to MIS-29, the abundance of the individual morphotypes did not vary considerably. It appears that the normal form of *Gs. ruber* is rare, only appearing during peak SST's (particularly MIS-31) and therefore the samples had insufficient specimens of each morphotype for a statistical comparison. However, the record suggests that the s.l. form is dominant and may be adapted to this unique setting, which is colder and more nutrient-rich than typical tropical to sub-tropical environments more common for *Gs. ruber* normal forms. The s.l. type is thought to be adapted to colder conditions; and has been found consistently more abundant at the margin of the distribution of *Gs. ruber* (M. Kucera, pers. comm., 2011).

5.4.2 Mg/Ca ratios and ocean palaeotemperatures recorded by Gs. ruber and G. bulloides

The pooled mean Mg/Ca ratios measured in *Gs. ruber* and *G. bulloides* are presented in Figure 5.4 and Appendix C, Tables C1 and C2. Individually, the Mg/Ca analyses for each sample scatter around the mean with the highest variability is found in *Gs. ruber* as it appears sporadically during MIS-33 and MIS-29, and prominently in MIS-31. It is absent throughout

the remainder of the record, except in very low numbers (*i.e.* n<9). To reflect more reliable temperatures, Mg/Ca or SST for *Gs. ruber* are subsequently shown where n>9 as red triangles and where n<9 as a black line. This was an arbitrary number but examination of the more larger datasets *e.g.* where n=22, a two-sample t-test did not show any significant difference between using the mean of 9 samples with the overall mean (see Supplementary Material 5.8.1, Tables 5.2a and b). This assumes that other samples share a similar relationship.

The pooled mean Mg/Ca was chosen to estimate SST as this is the traditional method with both solution and LA-ICP-MS *e.g. Anand et al.*, [2003]; *Sadekov et al.*, [2008]. It also minimises error in the prediction of any one value in the data set, such that it produces the lowest amount of error from all other values in the data set. Furthermore, all of the data can be included in the estimation. One of the issues with using the mean is that it is particularly susceptible to the influence of outliers. Outliers are values that are unusual compared to the rest of the data set by being especially small or large in numerical value. However, outliers can be statistically identified (see section 5.5.1).

It should be noted that Mg/Ca and subsequent temperatures that relate to lower numbers will be less reliable and should be interpreted with caution. Gaps between any *Gs. ruber* points indicate samples that did not have any *Gs. ruber* specimens present (Appendix C, Table C1). Also shown in Figure 5.4 are the 95% confidence intervals for the mean of each species (grey lines in A and B).



Figure 5.4: (A) Variability of mean Mg/Ca ratios in *Gs. ruber* (black line), red stars indicate where the number of samples (n) >9. (B) *G. bulloides* (black line) through the ODP Site 1123 sediment record. The grey lines represent the 95% confidence interval of the mean. For *Gs. ruber*, in some samples there were no individuals, although there were sporadic amounts within the deglacial and glacial intervals. For reference the grey shaded bars (top of figure) represents the MIS interglacial stages according to the *Lisiecki and Raymo*, [2005] global benthic stack.

G. bulloides was present during the entire sampling interval and generally records colder SSTs than *Gs. ruber* (where present) (Figure 5.5), except during the SH insolation maxima of MIS-31 (1080 kyr) where both species record the highest SSTs of ~18°C (*G. bulloides*) and ~19°C (*Gs. ruber*), which are 4 to 5 °C warmer than the present (annual) SSTs at the core site. While $SST_{Mg/Ca}$ from both species vary, they record a rapid warming of up to ~19°C at 1080 kyr in phase with the peak Southern Hemisphere insolation maxima. *G. bulloides* is the first to show

this warming, which from ~1100 kyr onwards increases from 9.2 to 16.2°C, although the warming appears to begin before the onset of local insolation. This is followed by a marked increase of subtropical taxa including *Gs. ruber*, which occurs at the expense of the Subantarctic taxa such as *N. pachyderma* and the eutrophic taxa *G. bulloides* [e.g. *Crundwell et al.*, 2008] (Fig 5.5). The appearance of *Gs. ruber* generally marks a change in SSTs to those at >14°C, (or greater), which is the minimum temperature tolerated for this species [*Bé*, 1977]. Throughout the record, *G. bulloides* gives mean glacial and interglacial temperatures of ~10.6 and 16°C respectively and during mid-glacial MIS-30 records temperatures up to 6.2°C lower than the modern temperature at this site. For comparison, SST data calculated using Artificial Neural Networks (ANN25) from the same core are shown [*Crundwell et al.*, 2008] and also temperature estimates using only the δ^{18} O compositions from the same samples. For the latter, the *Bemis et al.*, [1998] equation [Eq. 5.5] was used where T = 16.5 – 4.8(δ^{18} O_c – δ^{18} O_{sw}). The values of δ^{18} O_c were calculated by subtracting the modern mean ocean water reconstruction by *Waelboeck et al.*, [2002] from the foraminiferal δ^{18} O_c. For the δ^{18} O_{sw} modern measurements close to this studies core site were used averaging the values from 0-75m (Table 5.3).



Figure 5.5: (A) Orbital parameters eccentricity, precession and obliquity [*Laskar et al.*, 2004]. (B) Insolation at 42°S *Laskar et al.*, [2004]. (C) SST derived from Mg/Ca of *Gs. ruber* where n>9 (red triangles) and *G. bulloides* (blue diamonds) and δ^{18} O (black line) using the equation of *Bemis et al.*, [1998] where T = 16.5 – 4.8(δ^{18} O_c – δ^{18} O_{sw}) for *G. bulloides*. The standard mean ocean water reconstruction of *Waelbroeck et al.*, [2002] and modern estimates of δ^{18} O_{sw} from the Southwest Pacific Ocean (Helen Neil, unpublished data, Table 5.3) were used. (D) SST calculated from artificial neural network data in *Crundwell et al.*, [2008] re-calibrated onto this studies new age model. (E) Planktonic foraminiferal assemblage data also from *Crundwell et al.* [2008] showing the percentage abundance of *Gs. ruber*, *G. bulloides* and *N. incompta.* The horizontal orange line in B is the modern mean SST (14.7°C) at ODP Site 1123. Dotted lines indicate where peak SST(ANN) coincide with *Gs. ruber* maxima. For reference the grey shaded bars (top of figure) represents the MIS interglacial stages according to the *Lisiecki and Raymo*, [2005] global benthic stack.

5.4.3 Other trace element data (Al, Mn, Sr, Ba and Zn/Ca) in Gs. ruber and G. bulloides

Figure 5.6 shows the Mn, Sr, Ba and Zn/Ca ratios measured in *Gs. ruber* and *G. bulloides*. Al/Ca ratios can be used to screen for silicate contamination of foraminiferal tests, which may also affect Mg/Ca ratios. The average Al/Ca ratios for *Gs. ruber* and *G. bulloides* were 0.35 and 0.49 mmol/mol respectively and did not significantly co-vary with Mg/Ca suggesting that samples were unaffected by silicate/clay contamination. The Mg/Ca and Mn/Ca ratios in *G. bulloides* positively co-vary to some extent over the sampling period with Mn/Ca varying between ~0.1 and 0.4 mmol/mol (Figure 5.6). A similar relationship between Mg/Ca and Mn/Ca ratios is observed in the raw *Gs. ruber* data (not shown in Figure 5.6), although this is less clear compared to with *G. bulloides*, perhaps due to the smaller number of analysed *Gs. ruber* samples.



Figure 5.6 (previous page): (A) SST derived from Mg/Ca ratios of Gs. ruber (red triangles/line) and G. bulloides (blue line) (B) Sr/Ca ratios in Gs. ruber (grey triangles/line) and G. bulloides (black line) (C) Mn/Ca ratios in Gs. ruber (grey triangles/line) (D) Zn/Ca ratios measured in Gs. ruber (grey triangles/line) and G. bulloides (black line) and (E) Ba/Ca ratios measured in Gs. ruber (grey triangles/line) and G. bulloides (black line). For reference the grey shaded bars represent the MIS interglacial stages according to the Lisiecki and Raymo, [2005] global benthic stack. All samples are 3 –point moving averages.

In *G. bulloides*, Sr/Ca ratios throughout the entire record do not deviate from 1.20 to 1.35 mmol/mol. Similarly, Sr/Ca ratios for *Gs. ruber* show a restricted range from 1.24 to 1.56 mmol/mol. Zn/Ca ratios are low throughout the record with values typically $< 400 \,\mu$ mol/mol. However, after 1070 kyr, Zn/Ca ratios show consistently higher values than the remainder of the record. Correspondingly, the Ba/Ca ratios throughout the record are low, typically $< 50 \,\mu$ mol/mol. There are however, a number of excursions where the Ba/Ca is approximately three times higher during MIS-31 and throughout the glacial period of MIS-30 there are three excursions between $\sim 50{\text{-}100 \,\mu}$ mol/mol.

5.4.4 Stable isotope data and the $\delta^{18}O_{sw}$ 'salinity proxy' from G. bulloides

The estimated duration of MIS-31 from the planktic $\delta^{18}O_c$ record is ~20 kyr (1094 to 1074 kyr), as compared to 10-15 kyr in the benthic curve (1082 to 1067 kyr) (Figure 5.7). The *G. bulloides* $\delta^{18}O_c$ record over MIS32/31 displays a glacial–interglacial change from ~ -1.5 to 0.5‰. The $\delta^{18}O_c$ record from *G. bulloides* is similar to its paired SST_{Mg/Ca} record except that the $\delta^{18}O_c$ data are offset during the interglacial of MIS-31 when $\delta^{18}O_c$ lags the SST_{Mg/Ca} record by ~10 kyr (Figure 5.8).

The $\delta^{13}C_e$ data for *Gs. ruber* are sparse and not plotted on Figure 5.7 but are generally in phase with $\delta^{18}O_e$ *i.e.* where $\delta^{18}O_e$ is depleted, $\delta^{13}C_e$ is enriched. This pattern is not observed for *G. bulloides*, which during MIS-33 and from MIS-30 onwards has antiphased $\delta^{18}O_e$ and $\delta^{13}C_e$. During the MIS-31 peak, the planktic $\delta^{13}C_e$ and $\delta^{18}O_e$ are comparable to the benthic record, *i.e.* depleted in $\delta^{18}O_e$ and enriched $\delta^{13}C_e$ but are not in phase with the SST. The peak of MIS-31 is more prolonged than the benthic record, with the highest SST at ~1080 kyr, coincident with the peak summer hemisphere (SH) insolation maxima. The most depleted $\delta^{18}O_e$ indicates to an extent, the warmest temperatures are some 8 kyr later (1088 kyr). In *Gs. ruber*, the pattern prevalent in *G. bulloides* is not similar. The concurrent SSTs from both *Gs. ruber* and *G. bulloides* suggest a change in the upper surface waters during the peak of MIS-31 when these species record almost identical SST. However, at 1078 kyr, whilst the inferred SST's by *Gs. ruber* remain high, *G. bulloides* SST decrease until 1073 kyr when *Gs. ruber* disappears from the sediment record. By examining the difference in $\delta^{13}C_e$ from planktonic and benthic carbon isotopes measured *i.e.* $\Delta\delta^{13}C_{plk-ben}$ (Figure 5.7), a qualitative interpretation can be made. Large changes in $\Delta \delta^{13}C_{plk-ben}$ could indicate increased strength of export production and meridional overturning in the global ocean [*Oliver et al.*, 2009]. The $\Delta \delta^{13}C_{plk-ben}$ is enriched at the MIS-33/32 boundary and the glacial of MIS-29. However, from MIS-32/31 there is a general gradual increase in the $\Delta \delta^{13}C_{plk-ben}$.



Figure 5.7: (A) Orbital parameters [*Laskar et al.*, 2005]. (B) δ^{18} O (black curve) and δ^{13} C (green curve) from *Uvigerina* species along with (C) δ^{18} O (black) and δ^{13} C (green) for *G. bulloides* (3-pt mean). (D) The surface to deep water carbon isotope gradient as inferred from the Δ^{13} C from *Uvigerina* – *G. bulloides*. For reference the grey shaded bars (top of figure) represents the MIS interglacial stages according to the *Lisiecki and Raymo*, [2005] global benthic stack.

At the time of peak SH insolation at MIS-31 similar values of $\delta^{18}O_{sw}$ are obtained, 1.71 and 1.80 ‰ for *Gs. ruber* and *G. bulloides* respectively (Figure 5.8, Tables C4 and 5, Appendix C). The $\delta^{18}O_{sw}$ for both species are more enriched compared to modern annual $\delta^{18}O_{sw}$ values of 0.57‰ for 0.40‰ respectively (Supplementary Table 5.3). Following the SH insolation maxima (1080 kyr), the $\delta^{18}O_{sw}$ in *G. bulloides* rapidly depletes reaching its minima during the NH insolation maxima to ~0.15‰. This depletion in $\delta^{18}O_{sw}$ also occurs concurrently with a decrease in SST recorded in *G. bulloides*. Following the NH insolation maxima, the $\delta^{18}O_{sw}$ becomes more enriched, in concert with rapidly increasing SST. Depletion in $\delta^{18}O_{sw}$ is less variable, despite the overall decrease in SST. There is another brief depletion in $\delta^{18}O_{sw}$ MIS-29 which is also in phase with a small increase in NH insolation.



Figure 5.8: (A) Insolation at 42°S (red) and 42°N (blue) [*Laskar et al.*, 2004]. (B) SST calculated from Mg/Ca ratios in *G. bulloides*. (C) Calculated $\delta^{18}O_{sw}$ using the palaeotemperature equations from *Bemis et al*, [1998] where: T = 16.5 – 4.8($\delta^{18}O_c - \delta^{18}O_{sw}$) for *G. bulloides*. Blue solid line indicates 3-pt running mean *G. bulloides* and grey solid line show raw data. Blue and red lines indicate NH and SH insolation maxima. For reference the grey shaded vertical bars represent the MIS interglacial stages according to the *Lisiecki and Raymo*, [2005] global benthic stack.

5.4.5 Changes in size and weight of G. bulloides

The mean measurements of the width and height of each foraminiferal individual reveals a normal distribution with an average width (the normalisation parameter for weight), of 315 μ m for *Gs. ruber* and 343 μ m for *G. bulloides* (Appendix C, Table C6). Only *G. bulloides* weights are considered here as this species is present throughout the sampling interval.

Size-normalised weights (SNW) are heavier in glacial periods with lighter SNW in inter-glacial periods ranging from 2.1 to 5.7 ($10^2 \mu g/\mu m$) (Figure 5.9). The trend is more prominent during interglacial terminations, when decreasing SST coincides with increasing weight. However, from ~1100-1070 kyr the opposite trend is observed. The predicted SNW of *G. bulloides*, were derived from local core top data where predicted weight = [($\ln(SST_{Mg/Ca}/31.8)$]/-30.5 [*Marr et al.*, 2011] [Eqn. 5.6], confirm the deviation observed during the study interval. The predicted SNW are generally in-phase with the actual SNW throughout the record, but as described above become significantly offset at ~1100 until ~1070 kyr.



Figure 5.9: (A) *G. bulloides* derived SST versus (B) actual SNW and predicted SNW. Note that the (B) scale is reversed.

5.5 Discussion

5.5.1 Errors associated with the estimate

The uncertainties of average foraminiferal Mg/Ca ratios obtained by solution and LA-ICP-MS methods are not necessarily the same. LA-ICP-MS analysis of individual foraminifera allows examination of the components of mean Mg/Ca ratios. At first glance, the uncertainties of Mg/Ca ratios obtained from LA-ICP-MS methods appear to be larger than those from solution work. However, the reality is that unlike those obtained by LA-ICP-MS, the means obtained from solution work only contain analytical error, and do not give any information about variability. To compare the variances or 'errors' obtained from the two methods is therefore not appropriate. This issue highlights some key points:

- (1) The scatter from both species in this study is not attributable to analytical error as multiple analyses from a single chamber as measurement of Mg/Ca is typically (~±0.5°C). Larger 'errors' associated with each individual analysis largely reflect the environmental or biological variability within individual (intra) samples.
- (b) For down-core work, results from both solution and LA-ICP-MS methodologies are limited by the provenance of individual foraminifera down the core. Often, there is a trade-off between resolution and quantity. This is a problem shared by both methodologies, and it is often simply not possible to use more foraminifera, because simply there are none. Furthermore, in *Sadekov et al.*, [2008], a sample size of 15 *Gs. ruber* tests corresponded to an uncertainty of 2°C, (±1°C) which was almost identical to the sample size predicted by power analysis for an SST of 28°C (in that particular study location) and a target uncertainty of 2°C. Increasing the uncertainty to discern a 1°C difference in SST with 95% confidence, required the analysis of ~250 tests at a SST of 18°C and ~60 tests at 28°C.
- (c) 'Error' estimates from solution work are invariably smaller because these only contain measurement error -i.e. from repeated measurements of the same solution. They do not contain any information about the variability (environmental or biological) of the individual foraminifera that make up the sample. It is currently not possible to analyse

individual foraminifera by solution. However more recent studies are now using flow through techniques to clean tests followed by solution analysis on Gs. ruber using a smaller number of pooled specimens (e.g. 10 individuals) [Haarman et al., 2011]. The latter study showed the Mg/Ca ratios from the same sample ranged between the lowest (2.20 mmol/mol) and highest (4.94 mmol/mol). These Mg/Ca ratios are similar to those by Sadekov et al. [2008] for G. ruber from Sargasso Sea that ranged from 1.75 mmol/mol to 5.53 mmol/mol. This compares with a range of 1.29 mmol/mol to 3.79 mmol/mol (maximum range of 2.51 mmol/mol), from the down core measurements of Gs. ruber in this study (MIS-34 to 29). For G. bulloides the largest range through the MIS-29 to 34 was 3.86 mmol/mol (1.01 mmol/mol to 4.87 mmol/mol) compared to core top and plankton tow (some measured by LA-ICP-MS) which exhibited ranges of 4.3 mmol/mol [Ferguson et al., 2008] and 3.6 mmol/mol [Van Raden et al., 2011]. Although these comparisons are from different oceanographic settings they show reasonable variability between other samples that appear comparable to those in during the MIS-34 to 29 intervals. Similar comparisons with G. bulloides from other temperate regions will help reveal whether the variability down core is a reasonable representation compared to core top studies.

- (d) Calibrations should be based on assemblages of means rather than individuals, because the mean is the value most common, and produces the lowest amount of error from all other values in the data set. Given the inability to increase the numbers of foraminifera that make up each average, (see above), the other approach is to establish whether the sample mean is a reasonable estimate of the population mean. For this to be true, the sample mean should not contain outliers.
- (e) Examination of the individual measurements does not reveal any outliers. For example, if the highest and lowest 5% of the samples are removed from the mean, the value does not change by more than ~0.1 mmol/mol. A Dixon's Q test [*Miller and Miller*, 1984] can be performed to test this hypothesis. The test identifies rogue samples, which then should be eliminated from the rest of the sample as it would significantly bias the mean value. However application of this test on the dataset does not reveal any significant outliers. Therefore the variability of the individuals reflects the mean value (see Supplementary material 5.8.1, Table 5.6).

- (f) Additionally, the relationships found in *Bolton et al.*, [2011] and *Marr et al.*, [2011] that show significant differences between the older (*e.g.* F-2) chambers with the final chamber (F), still pertains (Appendix C, Tables C7 and C8).
- (g) It has been previously suggested that mean Mg/Ca variability of any given sample is partly controlled by biological factors [e.g. Bentov et al., 2005; 2006; Lea et al., 1999]. However, calibrations using the mean value still show a statistically significant relationship with temperature.
- (h) The Mg/Ca derived SST values compared to those measured by artificial neural networks (ANN) in the same core [*Crundwell et al.*, 2008] and calculated only from $\delta^{18}O_c$ show reasonably comparable trends (Figure 5.5). The main differences lie in the lower resolution of the ANN study, and the fact that their SST estimates are recording mean surface annual SST, and is thus more comparable to SST estimates of *Gs. ruber*. This can be seen particularly where the local solar insolation is high, as *Gs. ruber* numbers increase and are in phase with the peak SST recorded by ANN (Figure 5.5). The ANN-SST estimates were calibrated to surface temperatures where as *Gs. ruber* is calibrated at (0-50m), hence peak SST from ANN data appear to be more in phase with *G. ruber* SST. The $\delta^{18}O_c$ data however, show that the magnitudes between the two temperature proxies are comparable, except for the excursion during 1090-1080 (see below).

5.5.2 Palaeo-SSTs during MIS-34 to 29

During the cooling of MIS 33-32 (1110 to 1095 kyr) the lower $SST_{Mg/Ca}$ suggest the northward encroachment of SAW across the eastern end of Chatham Rise, where the absence of bathymetric constraints permit more water mass exchange compared to the main body of the Rise [*Chiswell and Sutton*, 1998] and with northward migration of SAW and a reduced Subtropical inflow [*Hayward et al.*, 2008]. During glacial stages movement of SAW northward is likely to occur with jetting of cold SAW across Mernoo Saddle where presently some exchange between northern STW and SAW occurs [*Nelson et al.*, 2000]. It was proposed that intensified current flows south of the Chatham Rise during the last glaciation, were a consequence of

more compressed SAW, lowered sea level, bathymetry, and expanded and stronger westerly winds [*Nelson et al.*, 2000; *Carter et al.*, 2004a]. These studies suggested that this system led to accelerated leakage to the north of Australasian SAW and upwelled Antarctic Intermediate Water (AIW) over Mernoo Saddle in a modified and intensified Southland Current with the expanded cold water masses displacing the south-flowing warm East Cape Current off the South-eastern North Island. Other possible movement may have occurred at the deep eastern end of Chatham Rise (*c.f. Chiswell and Sutton*, 1998). Additionally, Ba/Ca and Zn/Ca ratios at this time remain low, suggesting the presence of micro-nutrient low SAW. Microfaunal assemblage data from ODP Site 1123 show a comparable increase in the Subantarctic species *N. pachyderma* and eutrophic taxa whereas with a small decrease in Subtropical taxa [*Crundwell et al.*, 2008].

Warming of SST_{Mg/Ca} during MIS32/31 is concurrent with an increase in SH insolation, small (equivalent to ~3 m) increases in modelled sea level [Raymo et al., 2006; Pollard and DeConto, 2009], and perhaps precessional forcing of the SPSG [Villanueva et al., 1998; Herbert et al., 2001]. The increase in SST could also be reflecting changes in obliquity as the warming appears to begin at the onset of the increase in the obliquity phase (Figure 5.10). The near-identical SSTs of 18-19 °C recorded by *Gs. ruber* and *G. bulloides* during peak MIS-31 at ~1080 kyr are similar but slightly higher than those measured using artificial neural networks that estimate peak SST of 18-18.5°C [*Crundwell et al.*, 2008]. In comparison, the temperature estimates from δ^{18} O at the same time do not suggest a significant warming. This could be related to local regional hydrography and/or ice volume effects. For example local changes may also strongly influence the δ^{18} O water — salinity relationships [*Dekens et al.*, 2001].

As modern *G. bulloides* in the modern Southwest Pacific Ocean calcifies at $\sim 75 - 150$ m water depth and modern *Gs. ruber* at 0-50 m depth, one could surmise that the surface mixed layer was deeper or that *G. bulloides* calcified at similar (shallower) depths to *Gs. ruber* at this time. During the Antarctic Cold Reversal and Younger Dryas (~ 13.5 to 12 kyr), the range of planktic δ^{18} O from *Gs. ruber*, *G. bulloides* and *G. inflata* at Site MD2121, north of Chatham Rise (40°22.935'S; 177°59.68'E, 2314 m) had converged into a narrow band. This has been related to deeper mixed surface waters that were characteristic of the cooling trend driven from Antarctica, forcing a northward expansion of cold atmospheric and oceanic temperatures [*Carter et al.*, 2008]. Combined with the three fold increase in Zn/Ca and Ba/Ca (Figure 5.6), the data suggest an intensification of the micro-nutrient rich STW as a result of increased forcing at the pole (precession), such that the South Pacific Subtropical gyre [*Roemmich*, 2007] shifted southward. This shift in the water mass with increasing SST could explain the similar SST in both *Gs. ruber* and *G. bulloides* as a potential permanent shift in ENSO also occurred during this time in the Western tropical Pacific [*Russon et al.*, 2011]. It has been suggested that STW mass movement to the south is advected across from the East Cape Current and over Mernoo Saddle via the Southland Current (SC) (Figure 5.2). During other significantly warmer interglacials, such as MIS-11, the SC passed around the south end of New Zealand during MIS-11, 3 and 1 [*Hayward et al.*, 2008].

Other Southern Hemisphere studies from the same latitude to ODP Site 1123 located in the open ocean *e.g.* ODP Site 1090 in the SE Atlantic, (42 °54.8 'S, 8 °53.9'E, 3700 m) [*Becquey and Gersonde*, 2002; *Maiorano et al.*, 2009] or further south at ODP Site 704 (46°52.76'S, 07°25.23'E, 2350 m) [*Allen and Warnke*, 1991] and ODP Site 1094 (53.2°S, 5.1°E, 2818 m) [*Kanfoush et al.*, 2002] suggest a southward migration of the STF during MIS-31 that may have resulted from either modification of poleward heat transport and/associated zonal winds or polar amplification of an orbitally induced climate. During the Late Pleistocene, *Howard and Prell* [1992] in their reconstruction of the Southern Indian Ocean, found that the STF was north of its present position in the open ocean (40°S) for most of the past 500 kyr and south only during four major interglacial periods including MIS-11.

The warmest SSTs recorded during MIS-31 are also concomitant with a sudden increase in subtropical taxa that also suggest an enhanced subtropical inflow via SPSG, which is manifested by a small local increase in salinity (Figure 5.11). Following the peak SH insolation maxima, between 1080 and 1070 kyr, the SSTs recorded by *Gs. ruber* and *G. bulloides* slowly decrease. The minimum temperature recorded during MIS-30 is 6.7 °C (6.3 °C colder than modern interglacial temperatures). At the SH insolation minima, *Gs. ruber* disappears from the record. A second peak in planktic SSTs from *G. bulloides* occurs in conjunction with the precession maxima again suggesting an intensification of the SPSG accompanied by a southward movement of the STF (Fig 5.10). It can be argued that a third, but much lower amplitude SST warming occurred around 1040 kyr thus confirming precessional forcing of the warming at ODP 1123.



Figure 5.10: (A) Comparison between $SST_{Mg/Ca}$ with orbital precession. (B) Insolation values for 42°S and (C) comparison between $SST_{Mg/Ca}$ orbital obliquity over 1140 to 1000 kyr. Grey crosses and profile show *G. bulloides* SSTs, and black filled triangles show *Gs. ruber* SSTs where n>9. *Gs. ruber* appears during obliquity peaks whereas *G. bulloides* SSTs appear to be in phase partially with precession.

5.5.3 δ^{18} O and palaeo-salinity during MIS-33 to 29

The changes in SST lead the changes in δ^{18} O by as much as 10 kyr, suggesting that temperature changed before global ice volume and/or local hydrology [*Lea et al.*, 2000]. The paired measurements avoid any possible chronological offset due to seasonal or temporal bias, offsets in water column production depth, or from bioturbation. The main restriction lies in the accuracy of the absolute timing of events, which relies on the quality of the absolute chronology, of the δ^{18} O record to the benthic curve of *Lisiecki and Raymo* [2005].

Following conversion to an ice free residual, $\Delta \delta^{18}O_{IVF-sw}$, at ODP Site 1123 in *G. bulloides,* appears to record more positive values throughout the study period, thus indicating more saline conditions in this region than present day. During MIS-31, where the SST is highest, there is a concurrent increase in salinity, and Southern Hemisphere sea-level. This would indicate that any freshwater signal from melting Antarctica ice sheets is not observed at ODP

Site 1123. However, a decrease in $\Delta \delta^{18}O_{IVF-sw}$, related to a large freshening from global $\delta^{18}O_{sw}$ is observed during ~1080 to 1076 kyr, which coincides with peak NH insolation maxima (Figure 5.11). This suggests a significant contribution in freshwater from retreat of the NH ice sheets, with a concurrent shift to negative (fresher) conditions. There is strong evidence from other marine records that the timing of temperature and $\delta^{18}O_{sw}$ (ice volume) changes are not necessarily in phase, and that the phasing varies from place to place in the ocean [*Hays et al.*, 1976; Ruddiman and McIntyre, 1979; Lea et al., 2000].

The uncertainties in using these methods are much greater than those for calculating Mg/Ca as there is limited data on local $\delta^{18}O_{sw}$ *e.g.* [*Schmidt et al.*, 1999] with the implicit assumption that this relationship between salinity and $\delta^{18}O_{sw}$ remains constant through geologic time (*e.g. Rohling and Bigg*, 1998). In the absence of these data, the equations chosen appear to match reasonably well with core top data where independent equations using salinity and $\delta^{18}O_c$ were generated and compared (Supplementary Material, Figure 5.12).

In a core south of Chatham Rise (MD-2120) Pahnke et al., [2003] found similar albeit weaker $\delta^{18}O_c$ and SST_{Mg/Ca} from planktonic foraminifera reminiscent of the glacial climatic oscillations of Dansgaard-Oeschger and in the GISP2 ice core recorded in NH records. These oscillations coincided with orbital precession minima, analogous to this study's paired record and hence suggest that forcing from the NH is the cause of the large enrichment in $\delta^{18}O_{sw}$ following the SH insolation maxima. Similar oscillations to the timing of NH records have been found in other SH records, with the ocean conveyor as the most logical explanation [Charles et al., 1996]. Prior to the MPT the continental ice sheets were of limited size, and therefore more susceptible to rapid deglaciations [Maslin and Ridgwell, 2005]. Following the NH insolation maxima, a second SH insolation peak occurs at 1060 Kyr and marks a global shift in $\delta^{18}O_{sw}$ to more saline water, coinciding with a small SH sea level increase with a short reappearance in Gs. ruber that signal a brief excursion in STW. The duration of this is relatively short compared to the SH insolation maxima; G. bulloides records an increase in SST from ~10 to 15°C although the conditions were clearly not optimal for Gs. ruber which is either absent or present in small numbers. G. bulloides records the coldest temperatures during the glacial MIS-30 and appears to respond to small changes in NH insolation (1050 kyr) where both SST and $\delta^{18}O_c$ increase.



Figure 5.11: Changes in SST, $\delta^{18}O_{calcite}$ and $\delta^{18}O_{seawater}$ continental ice volume and local $\delta^{18}O_{sw}$ measured from *Gs. ruber* and *G. bulloides.* (A) Insolation at 42°N and 42°S. (B) SST converted from Mg/Ca ratios in *G. bulloides* (grey) and *Gs. ruber* (black triangles). Grey solid line indicates 3-pt running mean for *G. bulloides.* (C) The $\delta^{18}O_e$ measured in *G. bulloides* (black line) and *Gs. ruber* (black triangles). Black solid line indicates 3-pt running mean for *G. bulloides.* (D) Calculated $\delta^{18}O_{sw}$ using the palaeotemperature equations from *Bemis* [1998] where: T = 14.9 – 4.8($\delta^{18}O_e - \delta^{18}O_{sw}$) for *Gs. ruber* and T = 13.4 – 4.48($\delta^{18}O_e - \delta^{18}O_{sw}$) for *G. bulloides.* Blue solid line indicates 3-pt running mean *G. bulloides.* (E) The predicted $\delta^{18}O_{sw}$ from sea level from the Southern Hemisphere (red) and global sea level (blue) which was derived using the *Raymo et al.*, [2006] global sea level and converted to $\delta^{18}O_{sw}$ using the relationship from *Yokoyama et al.*, [2000] where $\delta^{18}O_{sw} =$ Sea Level * (1.1/-130 m). (F) $\Delta\delta^{18}O_{IVF-sw}$ (salinity excess), which represents regional hydrologic changes at ODP Site 1123 through MIS-34 to 29. Orange solid line indicates 3-pt running mean for *G. bulloides.* The red and blue vertical lines represent peak insolation at 42°S and 42°N respectively.

This significant amplitude in the planktic $\delta^{18}O_{sw}$ record provides evidence that the magnitude of millennial scale climatic oscillations is dependent on the state of the global climate. This study links the NH and SH and is consistent with a Late Pleistocene record to the south of ODP Site 1123 [*Pahnke et al.*, 2003]. This implies that although insolation was high in the SH, it did not have a significant effect (compared to the NH) to changes in global ice volume.

5.5.4 $\delta^{13}C$ during MIS-33 to 29

In G. bulloides the $\delta^{13}C_c$ is most enriched during the deglacial of MIS33/32, MIS-31 and during MIS-30 and was slightly more enriched than modern values of 0.27 ‰ (A. Bolton, unpubl. data). Over MIS-31 the $\delta^{13}C_c$ increases in concert with SST. These high $\delta^{13}C_c$ values are interpreted to indicate increased marine productivity from increases in photosynthesis at the surface. The events that show negative $\delta^{13}C_c$ excursions indicate the installation of a different regime dominated by more oligotrophic conditions. The largest $\Delta \delta^{13}C_{plk-ben}$ changes are observed at 1102 kyr (MIS33/32 transition), 1051 and 1043 kyr (MIS-32) kyr. These differences are partly due to a small lag between the planktic and the benthic signal, indicating an influence of older bottom water δ^{13} C but may also represent the merging of both STW and SAW above the core site. Weaker gradients on the other hand could indicate decreased export production, mixing between the deep and surface ocean, or a shift in downwelling [Oliver et al., 2009]. In addition to changes in the $\delta^{13}C_{DIC}$ the benthic record can also be affected from secondary overprints of extra ¹²C from areas of high productivity or shallow waters producing 'benthic fluff' productivity signal. High productivity at this site has occurred with frontal shifts as indicated by the changes in foraminiferal assemblages [Crundwell et al., 2008] and therefore needs to be taken into consideration.

5.5.5 Other trace elements (Ba, Mn, Zn and Sr/Ca)

Sr/Ca ratios remain relatively constant in all species throughout the entire record indicting that there is no detectable temperature dependence of this ratio in *Gs. ruber* or *G. bulloides*. Ba/Ca and Zn/Ca are low throughout the entire record. In the planktonic foraminifera of this thesis, there are 3 significant excursions of Ba/Ca to values > 100 μ mol/mol. These changes occur

shortly after the 1080 kyr in *Gs. ruber* and *G. bulloides* prior to the SH summer insolation minima and indicate increased fluxes in productivity [*Hönisch et al.*, 2011] (Figure 5.6). Increased productivity is supported by the marked increase in eutrophic mixed-layer taxa, especially *G. bulloides* (*e.g. Schiebel et al.*, 2001) and as shown in *Crundwell et al.*, [2008]. Assuming that Ba/Ca is a productivity indicator these changes would suggest a significant increase in productivity from 1060 and 1042 kyr. As the core site is north of Chatham Rise, presently a highly productive area, changes in productivity may be related to the intermixing of micro-nutrient poor and macro nutrient rich SAW with macro-nutrient poor but micro-nutrient rich STW [*Boyd et al.*, 2004]. Thus their mixing enhances productivity, as shown by present day chlorophyll concentrations [*Murphy et al.*, 2001].

The ratios of Zn/Ca have been suggested to correlate with silicic acid [*Lea*, 2003]. During the largest increase in Ba/Ca, the Zn/Ca ratio also increases from 1 to 25 µmol/mol, although this excursion is much shorter. However, apart from this excursion the Zn/Ca does not appear to vary with other trace elements or stable isotopes from this study. Although Zn concentrations are highest in surface waters they are not thought to be a limiting micro-nutrient for phytoplankton [*Ellwood*, 2004]. However, changes in Zn concentration may reflect shifts in surface water masses, which bring other limiting micro-nutrients such as iron [*Ellwood*, 2004]. *Marr et al.*, [2011] suggested changes in concentration of Zn in *G. bulloides* could be used to infer different water masses with elevated Zn/Ca ratios found in STW. If this interpretation is used, the Zn increases over MIS-30 it may imply that surface water mass exchange with the STF shifted south.

In *Gs. ruber* and *G. bulloides* the variation of Mn/Ca ratios is similar to that of Mg/Ca and to some extent $\delta^{18}O_c$ and this pattern is analogous to other studies. *Wei et al.*, [2009] showed climatic variations at ODP Site 1144 (South China Sea), where Mn/Ca ratios were roughly in phase with SST (Mg/Ca) and $\delta^{18}O_c$ in the planktonic foraminifer *Globigerinoides sacculifer*. Their Mn/Ca ratios varied from 0.02 to 0.49 mmol/mol (comparable to this work of 0.05 to 0.40 mmol/mol). *Klinkhammer et al.*, [2009] found co-variance of water column Mn and core top Mn/Ca from ODP Site 1242 (Panama Basin) and suggest that the partition coefficients for Mn (K_{Mn}) of the three species they studied were similar. However, there are *a priori* two potential sources of Mn to the tests, and hence two possible reasons for Mn-Mg correlations. Either the Mn was acquired in the upper oceans, hence potentially could be a tracer of ocean chemistry. Or, it was acquired from the sediments, in which case it is *post vivo* and could be viewed as contamination, albeit tracking changes in bottom water chemistry and potentially redox conditions.

LA-ICP-MS studies [Eggins et al., 2003; Reichart et al., 2003] have shown distinct enrichment of trace elements including Mn on outer and inner surfaces of selected foraminifera. These surface enrichments are often high in Cd and Ba as first observed by *Boyle* [1983]. The micro-analytic results of *Pena et al.*, [2008] report contamination of tests of *G. ruber* and *N. dutertrei* with Fe-Mn oxides and Mn-Mg carbonates. That work proposes that those species with more pores and spine holes (e.g. G. ruber) will carry more contamination, and that contamination is difficult to remove except by "reductive" cleaning. Unfortunately, this cleaning technique also induces partial dissolution of the actual foraminiferal calcite and thereby can cause a decrease in measured Mg/Ca ratios [*Boyle*, 1981; *Brown and Elderfield*, 1996; Rosenthal et al., 2000; Martin and Lea, 2002]. It may be that the results of *Pena et al.*, [2008] represent a "worst case" scenario – that work was carried out in a basin that is characterized by sediments that are somewhat anoxic and particularly rich in manganese minerals [*Pedersen and Price*, 1982; *Reimers*, 1987], conditions that promote manganese reduction reactions.

In this work, LA-ICP-MS was used to identify and exclude surface coatings such that the trace element ratios presented are those from the innermost biogenic calcite. Therefore the Mn/Ca ratios in this study are not likely to be Mn oxides or manganese carbonate overgrowths because LA-ICP-MS analyses were made on the internal layers of the foraminferal chamber and the external surfaces were excluded.

However, this is not to say that the foraminiferal Mn/Ca ratios reported in this work are unambiguously a signature of the surface oceans. Other data from plankton tow samples in *Gs. ruber*, report low Mn/Ca (*e.g.* Chapter 3). If there are sedimentary processes that can insert Mn into the calcite lattice, then the results reported here could be a diagenetic overprint. However, the generally low Mn/Ca ratios overall suggest this is not happening in this core.

5.5.6 Size-normalised weights – changes in carbonate chemistry during early MIS-31?

With regards to the size/ δ^{13} C relationship, the δ^{13} C difference for *G. bulloides* between the 250-300 and 300-350 µm size fractions was only 0.04 ‰ suggesting that size is unlikely to significantly influence the δ^{13} C. Culturing work on *G. bulloides* attributed changes in δ^{13} C to carbonate ion concentration [CO₃²⁻] [*Spero et al.*, 1997]. This could explain the apparent relationship between size-normalised weight (SNW) and δ^{13} C. However, recent work on cultured *G. bulloides* did not find a significant relationship with test weight and [CO₃²⁻] [*Beer et al.*, 2010]. The predicted weight relationship suggests a shift from the general trend indicating a significant change in the carbonate chemistry at this time.

SNW also generally correlate with SST in *G. bulloides* over glacial-interglacial cycles (Figure 5.8). The effect of SST on carbonate chemistry may be manifested from dissolution of tests although dissolution may also be a feature of post depositional change in pH brought about by organic material in the sediments. Evidence of dissolution was observed around 1096 kyr at the MIS-32 glacial maximum as evinced by fewer specimens, plus a minor increase in the planktic to benthic fragmentation ratios (~5) [*Crundwell et al.*, 2008]. Increased dissolution generally coincides with warm interglacial episodes [*Farrell and Prell*, 1989; *Le and Shackleton*, 1992] so that increasing dissolution lowers the Mg/Ca [*Brown and Elderfield*, 1996; *Rosenthal et al.*, 2000; *Dekens et al.*, 2002]. The SNW matches well with those from the predicted weights of *Marr et al.*, [2011] and although the apparent offset during early MIS-31 may indicate a dissolution artifact, the weights show a general increase towards MIS-31, converse to a dissolution effect.

SNW of planktic foraminifera have been previously linked to changes in surface ocean carbonate ion concentration $[CO_3^2]$ [Barker and Elderfield, 2002; Moy et al., 2009]. Different species may have different primary factors that govern changes in weight over glacial to interglacial cycles [Gonzalez-Mora et al., 2008]. Reductions in shell weights are thought to be related to changes in calcium carbonate (CaCO₃) export in the surface ocean and changes in atmospheric pCO₂ [Barker and Elderfield, 2002]. Increased pCO₂ results in the drawdown into the oceans, which in turn modifies the carbonate chemistry in the upper oceans [Petit et al., 1999]. The change in CO₂ results in the decrease of pH and [CO₃²] which has been linked to reduction of calcification rates in planktonic foraminifera [Moy et al., 2009]. Therefore the

weights of planktonic foraminifera may be indicative of changes to the carbonate system equilibrium related to atmospheric carbon released from greenhouse gases.

Recent culturing experiments on *Gs. ruber* and *G. bulloides* concluded that environmental influences other than $[CO_3^{2^2}]$ were most likely the dominant control on foraminifera calcification rate [*Beer et al.*, 2010]. In the culturing study by *Beer et al.*, [2010] *Gs. ruber* showed a statistically significant inverse correlation with $[CO_3^{2^2}]$, temperature, salinity and the SWN. $[CO_3^{2^2}]$ relationships observed were not necessarily indicative of causal relationships. *Gs. ruber* is a symbiotic species and therefore thought to be less sensitive to changes in $[CO_3^{2^2}]$ than those that do not harbour symbionts [*Lombard et al.*, 2010]. In this study, as with *G. bulloides*, changes with increased SST affected shell weights where the peak SH insolation maxima of MIS-31 coincided with lower shell weights including pCO₂ [*Gonzalez-Mora et al.*, 2008]. Previous data from core tops in the Southwest Pacific show the weights of *Gs. ruber* is weakly correlated to SST ($r^2 = 0.26$) (Chapter 4, Supplementary Material) where SNW is strongly inversely correlated in *G. bulloides* [*Marr et al.*, 2011].

Gametogenic calcite may bias the weights as traditionally the onset of gametogenesis occurs in colder waters [*Caron et al.*, 1990]. For example, although typically inhabiting the mixed-layer, during their life cycle, *Gs. ruber, G. sacculifer, G. bulloides* and *N. pachyderma* may produce gametogenic calcite, formed at greater depths [*Erez and Luz,* 1983; *Niebler et al.*, 1999]. Given that *Gs. ruber* disappears during glacial to early deglacial periods, *G. bulloides* is the only reliable indicator of weights throughout the entire glacial to interglacial cycles studied. *G. bulloides* produced gametogenic calcite in specimens larger than 150 µm in a study by *Schiebel et al.*, [1997] although this is converse to similar studies that claim this species (neither *Gs. ruber*) does not add a gametogenic calcite layer of significance [*Hamilton et al.*, 2008]. The presence or absence may be related to changes *i.e.* movement to colder waters. Therefore the changes in weights may be related to changes within the mixed layer (*i.e.* increased nutrients, or changes to $[CO_3^2]$ or a combination of both). However, during these colder temperatures, although the laser ablation profiles appear to record a small number of individuals with a lower initial Mg/Ca ratio which may indicate the presence of a gametogenic layer, it was generally thin, and therefore is unlikely to control the variability of weights.

This study has shown that the application of weights as a proxy for changing calcium carbonate chemistry may be limited and complicated by additional environmental factors (*e.g.*, temperature, nutrient availability, $\delta^{18}O_{sw}$ that appear to partially co-vary). Interestingly, size may also provide an alternative to weights as it is not affected by gametogenic calcite (typical thicknesses of this crust is negligible) and will not be affected by weight loss from potential dissolution (Appendix C, Table C6).

5.6 Summary and Implications for future global warming scenarios

Temperatures at ODP Site 1123 during MIS-31 were 4 to 4.5°C warmer than present day. Given the distribution of modern ocean temperatures under the present phase of global warming, it is likely that SSTs around Antarctica also increased and caused substantial melting. Indeed, *Pollard and DeConto* [2009] modelled a retreat and possible collapse of the WAIS with a 5°C warming of nearby seas. At ODP 1123, peak SSTs led ice volume changes by 10 kyr.

Insights into potential causes of warming at MIS-31 are suggested from observations of the modern and past ocean/climate system. In light of ODP 1123's proximity to the South Pacific Subtropical Gyre (SPSG), warm pulses are likely to be related to the strength of the gyre as well as to a general atmospheric warming of the ocean from increased precessional forcing. In the present phase of warming, the SPSG has spun-up mainly in response to an increase in the zonal westerly winds [Roemmich et al., 2007]. A more energetic gyre would affect transport within the East Australian Current (EAC) and its outflows to New Zealand (Tasman Front) and Tasmania (EAC extension) [Ridgway and Dunn, 2007; Hill et al., 2008]. Between 1944 and 2002 the intensification of the SPSG has indeed enhanced the EAC but transport has been focused on the EAC extension, which has shifted \sim 350 km poleward (Figure 5.2). In contrast, transport in the Tasman Front has declined although continues to maintain warm seas [Sasaki et al., 2008; Ridgway and Hill, 2009]. I suggest that during the MIS 32-31 deglaciation, the zonal westerly winds and SPSG migrated south from latitudes lower than present (e.g. Martinez, 1994) and during the course of this migration the Tasman Front inflow to New Zealand increased, perhaps in response to the finding of gaps in the Norfolk Ridge, to enhance its input to ODP 1123. With migration further south the Tasman Front inflow may have reduced although high insolation would have still maintained warmth in the overall ocean. Accompanying the warmth was a possible change in the surface ocean thermal structure where by *Gs. ruber* and *G. bulloides* either calcified at a similar depth implying a change from these species usual habitat depths, or that there was a change to the depth of the mixed layer from an intensified SPSG.

Glacial periods either side of MIS-31 show more intense forcing from the Southern Ocean, as the STF shifted further north. This is shown by the disappearance of *Gs. ruber*, decrease in $\delta^{18}O_{sw}$ and SSTs that were lower than 14°C reaching a minimum 7°C during MIS-30 as recorded by *G. bulloides*. Other studies also show that SSTs led benthic foraminiferal $\delta^{18}O_c$ by several thousand years during the Late Pleistocene [*Liu and Herbert*, 2004; *Medina-Elizalde and Lea*, 2005; *Herbert et al.*, 2010]. These studies infer the lead of SST over continental ice volume was not controlled by the direct radiative influence of Northern Hemisphere continental ice sheets. These studies show phasing of SSTs with SH precession in *G. bulloides* and suggest perhaps that the NH was out of phase, in agreement with *Raymo, et al.* [2006] and *Scherer, et al.* [2008].

5.7 Conclusions

Mg/Ca data for planktic foraminifera generated from the southern mid-latitude ODP Site 1123, on the Chatham Rise, east of New Zealand, indicates that MIS 31 was 4-5°C warmer than modern interglacial SST. As calculated from the Mg/Ca data measured in *Gs. ruber* and *G. bulloides* using available calibrations, SSTs reach up to 19°C compared to typical temperatures of ~14 to 13°C for each species, respectively. The timing of the SST peak in MIS 31, ~1081 kyr on the LR04 time scale [*Lisiecki and Raymo*, 2005], appears to precede the minimum in ice volume, as indicated by the δ^{18} O record, by ~10 kyr. MIS 31 as inferred from the benthic δ^{18} O lasts for 15 kyr compared to 20 kyr from the planktonic record. A warm subtropical intensification of the SPTG during MIS 31 is supported by elevated foraminiferal Zn/Ca and Ba/Ca ratios. To summarise, the SST and stable isotope recorded in foraminifera at ODP Site 1123 suggest that:

(1) During the peak MIS-31 interglacial, *G. bulloides* and *Gs. ruber* SSTs converged but outside this peak *G. bulloides* recorded lower temperatures than *Gs. ruber*. This implies a

change in the calcification habitat such that they both calcified close to the surface or a deeper mixed layer.

- (2) The increase in subtropical taxa and SST recorded at MIS-31 suggest a southward shift of the SPSG.
- (3) The ocean temperatures inferred from Gs. ruber appear to be in phase with obliquity but the lack of continuous data make the relationship between either orbital parameter difficult. G. bulloides appears to be in phase with precession which indicates a shift in the SPTG (and STF) to the south.
- (5) The SNW of *G. bulloides* correlate with SST, δ^{18} O and δ^{13} C. The general relationship with temperature is such that warmer temperatures result in lower SNW, except from early MIS-31. It is unclear as to which environmental variable(s) are the causes of these relationships but the data suggest that there is a significant shift in the carbonate chemistry in early MIS-31.
- (6) Mn/Ca ratios appear to co-vary with Mg/Ca. This is interpreted to reflect, in part, a change in surface ocean chemistry, although there is also a possibility of a diagenetic overprint.
- (7) Stable isotope records in planktonic foraminifera are partially in phase with Mg/Ca ratios. The SST in planktonic foraminifera lead the benthic stable isotope by 10 kyr inferring that SST variability is not controlled by continental ice sheets but local/regional changes in hydrography. The enriched $\delta^{13}C_c$ values during MIS-31 are interpreted to indicate higher marine productivity from increases in photosynthesis at the surface.

Supplementary Material

Table 5.1: Age control points for core ODP Site 1123

Depth	Age	Age Control Points	Calibration and references			
(mbsf)	(Kyr)					
		$\delta^{18}O_b$ tuned to $\delta^{18}O_b$ of Lisiecki and	$\delta^{18} O_b$ tuned to $\delta^{18} O_b$ of Lisiecki and			
40.073	1021.7720	<i>Raymo</i> [2005]	Raymo [2005]			
		$\delta^{18} O_b$ tuned to $\delta^{18} O_b$ of Lisiecki and	$\delta^{18} O_b$ tuned to $\delta^{18} O_b$ of Lisiecki and			
40.490	1033.8754	Raymo [2005]	Raymo [2005]			
		Palaeomagnetic reversal (base of				
		Jaramillo subchron @ 41.68 mbsf)				
41.247	1058.2485	interpolated at 1070 Kyr	Prof. G. Wilson, pers. comm.			
		$\delta^{18}O_b$ tuned to $\delta^{18}O_b$ of Lisiecki and	$\delta^{18} O_b$ tuned to $\delta^{18} O_b$ of Lisiecki and			
41.688	1069.9759	<i>Raymo</i> [2005]	<i>Raymo</i> [2005]			
		$\delta^{18}O_b$ tuned to $\delta^{18}O_b$ of Lisiecki and	$\delta^{18} O_b$ tuned to $\delta^{18} O_b$ of Lisiecki and			
42.366	1084.4456	Raymo [2005]	Raymo [2005]			
		$\delta^{18}O_{b}$ tuned to $\delta^{18}O_{b}$ of Lisiecki and	$\delta^{18}O_b$ tuned to $\delta^{18}O_b$ of Lisiecki and			
42.989	1108.1658	Raymo [2005]	Raymo [2005]			
		$\delta^{18}O_{b}$ tuned to $\delta^{18}O_{b}$ of Lisiecki and	$\delta^{18}O_b$ tuned to $\delta^{18}O_b$ of Lisiecki and			
43.184	1120.1347	Raymo [2005]	Raymo [2005]			
		$\delta^{18}O_{b}$ tuned to $\delta^{18}O_{b}$ of Lisiecki and	$\delta^{18}O_b$ tuned to $\delta^{18}O_b$ of Lisiecki and			
43.294	1128.1865	Raymo [2005]	Raymo [2005]			

5.8.1 Complementary data from ODP Site 1123

The original *Hall et al.*, [2001] and subsequent *Crundwell et al.*, [2008] age models were based on a spliced composite section where holes 1123B and 1123C were used. As this study uses only

data from the 1123C hole, data from hole 1123B was converted to the hole 1123C age model using the palaeomagnetic susceptibility data from both cores (Supplementary Figure 5.12). This then allows the other proxy data from *Crundwell et al.*, [2008] to be incorporated into this study.



Figure 5.12: Correlation of ODP Site 1123 palaeomagnetic susceptibility data from hole 'B' (grey curve) (A) to hole 1123'C' (black curve) (B) which was derived using Analyseries resulting in (C) which shows the palaeomagnetic data from both cores on the same scale (mbsf). The new age model derived was then correlated using the depths from the in 1123C core to give the age in (D). The U-channel palaeomagnetic susceptibility data from core 1123C was used to tie the base of the Jaramillo subchron (C1r.1n) at 41.68 mbsf to 1.072 Ma, black line in (B). Red squares represent visual tie points from 1123B to 1123C.

5.8.2 Estimation of $\delta^{18}O_{sw}$ from salinity relationships

The oxygen isotopic composition of seawater ($\delta^{18}O_{sw}$) has a demonstrated linear relationship with sea surface salinity and therefore has been used to reconstruct palaeosalinity [*Schmidt et al.*, 2006]. In some oceanographic regions these relationships are well established, particularly with the increased measurements of $\delta^{18}O_{sw}$ from studies such as GEOSECS [*Schmidt et al.*, 1999]. In the Southwest Pacific Ocean, local $\delta^{18}O_{sw}$ measurements are however more scarce. Therefore $\delta^{18}O_c$ in the foraminiferal tests of *Gs. ruber* and *G. bulloides* (A. Bolton, unpubl. data) were used in conjunction with estimated $\delta^{18}O_{sw}$ in order examine the palaeo-seawater equations available for *Gs. ruber* and *G. bulloides*. The derived $\delta^{18}O_{sw}$ values estimated from the salinity relationships were also compared to local measurements from north of Chatham Rise (Table 5.3) and some locations that were located close to GEOSECS stations [*LeGrande and Schmidt*, 2006].

The measured $\delta^{18}O_c$ coupled with estimated $SST_{Mg/Ca}$ and salinity measurements which were used to calculate $\delta^{18}O_{sw}$ using the following equations:

$$\delta^{18}O_{sw} = 0.687 * \text{site salinity} - 23.74 [Savin et al., 1985]$$
 [Eq. 5.7]

$$\delta^{18}O_{sw}$$
 (South Pacific) = -0.45 * site salinity - 15.29 [LeGrande and Schmidt, 2006] [Eq. 5.8]

$$\delta^{18}O_{sw} = 0.5 * \text{site salinity} - 35 [Craig and Gordon, 1965] [Eq. 5.9]$$

$$\delta^{18}O_{sw} = \text{site salinity} - 34/1.465 [Schmidt et al., 1999]$$
 [Eq. 5.10]

The averaged depth preference for *Gs. ruber* is assumed to be 0-50 m and 75 to 150 m for *G. bulloides* and the range of $\delta^{18}O_{sw}$ over this depth range is 0.57 to 0.39 ‰ (Table 5.6, Dr. H. Neil, unpubl. data). The $\delta^{18}O_{sw}$ estimates are shown in Tables 5.3 and 5.4 for *Gs. ruber* and for *G. bulloides*, respectively. Given the lack of $\delta^{18}O_{sw}$ measurements close to Chatham Rise, the equations by *Le Grande and Schmidt* [2006] and *Savin et al.*, [1985] appear to match well to those north of Chatham Rise. However for *G. bulloides* the estimated $\delta^{18}O_{sw}$ is much closer to $\delta^{18}O_{sw}$ values from the sea surface (Table 5.3).

Other GEOSECS $\delta^{18}O_{sw}$ measurements that lie close to tropical core tops show $\delta^{18}O_{sw}$ of -0.69 ‰ (AIMS1361) and 0.07 ‰ (AIMS3703) and highlight potential regional differences (*i.e.* local precipitation and evaporation processes in the tropics). Given this information the salinity

equations of *Le Grande and Schmidt* [2006] were chosen to estimate $\delta^{18}O_{sw}$ in *Gs. ruber* and *Savin et al.*, [1985] for *G. bulloides*.

n vs. all data	t stat	t-crit	df	р	different?
8	0.290	2.131	15.000	0.776	no
9	-0.112	2.120	16.000	0.912	no
10	-0.330	2.093	19.000	0.745	no
15	-0.066	2.045	29.000	0.948	no
18	-0.479	2.030	35.000	0.635	no

Table 5.2a: Two sample t-test (two-tailed) for Mg/Ca ratios from sample age 1081.8383 and n=19.

* Unequal variances were assumed.

Table 5.2b: Two sample t-test (two-tailed) for Mg/Ca ratios from sample age 1110.8879 and n=22.

n vs. all data	t stat	t-crit	df	р	different?
8	1.454	2.145	14	0.168	no
9	1.235	2.120	9	0.235	no
10	1.316	2.086	20	0.203	no
15	-0.132	2.045	29	0.896	no
20	-0.022	2.021	40	0.983	no

* Unequal variances were assumed.

For both Tables 5.2a and b if t stat is > t-crit then there is a significant difference between the means (n versus all the data). The data show that there is no significant difference between using 9 as a sample mean versus using all of the data.

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Depth	Measured $\delta^{18}O_{sw}(\%_0)$
10	0.57
20	0.55
30	0.51
50	0.52
75	0.46
100	0.4
150	0.39
200	0.33
300	0.23
500	-0.1
750	-0.28
1000	-0.36
1500	0.21
2000	0.13
2500	0.11
3085	0.14

Table 5.3: $\delta^{18}O_{sw}$ from north of Chatham Rise (courtesy of H. Neil, unpubl. data).

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Sample	Latitude	δ18Ο	Modern Annual SST (75-150 m)	Modern Salinity	<i>Savin</i> <i>et al.</i> , [1985]	Le Grande and Scmidt [2006]	Craig and Gordon [1965]	<i>Schmidt</i> <i>et al.,</i> [1999]
	°S	(°C)	(‰)	(‰)	δ ¹⁸ O _{sw} (‰)	δ ¹⁸ O _{sw} (‰)	δ ¹⁸ O _{sw} (‰)	δ ¹⁸ O _{sw} (‰)
AIMS1361	3.37	-2.59	27.62	34.5	-0.04	0.24	-0.25	0.34
AIMS3703	11.153	-2.81	22.16	34.4	-0.11	0.19	-0.30	0.27
TAN0706	29.355	-1.01	22.65	35.7	0.79	0.78	0.35	1.16
P71	33.855	-0.48	22.40	35.6	0.72	0.73	0.30	1.09
Z7003	36.69	-0.33	22.79	35.5	0.65	0.69	0.25	1.02
U2315	38.509	-0.96	20.97	35.6	0.72	0.73	0.30	1.09
ODP1123	41.786	0.63	12.28	35.1	0.37	0.51	0.05	0.75

Table 5.4: Estimation of $\delta^{18}O_{sw}$ using existing calibrations for Gs. ruber

						Le		Schmidt
						Grande		et al.,
					Savin	and	Craig and	[1999]
_					et al.,	Scmidt	Gordon	
Sample	Latitude	$\delta^{18}\mathbf{O}$	SST _(Mg/Ca)	Salinity	(1985)	(2006)	(1965)	
					5180	$\delta^{18}O_{\rm sw}$	$\delta^{18}O_{sw}$	$\delta^{18}O_{sw}$
	00		(0/)	(0/)	$0^{10} \mathbf{U}_{sw}$	(0/)	(0/)	(‰)
	-3	(*C)	(%00)	(%00)	(%00)	(%00)	(%00)	
P71	33.855	-0.26	17.40	35.64	0.74	0.75	0.32	1.11
P81	34.02	0.07	16.10	35.47	0.63	0.67	0.23	1.00
S793	36.3	0.32	15.40	35.42	0.59	0.65	0.21	0.99
S938	40.03	1.27	18.80	35.53	0.67	0.70	0.27	1.04
P69	40.4	0.75	19.10	35.57	0.70	0.72	0.29	1.07
R623	43.2	1.89	12.00	35.04	0.33	0.48	0.02	0.70
ODP1123	41.786	0.92	13.79	35.38	0.57	0.63	0.19	0.94
Q220	44.29	2.41	9.20	34.55	0.00	0.26	-0.23	0.37
D178	51.72	2.57	7.20	34.40	-0.11	0.19	-0.30	0.27
F111	48.95	2.22	7.30	34.45	-0.07	0.21	-0.27	0.30
B32	53.63	2.65	7.50	34.4	-0.11	0.19	-0.30	0.27

This study's independent estimate of temperature (SST_{Mg/Ca}) allows the substitution into a number of equations to rearrange for $\delta^{18}O_{sw}$ so as to compare previously established temperature relationships. *Bemis et al.*, [1998] in experiments on cultured *G. bulloides* developed a number of equations based on the test size (number of final chambers), showing a small enrichment of $\delta^{18}O_c$ with increasing ontogenetic calcite. However these experiments are limited to the culturing parameters, in this case their temperatures were set between 15 to
24°C. The variability of SSTs from ODP Site 1123 ranges from 9 to 19°C, and would therefore mean that extrapolation of these relationships would be required to estimate the δ^{18} O relationships at the colder end of the dataset. For colder oceanic temperatures, discrepancies can occur *e.g.* For *Bemis et al.* [1998] these were as much as 5°C.

G. bulloides 12-chambered shell [Bemis et al., 1998]:

$$T(^{\circ}C) = 13.2 - 4.89(\delta^{^{18}}O_{c} - \delta^{^{18}}O_{sw}) \qquad [Eq. 5.11]$$

G. bulloides (cultured) [Bemis et al., 2002]:

$$T(^{\circ}C) = 14.2 - 4.44(\delta^{18}O_{c} - \delta^{18}O_{sw})$$
 [Eq. 5.12]

G. bulloides [Mulitza et al., 2003]:

$$T(^{\circ}C) = 13.4 - 4.48(\delta^{18}O_{c} - \delta^{18}O_{sw})$$
 [Eq. 5.13]

Orbulina universa (high-light) used for Gs. ruber [Bemis et al., 1998]:

$$T = 14.9 - 4.8 \ (\delta^{18}O_c - \delta^{18}O_{sw}) \qquad [Eq. 5.14]$$

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The Orbulina universa equation was selected as it is a symbiotic foraminifera, as is Gs. ruber. So far no other suitable equations exist because Gs. ruber is difficult to sustain in culture. Figure 5.13 shows the derived equations for Gs. ruber from core top samples closely match those for O. universa [Bemis et al., 1998] and for G. bulloides the [Bemis et al., 2002].



Figure 5.13: Relationships between temperature and $(\delta^{18}O_c - \delta^{18}O_{sw})$ in (A) *Gs. ruber* and (B) *G. bulloides* core top derived data (Chapter 4) and unpublished $\delta^{18}O_c$ data (A. Bolton, 2009) from *G. bulloides* core tops (in addition to data from *Marr et al.*, [2011] with other extant calibrations.

Table 5.6: Dixons's Q test of outliers in the sample means

	age (kyr)	extreme low	next low	next high	extreme high	Q	Qcrit	Outliers?
1	1017.6033	2.17	2.44	2.45	2.73	0.51	0.83	no
2	1018.7824	1.66	2.18	2.62	2.80	0.45	0.83	no
3	1019.9615	1.60	1.72	3.06	4.28	0.45	0.83	no
4	1020.0015	1.55	1.83	2.50	3.52	0.52	0.83	no
5	1022.3198	1.55	1.76	2.35	3.00	0.45	0.83	no
6	1022.3598	1.23	1.23	2.75	3.22	0.24	0.83	no
7	1024.6781	1.76	1.89	2.48	3.08	0.45	0.83	no
8	1025.8572	1.19	1.56	2.00	3.24	0.60	0.83	no
9	1027.0363	1.71	2.06	2.23	2.78	0.51	0.83	no
10	1029.3946	1.36	1.64	2.35	2.70	0.26	0.83	no
11	1029.4346	1.32	3.07	3.07	3.60	0.77	0.83	no
12	1029.4746	1.11	2.36	2.72	2.72	0.78	0.83	no
13	1031.7529	1.05	2.25	3.44	3.65	0.46	0.83	no
14	1032.9320	2.74	2.89	3.31	3.31	0.27	0.83	no
15	1034.1111	1.35	2.16	2.16	3.22	0.57	0.83	no
16	1034.9955	0.72	1.53	2.60	2.89	0.37	0.83	no
17	1036.4694	1.03	1.52	1.76	2.62	0.54	0.83	no
18	1036.5033	0.87	0.87	1.94	2.40	0.30	0.83	no
19	1038.8276	1.02	1.23	1.56	3.03	0.73	0.83	no
20	1038.8616	1.45	1.45	2.35	3.57	0.57	0.83	no
21	1038.8955	1.02	2.07	4.31	4.31	0.32	0.83	no
22	1038.9294	1.12	1.39	2.25	2.86	0.35	0.83	no
23	1043.5442	1.26	1.41	4.65	4.65	0.04	0.83	no
24	1043.5842	1.17	1.86	2.31	2.40	0.56	0.83	no
25	1043.6242	1.14	1.43	2.67	3.09	0.22	0.83	no
26	1043.6642	1.23	1.40	2.01	3.06	0.57	0.83	no
27	1048.2607	1.32	1.63	2.17	4.70	0.75	0.83	no
28	1048.3007	1.88	1.88	2.28	2.93	0.62	0.83	no
29	1048.3407	1.50	2.20	2.60	3.28	0.39	0.83	no
30	1051.7981	1.25	2.41				0.83	
31	1051.8381	1.23	1.24	1.90	1.90	0.01	0.83	no
32	1051.8781	1.16	2.06	2.88	3.98	0.39	0.83	no
33	1051.9181	1.01	2.37	3.19	4.87	0.44	0.83	no
34	1056.5146	2.17	2.17	2.81	3.99	0.65	0.83	no
35	1056.5490	1.58	2.10	2.45	4.88	0.74	0.83	no
36	1058.8435	1.63	2.48	3.12			0.83	

	age (kyr)	extreme low	next low	next high	extreme high	Q	Qcrit	Outliers?
37	1058.8778	1.92	2.02	3.51	4.70	0.43	0.83	no
38	1060.0068	1.18	1.18	3.41	4.45	0.32	0.83	no
39	1060.0412	1.63	2.83	3.13	3.71	0.57	0.83	no
40	1060.0756	1.19	1.86	2.61	3.01	0.37	0.83	no
41	1061.7518	1.45	2.12	3.12	5.15	0.55	0.83	no
42	1061.7862	1.72	1.78	3.00	3.12	0.09	0.83	no
43	1062.9152	1.25	2.61	2.61	4.08	0.52	0.83	no
44	1063.4968	1.21	1.21	1.84	1.87	0.04	0.83	no
45	1063.5312	1.91	3.05	3.05	3.64	0.66	0.83	no
46	1064.6602	1.29	1.77	2.41	3.69	0.53	0.83	no
47	1065.2419	1.74	1.81	2.83	3.41	0.35	0.83	no
48	1065.8235	1.32	1.75	2.21	2.21	0.48	0.83	no
49	1066.4052	2.05	2.05	2.44	2.44	0.01	0.83	no
50	1066.9869	0.92	1.46	1.46	2.08	0.53	0.83	no
51	1067.5685	1.84	2.07	2.84	3.60	0.43	0.83	no
52	1068.1502	2.26	2.46	1.56	1.99	-0.74	0.83	no
53	1068.7319	1.13	2.11	1.72	3.17	0.71	0.83	no
54	1068.7663	2.07	1.57	3.03	4.59	0.62	0.83	no
55	1069.8952	1.24	1.50	1.86	3.38	0.71	0.83	no
56	1070.4452	1.65	1.33	5.02	2.25	-0.53	0.83	no
57	1070.9630	1.89	1.99	3.05	3.06	0.09	0.83	no
58	1071.0017	1.60	1.63	2.54	3.24	0.43	0.83	no
59	1071.9988	2.41	1.37				0.83	
60	1072.0374	3.15	2.20	0.98	1.16	0.48	0.83	no
61	1073.0345	1.49	1.88	2.79	4.17	0.51	0.83	no
62	1073.5524	1.41	1.84	3.02	3.09	0.26	0.83	no
63	1074.0702	1.04	2.03				0.83	
64	1074.5881	1.72	1.73	3.31	3.53	0.12	0.83	no
65	1075.1060	1.19	2.18	3.61	4.35	0.31	0.83	no
66	1075.6238	2.94	0.85				0.83	
67	1075.6625	3.65	2.07	3.83	4.10	0.61	0.83	no
68	1076.6596	1.48	2.33	3.02	3.58	0.40	0.83	no
69	1077.1774	0.15	2.81	1.15	3.54	0.79	0.83	no
70	1077.2161	1.54	2.43	3.23	4.19	0.36	0.83	no
71	1079.2489	1.69	1.88	3.12	3.76	0.31	0.83	no
72	1079.2875	2.17	4.03	4.36	4.54	0.78	0.83	no
73	1080.8025	1.69	2.35	2.58	5.10	0.74	0.83	no
74	1080.8411	1.47	1.81	4.59	4.76	0.10	0.83	no

	age (kyr)	extreme low	next low	next high	extreme high	Q	Qcrit	Outliers?
75	1081.8383	1.57	2.46	3.67	4.92	0.37	0.83	no
76	1081.8769	1.90	2.11	4.59	5.03	0.14	0.83	no
77	1082.8740	1.52	1.91	3.96	4.04	0.15	0.83	no
78	1082.9126	1.74	2.05	4.01	4.31	0.12	0.83	no
79	1082.9512	1.48	2.23	4.50	4.67	0.24	0.83	no
80	1084.4276	1.87	2.48	3.55	5.00	0.46	0.83	no
81	1084.4579	1.56	3.40	4.75	5.23	0.50	0.83	no
82	1084.4883	1.42	2.07	2.63	3.83	0.50	0.83	no
83	1086.3078	1.51	1.91	3.33	4.53	0.40	0.83	no
84	1086.3382	1.53	2.74	2.55	4.47	0.65	0.83	no
85	1087.6259	2.36	2.40	4.73	5.55	0.26	0.83	no
86	1087.6562	1.62	3.34	3.34	4.41	0.62	0.83	no
87	1090.2619	1.47	1.87	3.12	4.46	0.45	0.83	no
88	1090.2923	1.74	2.08	2.70	4.73	0.68	0.83	no
89	1092.8980	2.20	2.38	3.41	4.53	0.48	0.83	no
90	1092.9284	1.26	2.66	3.51	4.01	0.51	0.83	no
91	1092.9587	1.54	2.07	3.41	4.01	0.24	0.83	no
92	1096.8521	1.24	3.01	3.41	4.06	0.63	0.83	no
93	1096.8825	1.51	1.64	2.85	3.62	0.36	0.83	no
94	1096.9128	1.34	2.29				0.83	
95	1100.8062	1.46	1.82	2.95	3.91	0.39	0.83	no
96	1102.1242	1.41	2.91				0.83	
97	1102.1546	1.00	2.54	3.50	3.72	0.57	0.83	no
98	1104.7603	1.24	2.78	3.24	4.33	0.50	0.83	no
99	1104.7907	1.69	1.75	3.10	4.17	0.43	0.83	no
100	1107.3964	1.26	1.77	2.52	3.78	0.50	0.83	no
101	1108.8353	1.07	1.48	2.27	3.84	0.57	0.83	no
102	1110.8879	1.27	1.27	3.27	4.85	0.44	0.83	no
103	1110.9074	2.16	2.49	2.49	3.52	0.76	0.83	no
104	1114.9930	1.57	2.17	2.84	4.53	0.57	0.83	no
105	1115.0125	1.61	1.61	2.92	4.15	0.48	0.83	no
106	1119.0982	1.07	1.07	2.63	3.63	0.39	0.83	no
107	1121.1507	1.54	1.83	3.06	3.30	0.17	0.83	no
108	1121.1702	1.46	1.48	3.15	3.28	0.07	0.83	no
109	1125.2558	1.53	2.18	4.08	5.28	0.32	0.83	no
110	1127.3084	0.87	2.94	4.35	4.35	0.60	0.83	no

5.8.3 Analysis of means to identify outliers

In common with the bulk of other work in the field (e.g. Sadekov et al, [2008]; Anand et al., [2003]), means have been used to construct the calibration curve. In addition, the data was examined to identify potential outliers that may influence the mean value.

Each sample mean comprises of between 2 and 22 individual tests. There is no guarantee, especially in those means comprised of few data, that the sample means themselves are not affected by outliers, *i.e.* that these sample means are good estimates of the population sample means. Hence, each of the sample means (that were used in the calibration) was screened for outliers. If they contained no outliers, it might be reasonable to assume that they were appropriate estimates of the population sample means.

A Dixon's Q test was used to screen for outliers, employing a confidence interval of 95% (P=0.05). This means that there is a 95% certainty that average does not contain outliers, *i.e.* that the sample means are good estimates of the population sample means. If the Q statistic is less than the critical Q value (Q_{crit}), then with 95% confidence, there are no outliers. The Dixon Q statistic is defined as:

$$Q = \frac{(suspect \ value - nearest \ value)}{(largest \ value - smallest \ value)}$$
[Eq. 5.15]

For each sample mean, four of the data were chosen, comprising of the highest, next highest, and lowest, next lowest, thus allowing the full variation to be represented. A conservative approach was adopted by using the Q_{crit} value for n=4. Seven samples did not contain four points and hence could not be tested. The data are shown in Table 5.6. (N.B. the seven samples unable to be tested are in bold).

This analysis shows that the sample means tested did not (at the 95% CI) contain outliers, and hence they are good estimates of the population sample means.

Chapter 6

Conclusions and Suggestions for Future Work

The two main objectives of this thesis were to: (a) determine whether LA-ICP-MS is a useful analytical tool for the measurement of trace elements in foraminiferal calcite of Gs. ruber and N. incompta and can be used for reliable reconstruction of past ocean temperatures and, having demonstrated this, (b) reconstruct the ocean-climate conditions of MIS-34 to MIS-29 using these techniques. Trace element/Ca ratios were analysed in modern and fossil Gs. ruber, N. incompta and G. bulloides from core top, plankton tow and down-core material, which included the 'super-warm' interglacial period MIS-31 from sites in the Southwest Pacific Ocean.

6.1 Trace element determination in "modern" planktonic foraminifera (*Gs. ruber* and *N. incompta*) by LA-ICP-MS

Trace element/Ca ratios were measured by LA-ICP-MS in Gs. ruber and N. incompta from a wide range of core top and plankton tow samples in the Southwest Pacific Ocean with particular focus on linking measured Mg/Ca ratios to observed (near-) surface ocean temperatures.

6.1.1 Gs. ruber

The variability of Mg/Ca ratios within an individual *Gs. ruber* test show statistically significantly lower Mg/Ca ratios in the final chamber (F) compared to the two older final chambers (F-2 and F-1). Although the lower Mg/Ca in the final chamber could reflect a change in depth

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habitat, such as that typical during gametogenesis, data from plankton tow and other culturing studies also find lower Mg/Ca ratios in the final chamber of other planktonic foraminiferal species, which suggests that this may also be a biological or 'vital effect'. These vital effects could affect the incorporation of Mg between different chambers and suggests that biological internal regulation plays a more prominent role in the Mg/Ca intra-individual variability of foraminiferal tests than previously thought.

Inter-individual variability of Mg/Ca ratios between *Gs. ruber* from the same core top sites and plankton tows reveals a wide range of Mg/Ca values than cannot be explained by environmental conditions such as changes in seasonal near-surface ocean temperature or depth habitat, or reworking of modern and fossil foraminifera in core top samples. This variability requires that ocean temperature is not the only control on the incorporation of Mg into the tests of individual *Gs. ruber* and an as yet important control on Mg incorporation into *Gs. ruber* living under similar environmental conditions exists. Removal of the temperature effect on Mg/Ca ratios on *Gs. ruber* individuals from the same sample reveals a log-normal distribution that describes the variability of Mg/Ca ratios. However, the spread parameter of this distribution (*i.e.* the standard deviation of log [Mg/Ca] values) is not universal.

Regardless of this wide range of Mg/Ca within individual *Gs. ruber* populations, the mean site Mg/Ca value from each of the pooled final 3 chambers for each sample shows a positive correlation with annual SST at 0-50 m depth described by the following relationships:

$$\frac{Mg}{Ca_{chF-2}} = 0.798 \times \exp^{0.070 \times SST}$$
(r² = 0.94) [Eqn. 6.1]

$$\frac{Mg}{Ca_{chF-1}} = 0.891 \times \exp^{0.067 \times SST}$$
(r² = 0.89) [Eqn. 6.2]

$$\frac{Mg}{Ca_{chF}} = 0.798 \times \exp^{0.070 \times SST}$$
(r² = 0.90) [Eqn. 6.3]

These chamber-specific calibrations can be used as an alternative to bulk, solution-based, Mg/Ca analyses of foraminifera when analyses are performed by LA-ICP-MS. However, when LA-ICP-MS derived calibrations are compared to those derived from bulk solution ICP-MS studies, they are intermediate between the single chamber calibrations derived from F-2/F-1 and F from this study.

In summary, despite the intra-individual and inter-individual complexity observed in the Mg incorporation into *Gs. ruber*, LA-ICP-MS trace element analysis of this species of planktonic foraminifera can be used as a robust palaeocean thermometer provided the same chamber is analysed from each individual foraminifera.

6.1.2 N. incompta

In contrast to the LA-ICP-MS study of *Gs ruber*, individual *N. incompta* demonstrate far greater Mg/Ca heterogeneity that contrasts with previous work on this species. For example, outer calcite crusts in crystalline forms have an outer layer with very low Mg/Ca compared to the inner ontogenetic calcite. In reticulate or non-crystalline forms, this layer is either absent, or is only a thin layer with low Mg/Ca ratios. These individuals may represent intermediates of crystalline forms, but this is not obvious with SEM imaging. The majority of reticulate tests without an outer layer with low Mg/Ca have high and low Mg/Ca bands in the inner ontogenetic calcite layer(s), which are interpreted as reflecting organic layers of ontogenetic calcite.

The lack of correlation between Mg/Ca ratios of *N. incompta* with ocean temperature may suggest that this species does not dwell at the same depths at each core top site. Additionally, unlike *Gs ruber* there was no systematic difference in Mg/Ca found between the final four visible chambers at one core top site, nor between the F-3 and F chambers at any sites. This

may reflect migration within the water column that is not uni-directional, or points towards further unidentified controls on Mg incorporation into *N. incompta* that require further study.

In summary, trace element/Ca ratios measured by LA-ICP-MS on *N. incompta* from the Southwest Pacific Ocean cannot be used to extract reliable past-ocean temperatures and, as such, this species was not used in the reconstruction of the ocean-climate conditions of MIS-34 to MIS-29 in the second part of this thesis study.

6.2 Ocean-climate response at ODP Site 1123 during MIS-34 to 29

The trace element chemistry of *Gs. ruber* and *G. bulloides*, as well as size-normalised weights and the stable isotope composition (δ^{18} O, δ^{13} C) of *G. bulloides* were determined from Marine Isotope Stages 33 to 29 at ODP Site 1123. Palaeo-ocean temperatures were constructed using the calibration developed in the first part of this study (*Gs. ruber*) and using a calibration developed using the same techniques for *G. bulloides* [*Marr et al.*, 2011].

A new age model was generated for MIS-31 based on alignment of benthic δ^{18} O to the LR04 age model. The age model includes the revised position of the base of the Jaramillo palaeomagnetic sub-chron (C1r.1n).

G. bulloides is present throughout the sediment record and records the warmest SST at the peak of SH insolation maxima in concert with SST recorded by *Gs. ruber*. When compared to the δ^{18} O record, however, there is a 10 kyr offset that cannot be an artefact of a chronological offset as both Mg/Ca and stable isotope measurements were made on the same material. The lag between SST and δ^{18} O may indicate that these records are not in phase. The lead of the Southwest Pacific Ocean planktic SST's (Mg/Ca) over local (benthic δ^{18} O₂) ice volume change and a global (δ^{18} O_{sw}) change is consistent with other southern hemisphere SST records and infers that SST variability is not controlled by continental ice sheets.

The palaeo-SST from ODP Site 1123 show that during MIS-31 SST recorded by both *Gs. ruber* and *G. bulloides* reached a maximum of *ca.* 19°C, which is ca. 4-7°C warmer than the modern

spring/summer SST for each species, respectively, and in phase with the SH insolation maxima. As such, SST at southern mid-latitudes during MIS-31 in this "super-warm" interglacial were considerably higher than the present interglacial and consistent with sedimentary records that show a significant change in the Antarctic cryosphere at this time [*Naish et al.*, 2007b; *Scherer et al.*, 2008]. Modelled SST from Antarctica [*Pollard and DeConto*, 2009] predicts a SST increase of 5°C would be required to significantly melt the WAIS. The cause of this warming is suggested to be in part related to increased precessional forcing of the tropics, intensifying the SPTG and migration of STW to the south, as indicated by the increase in local salinity, and Zn/Ca and Ba/Ca ratios at ODP Site 1123. Additionally MIS-31 is characterised by high obliquity, which will have affected ice sheet expansion and contraction with a 40 kyr periodicity. Although the effect of ice growth in one hemisphere on sea level may thus be cancelled by melting in the other hemisphere through precessional forcing, the large depletion in $\delta^{18}O_{sw}$ and minimal SST recorded by *G. bulloides* that coincide with NH insolation maxima, suggest that NH ice sheets were more responsive to high latitude insolation than those in the SH.

Size-normalised weights of *G. bulloides* are generally lightest during interglacial periods and heaviest during glacial periods, and consistent with the temperature effect on size-normalised weights for modern *G. bulloides* from the Southwest Pacific [*Marr et al.*, 2011], but this relationship is not consistent throughout the record. During early MIS-31 the size-normalised test weights are consistently heavier than would be expected given the warm SST. This indicates that dissolution during this interglacial period is not the reason for this offset. This offset may be related to changes in ocean $[CO_3^{2-}]$ or other changes in water mass chemistry ($\delta^{13}C$, nutrient availability). Clearly, size-normalised weights of *G. bulloides* in the Southwest Pacific reflect a complex interplay of SST [*e.g. Marr et al.*, 2011], and other factors such as ocean $[CO_3^{2-}]$ and, in particular, during early MIS-31 the oceanographic and ocean chemistry of the Southwest Pacific was significantly perturbed compared to the present day when non-temperature controls became the dominant control on size-normalised weights of *G. bulloides*.

6.3 Suggestions for future work

This thesis has potentially identified a number of research directions that would be useful in improving the use of foraminiferal trace element chemistry as a proxy of palaeo-climatic and – oceanographic change both generally and in the Southwest Pacific.

(1) As LA-ICP-MS is a relatively new analytical technique in terms of its application to foraminifera, the comparison of LA-ICP-MS results versus those obtained by traditional solution-based ICP-MS techniques would be a useful avenue for further study to examine the comparability of the two techniques. This could be achieved by first analysing the same foraminifer's by LA-ICP-MS, which is essentially a non-destructive technique, followed by traditional solution-based ICP-MS analysis of the same individuals. In addition, it would be interesting to apply the cleaning techniques used during foraminifera preparation for solution-based methods and then analyse the foraminifera by LA-ICP-MS to critically assess the effects that various cleaning methods (oxidative, reductive and acid polishing) have on foraminiferal test chemistry.

(2) While the incorporation of Mg into planktic foraminifer tests as a palaeo-ocean thermometer has been the focus of this study, a wide range of other trace element/Ca ratios remain to be fully utilised for palaeo-climatic and –oceanographic reconstructions. For example, preliminary work in this study suggests that Mn and Zn/Ca ratios vary systematically between interglacial and glacial periods and work by others [*Yu et al.*, 2007; *Foster*, 2008] appear to show that B/Ca ratios may be able to be used to reconstruct past ocean $[CO_3^2]$ and pH. Application of new generation sector-field ICP-MS instruments which have much greater sensitivity than the analytical system used here, coupled to a laser ablation system, may result in significant advances in the application of other trace elements in foraminifera as palaeoenvironmental proxies.

(3) Finally, there is a lack of $\delta^{18}O_{sw}$ measurements in the Southwest Pacific, and therefore it is difficult to examine regional $\delta^{18}O_{sw}$ -salinity relationships with certainty and reconstruct past changes in $\delta^{18}O_{sw}$ that might be then linked to changes in global ice volume. As such, and assuming that modern relationships are maintained in the past, measurements of $\delta^{18}O_{sw}$ in the water column at different depths within the mixed layer and across a N-S transect of the Chatham Rise would be an important suite of data.

6.4 References

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Appendix A. Chapter 3

						Individu				WOA	
	Latitud	Longitu				al	F-2	F-1	F	05 SST	
Site	e	de	Core Type	Depth	Age	Number	Mg/Ca	Mg/Ca	Mg/Ca	(0-50m)	Salinity
	(degree	(degrees		(m)	(170)		(mmol/	(mmol/	(mmol/	(°C)	(2011)
	5))		(11)	()1)		1101)	1101)	morj	(C)	(psu)
AIMS1361	3.370	144.34	grab	1100		1	5.21	4.09	4.08	28.8	34.5
AIMS1361	3.370	144.34	grab	1100		2	5.44	5.90	5.89	28.8	34.5
AIMS1361	3.370	144.34	grab	1100		4	6.11	4.53	3.85	28.8	34.5
AIMS1361	3.370	144.34	grab	1100		6	5.36	6.06	4.18	28.8	34.5
AIMS1361	3.370	144.34	grab	1100		11	4.68	4.81	3.71	28.8	34.5
AIMS1361	3.370	144.34	grab	1100		12	4.44	5.14	4.44	28.8	34.5
AIMS1361	3.370	144.34	grab	1100		14	6.08	5.49	3.02	28.8	34.5
AIMS3703	11.153	125.02	grab	504	< 100	1	5.30	4.74	4.08	28.4	34.4
AIMS3703	11.153	125.02	grab	504	< 100	3	3.82	4.15	2.90	28.4	34.4
AIMS3703	11.153	125.02	grab	504	< 100	4	6.48	5.63	4.76	28.4	34.4
AIMS3703	11.153	125.02	grab	504	< 100	5	8.74	8.61	6.36	28.4	34.4
AIMS3703	11.153	125.02	erab	504	< 100	6	4.95	5.72	4.13	28.4	34.4
AIMS3703	11.153	125.02	erab	504	< 100	7	6.97	6.19	4.32	28.4	34.4
AIMS3703	11 153	125.02	orah	504	< 100	8	3 21	4 19	4 48	28.4	34.4
AIMS3703	11 153	125.02	orab	504	< 100	13	6.22	6.82	5.90	28.4	34.4
AIMS3703	11.153	125.02	grab	504	< 100	14	7.41	7 32	7.88	28.1	34.4
AIMS 2702	11.155	125.02	grab	504	< 100	14	5.49	5.69	5.12	20.4	34.4
AIM55705	11.155	125.02	grab	504	< 100	10	5.40	5.00	2.00	20.4	24.4
AIM\$5703	11.155	125.02	grab	504	< 100	17	6.56	5.95	5.99	28.4	34.4
AIMS3703	11.153	125.02	grab	504	< 100	18	6./3	8.85	5.94	28.4	34.4
AIMS3/03	11.153	125.02	grab	504	< 100	19	5.80	6.4/	5.37	28.4	34.4
AIMS1631	11.158	145.79	grab	1468		1	4.15	3.66	4.01	26.8	35.0
AIMS1631	11.158	145.79	grab	1468		4	5.13	5.98	4.62	26.8	35.0
AIMS1631	11.158	145.79	grab	1468		5	4.69	5.08	3.92	26.8	35.0
AIMS1631	11.158	145.79	grab	1468	01/0	7	4.77	4.56	3.91	26.8	35.0
AIMS2078	18.212	147.60	grab	880	± 50	1	5.36	4.59	3.57	26.4	35.0
			0		2160						
AIMS2078	18.212	147.60	grab	880	± 50	2	6.66	6.96	4.12	26.4	35.0
AIMS2078	18.212	147.60	grab	880	± 50	3	7.01	5.30	3.80	26.4	35.0
					2160						
AIMS2078	18.212	147.60	grab	880	± 50 2160	4	4.34	6.10	4.65	26.4	35.0
AIMS2078	18.212	147.60	grab	880	±50	6	5.82	6.07	2.33	26.4	35.0
	10.010	1.15.40	,	000	2160	0			2.54	244	25.0
AIMS20/8	18.212	14/.60	grab	880	± 50 2160	8	5.47	5.41	3./1	26.4	35.0
AIMS2078	18.212	147.60	grab	880	±50	9	5.49	5.99	3.60	26.4	35.0
A TM S 2079	10 212	147.60	anah	000	2160	14	4 70	E 45	4.10	26.4	25.0
AIM32078	16.212	14/.00	grab	000	<u>1</u> 50 2160	14	4.79	5.45	4.19	20.4	55.0
AIMS2078	18.212	147.60	grab	880	± 50	16	7.06	7.60	2.64	26.4	35.0
ATMS2078	18 21 2	147.60	arab	880	2160 +50	17	4 35	4 17	3.87	26.4	35.0
FR1/97/GC	10.212	147.00	grab	000	8995	17	4.55	4.17	5.02	20.4	55.0
12	23.577	153.79	core top	991	±25	1	5.30	5.74	2.40	24.7	35.4
FR1/97/GC 12	23 577	153 79	core top	991	8995 +25	2	4 26	4 77	3.81	247	35.4
FR1/97/GC	20.077	100.17	core top	, , i	8995	-			5.01	- 1.7	55.1
12 EB1/07/02	23.577	153.79	core top	991	±25	3	5.15	6.35	3.96	24.7	35.4
гкт/9//GC 12	23.577	153.79	core top	991	±25	5	5.86	5.97	4.22	24.7	35.4
FR1/97/GC			· · · r		8995	·			а и		
12 ER1/07/CC	23.577	153.79	core top	991	±25	7	4.44	4.95	4.15	24.7	35.4
12	23.577	153.79	core top	991	±25	10	3.86	6.81	4.13	24.7	35.4

Table A1: Core top and plankton tow Mg/Ca ratios for individual Globigernoides ruber ($250 - 355 \mu m$) from sites in the Southwest Pacific Ocean

Site	Latitud e	Longitu de	Core Type	Depth	Age	Individu al Number	F-2 Mg/Ca	F-1 Mg/Ca	F Mg/Ca	WOA 05 SST (0-50m)	Salinity
	(degree	(degrees		(m)	(vr)		(mmol/ mol)	(mmol/ mol)	(mmol/ mol)	(°C)	(nsu)
FR1/97/GC	3))		(III)	8995		moly	mory	mory	(0)	(psu)
12 FR1/97/GC	23.577	153.79	core top	991	±25 8995	11	4.70	4.89	2.62	24.7	35.4
12 FR1/97/GC	23.577	153.79	core top	991	±25 8995	12	5.35	5.71	5.68	24.7	35.4
12 FR1/97/GC	23.577	153.79	core top	991	±25 8995	13	5.06	4.79	3.92	24.7	35.4
12 FR1/97/GC	23.577	153.79	core top	991	±25 8995	14	5.20	6.48	4.09	24.7	35.4
12 FR1/97/GC	23.577	153.79	core top	991	±25 8995	15	3.73	2.31	6.78	24.7	35.4
12 TAN0706	23.577	153.79	core top	991	±25	16	5.05	4.67	2.78	24.7	35.4
C4 TAN0706	29.353	180.97	core top	2258		1	3.92	4.75	3.57	20.7	35.7
C4 TAN0706	29.353	180.97	core top	2258		2	6.57	7.11	4.48	20.7	35.7
C4 TAN0706	29.353	180.97	core top	2258		5	3.77	3.70	1.83	20.7	35.7
C4 TAN0706	29.353	180.97	core top	2258		6	4.05	4.55	2.50	20.7	35.7
C4 TAN0706	29.353	180.97	core top	2258		8	3.25	3.63	2.53	20.7	35.7
C4	29.353	180.97	core top	2258		9	2.73	3.19	1.90	20.7	35.7
C4	29.353	180.97	core top	2258		10	4.20	4.55	3.40	20.7	35.7
C4	29.353	180.97	core top	2258		11	4.42	4.18	3.02	20.7	35.7
C4	29.353	180.97	core top	2258		12	5.30	4.54	2.88	20.7	35.7
C4	29.353	180.97	core top	2258		13	2.78	3.24	2.62	20.7	35.7
TAN0/06 C4	29.353	180.97	core top	2258		14	2.41	2.89	2.33	20.7	35.7
TAN0/06 C4	29.353	180.97	core top	2258		15	5.25	5.43	3.00	20.7	35.7
TAN0706 C4	29.353	180.97	core top	2258		16	3.58	2.64	2.47	20.7	35.7
TAN0/06 C4	29.353	180.97	core top	2258		17	3.96	3.72	3.57	20.7	35.7
TAN0/06 C4	29.353	180.97	core top	2258		18	3.53	4.75	2.99	20.7	35.7
TAN0706 C4	29.353	180.97	core top	2258		19	2.45	2.20	1.66	20.7	35.7
TAN0706 C4	29.353	180.97	core top	2258		20	3.17	3.91	2.40	20.7	35.7
TAN0706 C4	29.353	180.97	core top	2258		21	6.59	6.34	3.87	20.7	35.7
TAN0706 C4	29.353	180.97	core top	2258		22	2.54	2.44	1.67	20.7	35.7
TAN0706 C4	29.353	180.97	core top	2258		23	2.39	2.46	1.77	20.7	35.7
TAN0706 C4	29.353	180.97	core top	2258		24	2.61	2.88	4.26	20.7	35.7
TAN0706 C4	29.353	180.97	core top	2258		25	2.61	2.27	1.86	20.7	35.7
TAN0706 C4	29.353	180.97	core top	2258		26	4.91	3.93	3.24	20.7	35.7
TAN0706 C4	29.353	180.97	core top	2258		27	3.47	4.21	3.77	20.7	35.7
TAN0706 C4	29 353	180.97	core top	2258			3.03	2.65	2.18	20.7	35.7
TAN0706	29.353	180.97	core top	2258		20	3.08	3.60	2.10	20.7	35.7
D71	33.855	174.60	core top	1910	5715 ± 40	1	2.45	2.80	2.27	18.8	35.6
1 / 1 D71	33.055	174.60	core top	1010	5715 ±	1 2	2.70	2.00	2.00	10.0	35.0
P/1	33.855	1/4.69	core top	1919	5715 ±	2	2.12	2.78	2.31	18.8	35.0
P71	33.855	174.69	core top	1919	40 5715 ±	2	2.66	3.18	2.28	18.8	35.6
P71	33.855	174.69	core top	1919	40	3	4.16	4.04	2.90	18.8	35.6

Site	Latitud e (degree	Longitu de (degrees	Core Type	Depth	Age	Individu al Number	F-2 Mg/Ca (mmol/	F-1 Mg/Ca (mmol/	F Mg/Ca (mmol/	WOA 05 SST (0-50m)	Salinity
	s))		(m)	(yr)		mol)	mol)	mol)	(°C)	(psu)
P71	33.855	174.69	core top	1919	5715 <u>+</u> 40	3	4.13	3.76	2.36	18.8	35.6
P71	33.855	174.69	core top	1919	5715 ± 40	4	2.89	2.76	2.39	18.8	35.6
P71	33.855	174.69	core top	1919	5715 ± 40	4	2.54	2.83	2.55	18.8	35.6
P71	33.855	174.69	core top	1919	5/15 ± 40	5	4.29	3.40	2.35	18.8	35.6
P71	33.855	174.69	core top	1919	5/15 ± 40	7	3.41	2.44	3.14	18.8	35.6
P71	33.855	174.69	core top	1919	5/15 ± 40	8	2.38	3.02	3.29	18.8	35.6
P71	33.855	174.69	core top	1919	$5/15 \pm 40$	9	2.51	2.60	1.53	18.8	35.6
P71	33.855	174.69	core top	1919	5715 ± 40	9	2.92	2.44	2.32	18.8	35.6
P71	33.855	174.69	core top	1919	5715 ± 40	10	3.44	3.33	2.13	18.8	35.6
P71	33.855	174.69	core top	1919	5715 ± 40	11	3.91	3.51	2.53	18.8	35.6
P71	33.855	174.69	core top	1919	5715 ± 40	13	3.18	4.21	2.80	18.8	35.6
P71	33.855	174.69	core top	1919	5715 ± 40	13	4.37	3.13	2.58	18.8	35.6
P71	33.855	174.69	core top	1919	5715 ± 40	14	3.82	3.12	2.38	18.8	35.6
P71	33.855	174.69	core top	1919	5715 ± 40	14	4.09	2.91	2.76	18.8	35.6
P71	33.855	174.69	core top	1919	5715 ± 40	16	2.11	2.19	2.15	18.8	35.6
P81	34.020	173.51	core top	2036	5/15 ± 40	1	2.54	2.90	1.55	18.1	35.6
P81	34.020	173.51	core top	2036	5/15 ± 40	2	2.98	2.64	2.34	18.1	35.6
P81	34.020	173.51	core top	2036	40 5715 ±	3	4.77	4.20	4.53	18.1	35.6
P81	34.020	173.51	core top	2036	40 5715 ±	5	2.21	2.48	1.99	18.1	35.6
P81	34.020	173.51	core top	2036	40 5715 ±	6	2.96	3.54	2.24	18.1	35.6
P81	34.020	173.51	core top	2036	40 5715 ±	7	4.28	4.62	3.93	18.1	35.6
P81	34.020	173.51	core top	2036	40 5715 ±	10	3.77	3.11	2.78	18.1	35.6
P81	34.020	173.51	core top	2036	40	12	4.18	3.83	3.41	18.1	35.6
P81	34.020	173.51	core top	2036	40 5715 ±	14	2.59	3.34	1.48	18.1	35.6
P81	34.020	173.51	core top	2036	40 5715 ±	15	2.01	2.07	1.60	18.1	35.6
P81	34.020	173.51	core top	2036	40 5715 ±	16	2.19	2.49	1.39	18.1	35.6
P81	34.020	173.51	core top	2036	40 5715 ±	17	2.94	2.53	1.81	18.1	35.6
P81	34.020	173.51	core top	2036	40 5715 ±	18	2.46	2.73	1.99	18.1	35.6
P81	34.020	173.51	core top	2036	40	20	1.88	1.40	1.33	18.1	35.6
P81	34.020	173.51	core top	2036	5715 <u>±</u> 40	21	2.34	2.27	1.38	18.1	35.6
P81	34.020	173.51	core top	2036	5715 ± 40 5715 +	25	3.66	3.15	2.38	18.1	35.6
P81	34.020	173.51	core top	2036	40 5715 +	26	1.41	1.49	1.12	18.1	35.6
P81	34.020	173.51	core top	2036	40	27	2.73	2.90	1.93	18.1	35.6
Z7003	36.693	176.24	core top	430	±55	2	1.98	2.82	3.33	18.1	35.5

						Individu				WOA	
	Latitud	Longitu				al	F-2	F-1	F	05 SST	
Site	e	de	Core Type	Depth	Age	Number	Mg/Ca	Mg/Ca	Mg/Ca	(0-50m)	Salinity
	(degree	(degrees		()			(mmol/	(mmol/	(mmol/	(90)	()
	s))		(m)	(yr) 5022		mol)	mol)	mol)	(°C)	(psu)
Z7003	36.693	176.24	core top	430	±55	4	2.49	2.05	3.22	18.1	35.5
					5932						
Z7003	36.693	176.24	core top	430	±55	6	2.34	3.41	3.52	18.1	35.5
					5932						
Z/003	36.693	176.24	core top	430	±55 5022	8	3.30	0.84	2.40	18.1	35.5
Z7003	36 693	176 24	core top	430	+55	10	2.84	3.83	2.67	18.1	35.5
			tort top		5932						
Z7003	36.693	176.24	core top	430	±55	15	3.09	4.10	4.17	18.1	35.5
77002	26,602	174.04		120	5932	16	0.40	2.01	174	10.1	25.5
Z/003	36.693	1/6.24	core top	430	±55 5032	16	2.49	2.01	1./4	18.1	35.5
Z7003	36.693	176.24	core top	430	±55	17	3.34	3.26	1.39	18.1	35.5
					5932						
Z7003	36.693	176.24	core top	430	±55	18	2.29	1.94	1.37	18.1	35.5
77002	26 (02	176.04		120	5932	10	0.25	0.75	2.04	10.1	25.5
Z/005	30.093	1/6.24	core top	430	±00 5932	19	2.35	2.75	2.04	18.1	33.5
Z7003	36.693	176.24	core top	430	±55	20	2.67	2.80	1.60	18.1	35.5
			1		5932						
Z7003	36.693	176.24	core top	430	±55	21	5.27	4.49	2.46	18.1	35.5
77003	36 603	176.24	core too	430	5932 +55	22	3.00	2 20	1.64	101	25.5
27005	30.093	1/0.24	core top	430	<u>+</u> 55 5932	22	5.09	5.50	1.04	10.1	55.5
Z7003	36.693	176.24	core top	430	±55	23	3.09	2.87	1.47	18.1	35.5
			1		5932						
Z7003	36.693	176.24	core top	430	±55	24	2.70	3.18	1.80	18.1	35.5
77003	36 603	176.24	core top	430	5932 +55	25	3 11	4.04	2.23	181	35.5
27005	50.075	1/0.24	plankton	450	April	25		4.04	2.2.)	10.1	55.5
U2315	38.509	179.02	tow	100-50	2001	2	2.42	4.06	1.36	18.7	35.6
			plankton		April						
U2315	38.509	179.02	tow	100-50	2001	3	5.91	6.08	3.10	18.7	35.6
U2315	38 500	170.02	plankton	100.50	2001	4	3.26	4.68	2.50	187	35.6
02515	50.507	179.02	plankton	100-50	April	7	5.20	4.00	2.50	10.7	55.0
U2315	38.509	179.02	tow	100-50	2001	5	2.29	3.16	2.18	18.7	35.6
			plankton		April						
U2315	38.509	179.02	tow	100-50	2001	6	3.67	3.44	2.77	18.7	35.6
U2315	38 509	179.02	tow	100-50	2001	9	2.62	2.96	1.87	187	35.6
02010	50.507	172102	plankton	100 00	April	-	2.02	2.00	1107	1011	5510
U2315	38.509	179.02	tow	100-50	2001	10	3.56	3.51	3.13	18.7	35.6
110015	20 500	150.02	plankton	100 50	April		2.20	2.02	0.01	10 7	25.4
U2315	38.509	1/9.02	tow	100-50	2001 April	11	2.29	2.93	0.91	18./	35.6
U2315	38,509	179.02	tow	100-50	2001	12	3.30	3.93	2.19	18.7	35.6
			plankton		April						
U2315	38.509	179.02	tow	100-50	2001	13	3.36	2.80	2.55	18.7	35.6
110215	29 500	170.02	plankton	100 50	April 2001	14	2.07	4.24	1.02	107	25.6
U2315	38.509	1/9.02	tow	100-50	2001 April	14	2.97	4.24	1.83	18./	35.0
U2315	38,509	179.02	tow	100-50	2001	15	2.09	3.84	3.25	18.7	35.6
			plankton		April						
U2315	38.509	179.02	tow	100-50	2001	16	2.60	2.84	2.09	18.7	35.6
112222	41 (01	179.05	plankton	100 50	April 2001	1	2.02	4.60	2 (0	10.2	25.6
U2322net6	41.601	1/8.05	tow	100-50	2001 April	1	5.95	4.60	2.69	18.5	35.0
U2322net6	41.601	178.05	tow	100-50	2001	3	2.16	2.69	2.08	18.3	35.6
			plankton		April						
U2322net6	41.601	178.05	tow	100-50	2001	4	2.97	4.37	4.24	18.3	35.6
112322-act	<u>/1 601</u>	178.05	plankton	100 50	April 2001	5	260	3.02	1.90	18.3	35.6
UZJZZIICIO	41.001	1/0.03	plankton	100-30	April	3	2.00	5.02	1.00	10.3	55.0
U2322net6	41.601	178.05	tow	100-50	2001	6	3.02	3.29	2.96	18.3	35.6
			plankton		April						
U2322net6	41.601	178.05	tow	100-50	2001	8	3.07	2.34	3.09	18.3	35.6
12322not6	41 601	178.05	plankton	100-50	April 2001	0	2 37	3 32	2 52	183	35.6
0252211010	+1.001	170.05	plankton	100-50	April	,	2.31	5.55	4.34	10.5	55.0
U2322net7	41.601	178.05	tow	50-10	2001	1	3.37	3.05	2.16	18.8	35.6

						Individu				WOA	
	Latitud	Longitu				al	F-2	F-1	F	05 SST	
Site	e	de	Core Type	Depth	Age	Number	Mg/Ca	Mg/Ca	Mg/Ca	(0-50m)	Salinity
	(degree	(degrees					(mmol/	(mmol/	(mmol/		
	s))		(m)	(yr)		mol)	mol)	mol)	(°C)	(psu)
			plankton		April						
U2322net7	41.601	178.05	tow	50-10	2001	5	4.01	3.25	2.55	18.8	35.6
			plankton		April			• • •		40.0	
U2322net/	41.601	178.05	tow	50-10	2001	2	2.96	3.08	1.48	18.8	35.6
L12222	41 (01	179.05	plankton	50.10	2001	(2.46	2.01	1 40	10.0	25.6
U2322fiet/	41.001	1/6.05	plankton	50-10	April	0	2.40	2.91	1.40	10.0	55.0
L12322net7	41 601	178.05	tow	50-10	2001	3	1 78	2 21	1.86	18.8	35.6
0252211017	11.001	170.05	plankton	50 10	April	5	1.70	2.21	1.00	10.0	55.0
U2322net7	41.601	178.05	tow	50-10	2001	7	2.98	3.27	2.69	18.8	35.6
			plankton		April						
U2322net7	41.601	178.05	tow	50-10	2001	4	3.25	3.42	2.50	18.8	35.6
			plankton		April						
U2322net7	41.601	178.05	tow	50-10	2001	8	2.51	2.71	1.30	18.8	35.6
ODP1123	41.942	188.50	core top	3290		1	2.24	2.31	1.24	14.7	36.2
ODP1123	41.942	188.50	core top	3290		2	1.53	2.15	1.06	14.7	36.2
ODP1123	41.942	188.50	core top	3290		3	2.94	2.54	2.62	14.7	36.2
ODP1123	41.942	188.50	core top	3290		5	1.47	1.53	1.44	14.7	36.2
ODP1123	41.942	188.50	core top	3290		7	1.53	1.85	1.45	14.7	36.2
ODP1123	41.942	188.50	core top	3290		9	1.44	1.42	1.35	14.7	36.2
ODP1123	41.942	188.50	core top	3290		11	1.41	2.03	1.30	14.7	36.2
ODP1123	41.942	188.50	core top	3290		12	1.62	1.65	1.24	14.7	36.2
ODP1123	41.942	188.50	core top	3290		13	2.21	2.29	1.70	14.7	36.2
ODP1123	41.942	188.50	core top	3290		14	2.11	2.06	1.56	14.7	36.2
ODP1123	41.942	188.50	core top	3290		15	1.65	1.55	1.20	14.7	36.2
ODP1123	41.942	188.50	core top	3290		18	2.85	3.03	2.14	14.7	36.2

N.B. In order to perform paired t-tests, those individuals where 1 or more chambers were excluded post-analysis, were not included in the above table.

Table A2: Core top and plankton tow morphotypes, height, length and weight data for individual *Globigernoides ruber* ($250 - 355 \mu m$) from sites in the Southwest Pacific Ocean

					Individual				
Site	Latitude	Longitude	Depth	Age	Number	Morphotype	Х	Υ	Weight
	(degrees)	(degrees)	(metres)	(yr)			(µm)	(µm)	(µg)
AIMS1361	3.370	144.34	1100		1	s.s.	251	280	5.7
AIMS1361	3.370	144.34	1100		2	s.s.	214	249	6.9
AIMS1361	3.370	144.34	1100		4	s.s.	259	290	7.5
AIMS1361	3.370	144.34	1100		6	s.l.	277	294	6.8
AIMS1361	3.370	144.34	1100		11	s.l.	280	270	9.9
AIMS1361	3.370	144.34	1100		12	s.s.	215	266	8.5
AIMS1361	3.370	144.34	1100		14	s.l.	279	283	9.0
AIMS3703	11.153	125.02	504	< 100	1	s.s.	343	384	11.6
AIMS3703	11.153	125.02	504	< 100	3	s.l.	414	410	18.5
AIMS3703	11.153	125.02	504	< 100	4	s.s.	341	381	13.7
AIMS3703	11.153	125.02	504	< 100	5	s.s.	254	321	11.6
AIMS3703	11.153	125.02	504	< 100	6	s.s.	369	421	16.3
AIMS3703	11.153	125.02	504	< 100	7	s.l.	336	352	10.3
AIMS3703	11.153	125.02	504	< 100	8	s.s.	261	308	7.5
AIMS3703	11.153	125.02	504	< 100	13	s.l.	283	317	5.8
AIMS3703	11.153	125.02	504	< 100	14	s.s.	397	408	5.8
AIMS3703	11.153	125.02	504	< 100	16	s.s.	273	338	7.5

					Individual				
Site	Latitude	Longitude	Depth	Age	Number	Morphotype	Х	Y	Weight
	(degrees)	(degrees)	(metres)	(yr)			(µm)	(µm)	(µg)
AIMS3703	11.153	125.02	504	< 100	17	s.l.	308	303	9.8
AIMS3703	11.153	125.02	504	< 100	18	s.l.	335	253	13.0
AIMS3703	11.153	125.02	504	< 100	19	s.l.	288	283	11.0
AIMS1631	11.158	145.79	1468		1	S.S.	344	350	25.1
AIMS1631	11.158	145.79	1468		4	S.S.	320	353	15.0
AIMS1631	11.158	145.79	1468		5	S.S.	283	318	10.0
AIMS1631	11.158	145.79	1468		7	s.s.	257	264	5.5
AIMS2078	18.212	147.60	880	2160 ± 50	1	s.l.	307	295	10.3
AIMS2078	18.212	147.60	880	2160 ± 50	2	s.s.	336	353	8.7
AIMS2078	18.212	147.60	880	2160 ± 50	3	s.l.	270	291	10.6
AIMS2078	18.212	147.60	880	2160 ± 50	4	s.l.	263	301	7.8
AIMS2078	18.212	147.60	880	2160 ± 50	6	s.l.	242	256	9.6
AIMS2078	18.212	147.60	880	2160 ± 50	8	S.S.	302	328	8.8
AIMS2078	18.212	147.60	880	2160 ± 50	9	s.l.	322	290	7.7
AIMS2078	18.212	147.60	880	2160 ± 50	14	s.s.	275	289	5.3
AIMS2078	18.212	147.60	880	2160 ± 50	16	s.l.	249	267	5.2
AIMS2078	18.212	147.60	880	2160 ± 50	17	s.l.	230	233	6.2
FR1/97/GC12	23.577	153.79	991	8995 ±25	1	s.s.	211	255	8.8
FR1/97/GC12	23.577	153.79	991	8995 ±25	2	s.l.	224	244	9.8
FR1/97/GC12	23.577	153.79	991	8995 ±25	3	s.l.	260	273	7.4
FR1/97/GC12	23.577	153.79	991	8995 ±25	5	s.l.	251	294	11.3
FR1/97/GC12	23.577	153.79	991	8995 ±25	7	s.l.	256	284	10.3
FR1/97/GC12	23.577	153.79	991	8995 ±25	10	s.l.	268	222	7.2
FR1/97/GC12	23.577	153.79	991	8995 ±25	11	s.l.	218	252	13.3
FR1/97/GC12	23.577	153.79	991	8995 ±25	12	s.l.	244	261	10.1
FR1/97/GC12	23.577	153.79	991	8995 ±25	13	s.l.	208	232	6.5
FR1/97/GC12	23.577	153.79	991	8995 ±25	14	s.l.	189	232	10.4
FR1/97/GC12	23.577	153.79	991	8995 ±25	15	s.l.	194	237	10.1
FR1/97/GC12	23.577	153.79	991	8995 ±25	16	s.l.	180	194	7.5
TAN0706 C4	29.353	180.97	2258		1	s.s.	260	294	13.0
TAN0706 C4	29.353	180.97	2258		2	s.s.	272	315	22.4
TAN0706 C4	29.353	180.97	2258		5	s.l.	344	377	10.1
TAN0706 C4	29.353	180.97	2258		6	s.l.	273	270	12.1
TAN0706 C4	29.353	180.97	2258		8	s.l.	246	248	10.9
TAN0706 C4	29.353	180.97	2258		9	s.s.	203	227	6.0
TAN0706 C4	29.353	180.97	2258		10	s.s.	224	245	7.9
TAN0706 C4	29.353	180.97	2258		11	s.l.			24.4
TAN0706 C4	29.353	180.97	2258		12	s.l.			12.3
TAN0706 C4	29.353	180.97	2258		13	s.l.			13.8
TAN0706 C4	29.353	180.97	2258		14	s.l.			12.3
TAN0706 C4	29.353	180.97	2258		15	s.l.			16.7
TAN0706 C4	29.353	180.97	2258		16	s.s.			15.0
TAN0706 C4	29.353	180.97	2258		17	s.l.			16.2
TAN0706 C4	29.353	180.97	2258		18	s.s.			22.4
TAN0706 C4	29.353	180.97	2258		19	s.l.			7.6
TAN0706 C4	29.353	180.97	2258		20	s.l.			16.1
TAN0706 C4	29.353	180.97	2258		21	s.l.			14.7
TAN0706 C4	29.353	180.97	2258		22	s.s.			8.9
TAN0706 C4	29.353	180.97	2258		23	s.s.			10.2
TAN0706 C4	29.353	180.97	2258		24	s.l.			15.5
TAN0706 C4	29.353	180.97	2258		25	s.l.			12.3

					Individual				
Site	Latitude	Longitude	Depth	Age	Number	Morphotype	Х	Υ	Weight
	(degrees)	(degrees)	(metres)	(yr)			(µm)	(µm)	(µg)
TAN0706 C4	29.353	180.97	2258		26	s.l.			14.5
TAN0706 C4	29.353	180.97	2258		27	s.s.			7.0
TAN0706 C4	29.353	180.97	2258		28	s.s.			8.5
TAN0706 C4	29.353	180.97	2258		29	s.s.			7.7
P71	33.855	174.69	1919	5715 ± 40	1		368	396	10.4
P71	33.855	174.69	1919	5715 ± 40	2		271	300	9.0
P71	33.855	174.69	1919	5715 ± 40	2		271	300	9.0
P71	33.855	174.69	1919	5715 ± 40	3		257	296	8.4
P71	33.855	174.69	1919	5715 ± 40	3		257	296	8.4
P71	33.855	174.69	1919	5715 ± 40	4		311	327	14.2
P71	33.855	174.69	1919	5715 ± 40	4		311	327	14.2
P71	33.855	174.69	1919	5715 ± 40	5		270	299	6.3
P71	33.855	174.69	1919	5715 ± 40	7		268	315	9.0
P71	33.855	174.69	1919	5715 ± 40	8		210	223	4.4
P71	33.855	174.69	1919	5715 ± 40	9		353	340	8.7
P71	33.855	174.69	1919	5715 ± 40	9		353	340	8.7
P71	33.855	174.69	1919	5715 ± 40	10		297	338	10.3
P71	33.855	174.69	1919	5715 ± 40	11		253	286	9.2
P71	33.855	174.69	1919	5715 ± 40	13		254	250	4.9
P71	33.855	174.69	1919	5715 ± 40	13		254	250	4.9
P71	33.855	174.69	1919	5715 ± 40	14		192	233	8.4
P71	33.855	174.69	1919	5715 ± 40	14		192	233	8.4
P71	33.855	174.69	1919	5715 ± 40	16		299	321	4.1
P81	34.020	173.51	2036	5715 ± 40	1	s.l.	309	305	2.3
P81	34.020	173.51	2036	5715 ± 40	2	s.l.	293	291	3.3
P81	34.020	173.51	2036	5715 ± 40	3		289	294	3.5
P81	34.020	173.51	2036	5715 ± 40	5		296	344	4.3
P81	34.020	173.51	2036	5715 ± 40	6		282	272	3.1
P81	34.020	173.51	2036	5715 ± 40	7	S.S.	211	243	3.4
P81	34.020	173.51	2036	5715 ± 40	10	s.l.	188	234	2.6
P81	34.020	173.51	2036	5715 ± 40	12	S.S.	225	245	3.1
P81	34.020	173.51	2036	5715 ± 40	14	s.s.			2.1
P81	34.020	173.51	2036	5715 ± 40	15	s.l.			
P81	34.020	173.51	2036	5715 ± 40	16	s.l.			
P81	34.020	173.51	2036	5715 ± 40	17	s.l.			
P81	34.020	173.51	2036	5715 ± 40	18	s.s.			
P81	34.020	173.51	2036	5715 ± 40	20	s.l.			
P81	34.020	173.51	2036	5715 ± 40	21	s.l.			
P81	34.020	173.51	2036	5715 ± 40	25	s.l.			
P81	34.020	173.51	2036	5715 ± 40	26	-			
P81	34.020	173.51	2036	5715 ± 40	27				
Z7003	36.693	176.24	430	5932 ±55	2	s.l.	265	281	9.9
Z7003	36.693	176.24	430	5932 ±55	4	s.l.	319	315	16.1
Z7003	36.693	176.24	430	5932 ±55	6	s.l.	294	301	13.7
Z7003	36.693	176.24	430	5932 ±55	8	s.s.	261	296	10.1
Z7003	36.693	176.24	430	5932 ±55	10	s.l.	279	328	13.1
Z7003	36.693	176.24	430	5932 ±55	15	s.s.	246	279	9.6
Z7003	36.693	176.24	430	5932 ±55	16	s.s.			8.3
Z7003	36.693	176.24	430	5932 ±55	17	s.l.			6.8
Z7003	36.693	176.24	430	5932 ±55	18	s.l.			5.7
Z7003	36.693	176.24	430	5932 ±55	19	s.l.			10.0

					Individual				
Site	Latitude	Longitude	Depth	Age	Number	Morphotype	Х	Y	Weight
	(degrees)	(degrees)	(metres)	(yr)			(µm)	(µm)	(µg)
Z7003	36.693	176.24	430	5932 ±55	20	s.s.			crushed
Z7003	36.693	176.24	430	5932 ±55	21	s.s.			crushed
Z7003	36.693	176.24	430	5932 ±55	22	s.s.			15.8
Z7003	36.693	176.24	430	5932 ±55	23	s.s.			11.2
Z7003	36.693	176.24	430	5932 ±55	24	s.s.			12.0
Z7003	36.693	176.24	430	5932 ±55	25	s.s.			9.1
U2315	38.509	179.02	100-50	April 2001	2	s.l.	263	255	9.7
U2315	38.509	179.02	100-50	April 2001	3	s.l.	216	225	8.0
U2315	38.509	179.02	100-50	April 2001	4	s.l.	214	228	6.2
U2315	38.509	179.02	100-50	April 2001	5	s.l.	235	257	8.7
U2315	38.509	179.02	100-50	April 2001	6	s.s.	174	216	4.3
U2315	38.509	179.02	100-50	April 2001	9	s.s.	171	188	4.4
U2315	38.509	179.02	100-50	April 2001	10	s.s.	180	224	4.8
U2315	38.509	179.02	100-50	April 2001	11	s.l.	230	264	7.1
U2315	38.509	179.02	100-50	April 2001	12	s.s.	206	237	5.9
U2315	38.509	179.02	100-50	April 2001	13	s.s.	198	208	6.0
U2315	38.509	179.02	100-50	April 2001	14	s.s.	274	307	10.9
U2315	38.509	179.02	100-50	April 2001	15	s.l.	187	216	5.7
U2315	38.509	179.02	100-50	April 2001	16	s.s.	140	160	2.6
U2322net6	41.601	178.05	100-50	April 2001	1	s.l.	206	197	4.4
U2322net6	41.601	178.05	100-50	April 2001	3	s.l.	239	272	5.4
U2322net6	41.601	178.05	100-50	April 2001	4	s.s.	191	219	3.7
U2322net6	41.601	178.05	100-50	April 2001	5	s.s.	201	209	2.6
U2322net6	41.601	178.05	100-50	April 2001	6	s.s.	190	231	4.5
U2322net6	41.601	178.05	100-50	April 2001	8	s.s.	107	158	1.1
U2322net6	41.601	178.05	100-50	April 2001	9	s.s.	207	199	4.7
U2322net7	41.601	178.05	50-10	April 2001	1	s.s.	243	269	5.3
U2322net7	41.601	178.05	50-10	April 2001	2	s.s.	200	225	5.5
U2322net7	41.601	178.05	50-10	April 2001	3	s.s.	216	245	4.0
U2322net7	41.601	178.05	50-10	April 2001	4	s.l.	216	203	n.d.
ODP1123	41.942	188.50	3290		1	s.l.	250	261	6.8
ODP1123	41.942	188.50	3290		2	s.s.	180	174	3.8
ODP1123	41.942	188.50	3290		3	s.l.	190	188	4.8
ODP1123	41.942	188.50	3290		5	s.l.	179	216	2.7
ODP1123	41.942	188.50	3290		7	s.s.	188	217	2.5
ODP1123	41.942	188.50	3290		9	s.l.	189	232	6.3
ODP1123	41.942	188.50	3290		11	s.l.	180	194	4.4
ODP1123	41.942	188.50	3290		12	s.l.	194	218	5.9
ODP1123	41.942	188.50	3290		13	s.s.	150	203	4.4
ODP1123	41.942	188.50	3290		14	s.l.	125	200	3.5
ODP1123	41.942	188.50	3290		15	s.l.	171	195	2.2
ODP1123	41.942	188.50	3290		18	s.l.	148	193	2.2

N.B. In order to perform paired t-tests, those individuals where 1 or more chambers were excluded post-analysis, were not included in the above table. Cells in bold

Site	Individual Number	Chamber	Mg/Ca	Al/Ca	Mn/Ca	Sr/Ca	Zn/Ca	Ba/Ca
	1 tuilibel		(mmol/mol)	(µmol/mol)	(µmol/mol)	(mmol/mol)	(µmol/mol)	(µmol/mol)
AIMS1361	1	F	4.076	-0.4	32.4	1.429	10.7	1.1
AIMS1361	1	F-1	4.086	27.2	28.2	1.356	2.1	1.0
AIMS1361	1	F-2	5.213	54.1	42.2	1.477	2.4	1.1
AIMS1361	2	F	5.888	126.1	60.6	1.383	11.0	3.4
AIMS1361	2	F-1	5.905	479.5	64.6	1.424	12.0	1.9
AIMS1361	2	F-2	5.443	161.7	67.4	1.400	11.0	2.9
AIMS1361	3	F	4.695	2.1	56.3	1.458	2.9	1.0
AIMS1361	3	F-1	4.711	438.7	49.5	1.377	8.1	1.3
AIMS1361	4	F	3.849	33.3	51.3	1.411	14.7	1.1
AIMS1361	4	F-1	4.531	9.3	64.8	1.365	16.9	1.1
AIMS1361	4	F-2	6.111	328.1	53.7	1.403	13.2	1.5
AIMS1361	5	F	3.210	66.1	24.8	1.435	9.3	1.8
AIMS1361	5	F-1	5.487	370.4	34.7	1.406	9.9	3.4
AIMS1361	6	F	4.183	99.3	40.1	1.277	9.3	1.6
AIMS1361	6	F-1	6.057	580.1	70.2	1.375	5.2	3.6
AIMS1361	6	F-2	5.360	177.2	59.2	1.368	4.3	2.0
AIMS1361	7	F	4.241	148.7	2.7	1.422	6.7	0.9
AIMS1361	7	F-1	6.145	676.4	14.0	1.510	5.1	1.0
AIMS1361	8	F	3.474	148.9	55.9	1.346	12.7	1.8
AIMS1361	9	F	4.652	450.7	40.2	1.591	4.4	2.0
AIMS1361	10	F	4.435	9.6	27.7	1.435	7.0	1.2
AIMS1361	10	F-2	4.514	14.4	21.9	1.464	7.3	1.4
AIMS1361	11	F	3.708	74.8	5.9	1.415	3.3	0.7
AIMS1361	11	F-1	4.814	158.1	7.1	1.465	3.4	0.8
AIMS1361	11	F-2	4.680	73.3	6.8	1.494	2.8	1.1
AIMS1361	12	F	4.444	1.3	23.6	1.385	12.7	1.2
AIMS1361	12	F-1	5.140	150.1	26.9	1.487	11.9	1.4
AIMS1361	12	F-2	4.445	57.1	21.5	1.421	7.2	1.3
AIMS1361	13	F	3.508	399.4	37.3	1.348	8.4	1.3
AIMS1361	14	F	3.022	22.8	9.1	1.476	8.6	0.8
AIMS1361	14	F-1	5.489	35.1	18.6	1.459	4.6	1.4
AIMS1361	14	F-2	6.085	303.3	17.2	1.578	7.1	1.6
AIMS1631	1	F	4.008	29.9	23.4	1.463	13.3	1.1
AIMS1631	1	F-1	3.663	-7.3	24.1	1.645	19.8	1.1
AIMS1631	1	F-2	4.148	0.6	54.9	1.489	36.8	1.6
AIMS1631	2	F	3.059	36.7	13.5	1.432	15.2	1.4
AIMS1631	2	F-2	3.834	81.6	13.4	1.406	11.4	1.1
AIMS1631	3	F	3.458	12.7	20.8	1.415	16.3	1.1
AIMS1631	3	F-2	5.948	5.3	22.9	1.652	15.4	1.6
AIMS1631	4	F	4.624	17.5	6.2	1.400	42.1	0.8
AIMS1631	4	F-1	5.981	16.6	8.6	1.586	20.4	1.2
AIMS1631	4	F-2	5.130	23.9	4.6	1.482	16.3	0.9
AIMS1631	5	F	3.925	10.4	11.3	1.387	27.7	1.1
AIMS1631	5	F-1	5.078	8.3	16.8	1.456	34.9	1.1
AIMS1631	5	F-2	4.687	9.6	15.4	1.466	26.3	1.1
AIMS1631	6	F	4.069	10.3	13.7	1.407	13.1	0.8
AIMS1631	6	F-1	5.107	26.2	19.1	1.323	32.5	1.0
AIMS1631	.7	F	3.909	1.5	72.1	1.418	22.7	1.0
AIMS1631	./	F-1	4.562	-1.7	64.9	1.419	24.8	1.1
AIMS1631	./	F-2	4.773	3.7	99.6	1.393	19.2	2.0
AIMS1631	8	F-2	4.011	9.2	25.1	1.428	20.3	0.9
AIMS2078	1	F	3.5/1	197.1	2.2	1.675	2.4	1.3
AIMS2078	1	F-1	4.591	385.3	9.6	1.692	5.7	2.3
AIMS2078	1	F-2	5.361	1263.0	34.9	1.585	5.6	3.4
AIMS2078	2	F	4.116	134.2	5.4	1.663	6.1	1.8

Table A3: Other trace element data for *Globigernoides ruber* ($250 - 355 \mu m$) for core top and plankton tow sites in the Southwest Pacific Ocean

Site	Individual Number	Chamber	Mg/Ca	Al/Ca	Mn/Ca	Sr/Ca	Zn/Ca	Ba/Ca
			(mmol/mol)	(µmol/mol)	(µmol/mol)	(mmol/mol)	(µmol/mol)	(µmol/mol)
AIMS2078	2	F-1	6.960	216.1	24.5	1.651	7.1	2.7
AIMS2078	2	F-2	6.655	174.3	7.8	1.642	6.0	1.4
AIMS2078	3	F	3.798	917.0	13.0	1.571	668.0	2.0
AIMS2078	3	F-1	5.296	959.9	3.8	1.661	27.3	2.1
AIMS2078	3	F-2	7.007	740.4	5.5	1.612	6.0	2.6
AIMS2078	4	F	4.655	1150.2	41.0	1.511	13.1	2.4
AIMS2078	4	F-1	6.103	599.2	32.8	1.557	9.7	2.6
AIMS2078	4	F-2	4.340	922.4	45.9	1.521	33.9	3.0
AIMS2078	5	F-1	6.790	1194.8	19.0	1.466	6.7	1.4
AIMS2078	6	F	2.333	290.0	8.1	1.517	7.4	1.1
AIMS2078	6	F-1	6.067	507.0	23.4	1.531	5.7	3.1
AIMS2078	6	F-2	5.821	680.2	12.0	1.504	8.4	2.0
AIMS2078	7	F-1	6.563	1104.4	9.5	1.660	28.9	2.2
AIMS2078	7	F-2	6.645	141.8	8.7	1.594	3.9	1.4
AIMS2078	8	F	3.708	151.1	5.7	1.528	5.7	1.4
AIMS2078	8	F-1	5.413	340.8	17.0	1.393	19.1	2.4
AIMS2078	8	F-2	5.469	440.6	12.0	1.505	7.8	1.5
AIMS2078	9	F	3.604	330.2	5.9	1.403	5.1	1.0
AIMS2078	9	F-1	5.987	208.3	6.2	1.432	5.6	1.5
AIMS2078	9	F-2	5.488	93.8	5.3	1.498	1.8	1.1
AIMS2078	14	F	4.190	57.3	7.8	1.415	5.4	1.3
AIMS2078	14	F-1	5.452	140.7	15.6	1.469	14.0	2.8
AIMS2078	14	F-2	4.794	140.5	0.2	1.419	13.5	1.7
AIMS2078	15	F	4.661	455.7	9.3	1.464	38.3	1.4
AIMS2078	15	F-2	6.601	737.6	2.7	1.578	11.8	2.7
AIMS2078	16	F	2.642	29.6	4.0	1.332	9.2	1.1
AIMS2078	16	F-1	7.605	37.2	2.2	1.473	10.5	1.1
AIMS2078	16	F-2	7.064	150.0	4.9	1.435	7.5	1.7
AIMS2078	17	F	3.823	64.3	5.7	1.451	7.1	1.5
AIMS2078	17	F-1	4.167	184.9	3.7	1.380	5.4	1.4
AIMS2078	17	F-2	4.347	699.1	9.7	1.466	5.4	1.6
AIMS2078		F-3	3.799	917.5	13.4	1.568	668.2	1.3
AIMS2078		F-3	3.926	183.8	21.2	1.572	7.6	2.9
AIMS3703	1	F	4.085	432.2	66.9	1.534	36.9	3.1
AIMS3703	1	F-1	4.740	526.0	65.3	1.494	19.7	2.8
AIMS3703	1	F-2	5.302	187.3	50.2	1.507	14.6	2.4
AIMS3/03	2	F F	4.240	332.8	53.2	1.464	8.6	1./
AIMS3/03	2	F-1	5.298	429.7	/1.5	1.516	10.3	2.2
AIM53/03	3		2.897	155.3	51.1	1.424	18.2	1.3
AIM55/05	3	F-1 E 2	4.155	287.9	42.6	1.397	12.0 E 9	1./
AIM55705	5	Г-2 Г	3.621	25.8	20.7	1.415	5.8	0.9
AIM55/05	4	F F 2	4./58	255.9	55.7	1.415	10.2	1.3 1 E
AIM53703	4	Г-2 Г	0.4/0	1790.2	50.5 70.7	1.439	12.5	1.5
AIM53703	5	Г Е 2	0.303	1/69.2	/9./	1.439	21.0 16.2	2.9
AIM53703	5	Г-2 Г	0./41	1419.0 691 2	110.7	1.433	10.5	2.0
AIMS3703	0	г Е 1	4.131 5.715	001.2 951.2	07 C	1.022	25.2	0.0 2.0
AIM\$3703	0	Г-1 Е 2	J./15	001.0 228.4	07.0 40.4	1.400	23.3	3.0 1.8
AIM\$3703	0 7	F-2	4.940	58.2	19.4	1.495	19.5	1.0
AIMS3703	7	Е-1	4. <i>322</i> 6 194	15.2	58.0	1.544	16.3	2.0
AIM\$3702	7	F-2	6 969	38.7	21 0	1.505	8.0	2.0
AIMS3703	, 8	 F	4 484	874 5	58.1	1.505	0.7 22 7	27
AIMS3703	8	F-1	4 191	477.8	53.4	1 548	19.9	2.0
AIMS3703	8	F-2	3.208	-2523.9	58.1	1.504	-0.6	07
AIMS3703	11	F F	4.719	224.4	79.0	1.460	29.0	2.5
AIMS3703	13	F	5.899	16.2	29.0	1.626	9.0	1.5
AIMS3703	13	F-1	6.822	252.7	80.2	1.444	12.6	1.6
AIMS3703	13	F-2	6.221	74.6	54.7	1.444	9.3	1.4

Site	Individual Number	Chamber	Mg/Ca	Al/Ca	Mn/Ca	Sr/Ca	Zn/Ca	Ba/Ca
			(mmol/mol)	(µmol/mol)	(µmol/mol)	(mmol/mol)	(µmol/mol)	(µmol/mol)
AIMS3703	14	F	7.875	479.0	71.0	1.677	84.0	3.0
AIMS3703	14	F-1	7.319	949.1	93.3	1.497	47.5	4.4
AIMS3703	14	F-2	7.412	517.4	46.1	1.507	24.4	2.2
AIMS3703	15	F	4.849	108.8	30.7	1.480	12.6	1.7
AIMS3703	15	F-1	6.323	1030.9	41.6	1.552	18.7	2.2
AIMS3703	16	F	5.117	840.5	21.6	1.468	26.4	1.5
AIMS3703	16	F-1	5.678	1459.1	42.5	1.428	32.4	2.5
AIMS3703	16	F-2	5.476	80.8	21.5	1.448	45.4	1.7
AIMS3703	17	F	3.990	139.9	13.3	1.717	25.9	0.9
AIMS3703	17	F-1	5.934	240.6	51.3	1.465	65.7	2.5
AIMS3703	17	F-2	6.560	148.9	27.8	1.545	35.6	2.3
AIMS3703	18	F	5.940	-502.2	47.2	1.560	24.9	-0.8
AIMS3703	18	F-1	8.827	-9.3	65.3	1.541	10.4	1.8
AIMS3703	18	F-2	6.726	-19.1	39.7	1.525	6.7	1.4
AIMS3703	19	F	5.375	1668.2	62.3	1.579	44.2	2.2
AIMS3703	19	F-1	6.472	610.1	94.9	1.519	11.2	1.4
AIMS3703	19	F-2	5.804	2.6	39.6	1.486	6.8	1.1
FR1/97/GC12	1	F	2.398	121.7	36.6	1.425	6.2	1.2
FR1/97/GC12	1	F-1	5.738	1799.5	63.5	1.436	4.0	5.2
FR1/97/GC12	1	F-2	5.302	1716.8	83.6	1.411	4.3	4.3
FR1/97/GC12	2	F	3.811	861.6	47.1	1.575	88.5	3.2
FR1/97/GC12	2	F-2	4.256	460.5	28.3	1.500	5.6	1.5
FR1/97/GC12	3	F	3.958	230.5	15.4	1.571	8.3	2.4
FR1/97/GC12	3	F-1	6.348	653.5	11.6	1.545	4.8	2.0
FR1/97/GC12	3	F-2	5.151	74.0	36.5	1.482	4.2	1.6
FR1/97/GC12	4	F	4.318	566.1	17.0	1.529	5.1	1.3
FR1/97/GC12	5	F	4.216	33.2	21.5	1.583	1.7	3.0
FR1/97/GC12	5	F-1	5.969	416.8	16.4	1.554	2.7	2.8
FR1/97/GC12	5	F-2	5.860	373.3	50.8	1.379	2.7	1.5
FR1/97/GC12	6	F	2.957	1192.7	41.1	1.533	3.4	2.2
FR1/97/GC12	6	F-2	6.455	1562.7	41.1	1.489	3.4	1.8
FR1/97/GC12	7	F	4.146	479.3	26.8	1.608	3.8	5.8
FR1/97/GC12	7	F-1	4.954	696.1	21.5	1.452	2.0	8.1
FR1/97/GC12	7	F-2	4.439	799.7	37.4	1.375	9.8	1.7
FR1/97/GC12	9	F-1	5.086	1269.2	31.2	1.464	5.8	3.7
FR1/97/GC12	10	F	4.129	1023.8	54.5	1.448	133.2	2.0
FR1/97/GC12	10	F-2	3.863	1078.4	46.0	1.487	5.5	2.5
FR1/97/GC12	11	F	2.625	69.8	16.2	1.445	2.6	1.4
FR1/97/GC12	11	F-2	4.703	1744.8	33.7	1.359	8.0	1.7
FR1/97/GC12	12	F	5.684	1660.7	27.4	1.625	3.3	1.5
FR1/97/GC12	12	F-2	5.353	831.1	48.7	1.435	4.9	1.9
FR1/97/GC12	13	F	3.921	-40.6	52.2	1.368	3.2	1.5
FR1/97/GC12	13	F-1	4.788	-3586.4	0.0	1.365	-12.1	3.7
FR1/97/GC12	13	F-2	5.064	288.5	33.4	1.506	-0.9	3.3
FR1/97/GC12	14	F	4.090	63.5	23.9	1.614	2.0	1.6
FR1/97/GC12	14	F-1	6.477	-454.6	0.0	1.625	-1.4	1.6
FR1/97/GC12	14	F-2	5.205	1912.1	19.7	1.491	-8.4	1.8
FR1/97/GC12	15	F	6.784	-20.7	46.2	1.621	2.5	1.9
FR1/97/GC12	15	F-1	2.314	-6700.4	0.0	1.534	-14.4	1.9
FR1/97/GC12	15	F-2	3.728	685.0	44.8	1.574	2.4	2.1
FR1/97/GC12	16	F	2.779	462.0	26.1	1.508	-1.3	2.1
FR1/97/GC12	16	F-1	4.673	726.0	7.7	1.463	2.7	7.5
FR1/97/GC12	16	F-2	5.046	682.2	55.2	1.362	4.4	2.6
ODP1123	1	F	1.241	105.0	48.3	1.490	43.8	4.2
ODP1123	1	F-1	2.314	959.4	46.8	1.357	34.6	7.6
ODP1123	1	F-2	2.235	771.6	57.3	1.388	40.2	6.5
ODP1123	2	F	1.059	294.7	26.5	1.454	41.8	3.3
ODP1123	2	F-1	2.145	259.1	100.8	1.453	44.9	4.1

Site	Individual Number Chamber		Mg/Ca	Al/Ca	Mn/Ca	Sr/Ca	Zn/Ca	Ba/Ca
			(mmol/mol)	(µmol/mol)	(µmol/mol)	(mmol/mol)	(µmol/mol)	(µmol/mol)
ODP1123	2	F-2	1.533	132.6	31.1	1.414	47.1	3.3
ODP1123	3	F	2.618	310.1	12.4	1.418	23.4	2.9
ODP1123	3	F-1	2.541	95.6	9.7	1.475	15.7	2.7
ODP1123	3	F-2	2.938	236.2	9.2	1.425	17.3	2.7
ODP1123	4	F	1.176	653.2	108.5	1.479	51.6	6.6
ODP1123	4	F-2	1.806	597.6	68.6	1.424	83.3	6.4
ODP1123	5	F	1.435	382.3	17.5	1.493	51.8	2.9
ODP1123	5	F-1	1.525	825.1	11.9	1.468	36.5	8.9
ODP1123	5	F-2	1.473	464.7	7.7	1.501	33.4	2.0
ODP1123	7	F	1.448	254.9	162.9	1.484	64.0	8.3
ODP1123	7	F-2	1.528	322.7	126.1	1.533	71.5	6.9
ODP1123	8	F	1.612	69.2	18.2	1.497	9.0	4.3
ODP1123	9	F	1.350	/45./	41.9	1.398	54.9	7.8
ODP1123	9	F-1	1.417	180.2	17.9	1.370	33.3	4.5
ODP1123	9	F-2	1.442	2/4.9	14.7	1.384	26.1	3.7
ODPI123	10	F F 1	1.463	299.6	47.3	1.453	65.5	8.2
ODPI123	10	F-1 E	1.556	3/4./	27.0	1.453	44.1	/.3
ODP1123	11	Г Е 1	1.500	154.9	43.0	1.555	40.2	5.0
ODP1123	11	Г-1 Е 2	2.032	400.9	45.6	1.340	02.2	6.8
ODP1123	11	F-2	1.415	1271.0	43.0 55.1	1.505	37.2	0.8
ODP1123	12	Г Е 1	1.239	720.4	39.1	1.526	37.2	9.3
ODP1123	12	F-1	1.040	80.8	50.8	1.499	57.0	6.3
ODP1123	13	F_1	2 295	347.4	241.1	1.330	68.5	0.5
ODP1123	13	F	1 556	120.4	14.0	1.550	29.6	2.6
ODP1123	14	F-1	2.061	859.1	37.6	1.437	34.9	4.3
ODP1123	14	F-2	2.001	238.3	17.5	1.419	31.8	2.9
ODP1123	15	F	1.201	6.2	5.0	1.504	14.1	1.3
ODP1123	15	F-1	1.549	23.4	8.9	1.423	19.0	1.3
ODP1123	15	F-2	1.645	11.9	11.5	1.347	24.1	1.8
ODP1123	17	F-1	1.512	337.3	50.1	1.440	130.5	8.4
ODP1123	17	F-2	1.734	335.7	111.4	1.422	90.6	7.6
ODP1123	18	F	2.135	39.3	10.2	1.502	29.2	2.4
ODP1123	18	F-1	3.032	294.9	29.0	1.495	33.9	3.3
ODP1123	18	F-2	2.850	182.8	21.6	1.507	36.9	3.9
ODP1123	19	F	1.511	456.6	140.6	1.372	93.9	9.9
P71	1	F	2.056	62.1	27.4	1.347	23.5	2.0
P71	1	F-1	2.798	19.9	14.6	1.482	16.2	0.9
P71	1	F-2	2.446	40.5	24.1	1.405	19.3	1.8
P71	2	F	2.372	45.2	34.9	1.446	55.2	1.4
P71	2	F	2.256	43.6	44.6	1.449	45.0	1.4
P71	2	F-1	2.777	76.1	33.7	1.345	64.4	1.5
P 71	2 rep	F-1	3.185	42.5	35.8	1.391	90.6	1.7
P71	2	F-2	2.716	27.6	31.4	1.374	48.3	1.5
P71	2 rep	F-2	2.658	1.2	28.2	1.380	44.5	2.4
P/1	3	F	2.283	-2.2	5.7	1.533	16.7	1.1
P71	3 rep	F	2.901	73.7	17.9	1.572	54.9	1.4
P/1	3	F-1	4.040	65.9	21.3	1.598	43.5	1.3
P71	3 rep	F-1	3. 757	23.1	16.5	1.553	35.3	11.1
P/1 D71	3	F-2	4.165	21.0	25.4	1.513	4/.2	8.5
P/1 D71	3 rep	F-2	4.127	38.0	40.3	1.467	5 7.2	5.9
P/1 D71	4	F F	2.356	123.1	30.0	1.3/5	40.2	5.4 E 1
F/I D71	4 rep	F	2 .394	1/0.9	82.6	1.384	21.2	5.1
17/1 D71	4	г-1 Б 1	2.704	0/4.2	26.0	1.438	20.9	5.5 E 9
I'/I D71	4 rep	Г-1 Б 2	2.83U	58.5 300 7	29. 1	1.415	2 0.4	5.8
1'/1 D71	4	г-2 Е Э	2.00/ 2 E20	500.7	32.9 20 7	1.365	04.1 22 1	1.9 1 E
171 P71	4 rep	1'-4 F	2.339 2.551	52.1 65.8	4 9. 1 0.2	1 081	99.1 82.7	-1.3 1 4
1 / 1	5	1	2.331	05.0	1.4	1.701	04.1	1.4

Site	Individual Number	r Chamber	Mg/Ca	Al/Ca	Mn/Ca	Sr/Ca	Zn/Ca	Ba/Ca
			(mmol/mol)	(µmol/mol)	(µmol/mol)	(mmol/mol)	(µmol/mol)	(µmol/mol)
P71	5 rep	F	2.352	196.7	68.4	1.877	70.8	1.6
P71	5	F-1	3.404	30.6	14.7	1.805	47.8	1.6
P71	5 rep	F-1	3.129	74.6	13.4	1.797	40.3	2.4
P71	5	F-2	3.994	125.9	42.3	1.719	56.9	2.7
P71	6	F-1	3.121	19.3	55.9	1.394	31.3	1.6
P71	6	F-2	2.405	42.6	20.2	1.367	25.6	4.0
P71	6 rep	F-2	3.139	911.6	71.2	1.389	26.2	1.6
P71	7	F	2.988	72.1	14.9	1.393	33.8	1.5
P71	7 rep	F	3.137	1469.9	41.1	1.405	44.5	1.6
P71	7	F-1	2.442	70.2	8.0	1.451	16.2	1.9
P71	7 rep	F-1	3.021	672.0	34.5	1.391	21.0	6.9
P71	7	F-2	2.016	13.2	4.1	1.479	7.4	5.5
P71	7 rep	F-2	3.414	241.4	50.4	1.359	18.8	4.2
P71	8	F	3.291	37.5	52.9	1.488	33.9	5.4
P7 1	8 rep	F	1.388	98.3	26.0	1.440	15.6	1.4
P71	8	F-1	2.208	158.5	47.1	1.405	12.6	2.3
P71	8	F-2	2.377	10.5	34.0	1.417	21.5	1.4
P71	8 rep	F-2	3.258	46.4	65.4	1.336	12.4	15.3
P71	9	F	1.530	1297.4	29.9	1.418	19.3	1.0
P71	9 rep	F	2.320	112.6	46.3	1.443	25.3	0.8
P71	9	F-1	2.596	71.3	61.4	1.338	31.8	1.0
P71	9 rep	F-1	2.436	24.5	15.6	1.419	18.2	2.0
P71	9	F-2	2.511	61.6	20.2	1.423	30.7	9.7
P71	9 rep	F-2	2.924	89.3	18.5	1.623	10.7	2.7
P71	10	F	2.131	890.9	15.1	1.523	23.4	1.4
P71	10 rep	F	2.078	443.9	16.4	1.565	22.5	3.0
P71	10 rep	F	2.411	116.5	70.5	1.360	42.1	1.2
P71	10	F-1	3.327	22.9	15.2	1.493	17.9	3.9
P71	10 rep	F-1	3.390	29.8	14.0	1.514	14.1	3.2
P 71	10 rep	F-1	2.535	202.5	62.7	1.382	32.2	3.5
P71	10	F-2	3.443	46.1	16.6	1.498	16.9	1.5
P71	11	F	2.527	308.3	15.2	1.442	17.4	2.4
P71	11	F-1	3.512	724.8	55.7	1.480	21.0	2.9
P71	11	F-2	3.911	422.4	166.1	1.498	24.1	5.0
P71	12	F	1.241	43.5	8.3	1.602	3.0	0.5
P71	12	F-1	1.832	158.1	34.4	1.437	7.2	0.6
P71	13	F	2.803	41.3	25.4	1.547	27.1	1.3
P 71	13 rep	F	2.577	24.9	11.5	1.421	16.6	1.0
P71	13	F-1	4.212	60.1	45.1	1.450	37.7	1.7
P71	13 rep	F-1	3.131	57.4	24.5	1.392	15.6	1.2
P/1	13	F-2	3.176	28.1	23.5	1.465	15.0	1.3
P71	13 rep	F-2	4.371	106.4	53.8	1.424	34.7	1.5
P/1	14	F	2.384	17.5	56.4	1.472	22.8	3.8
P71	14 rep	F	2.757	23.2	38.9	1.448	25.3	18.1
P/1	14	F-I E 4	3.123	219.0	/9.0	1.419	37.6	0.9
P/I	14 rep	F-1	2.915	44.1	61.1	1.535	30.9	-3.3
P/I D71	14	F-2	3.818	25.9	49.9	1.429	24.6	1.5 F 2
P/I D71	14 rep	F-2	4.090	44.Z	55.0	1.490	30.8	5.3
17/1 D71	15	Г Е 1	2.813	119.2	43./ 01.2	1.333	40.0 55 1	4.0
17/1 1074	15	Г-1 Г	2.700	377.4 07.0	91.3 42 F	1.408	27.0	4.0
P/1 D74	16	Г Е 1	2.154	δ/.δ 114.0	43.5	1.399	3/.9 10.4	3.4 1 5
17/1 D71	10	Г-1 Г 2	2.193	114.8	15.4	1.314	19.4	1.5
1'/l D01	10	г-2 Б	2.107	922.9 136.0	10.0	1.269	14.3	1./ 5.1
Гð1 D04	1	Г Е 1	1.550	125.9	07.0	1.491	00.9 27 4	J.1
1781 D01	1	Г-1 БЭ	2.903	100.9	97.9 112 7	1.470	5/.4 16 2	0.5
F 01 D01	1	1'-2 E	2.340	40.4 220.6	20.0	1.401	40.J	0.5
P01	2	Г Г 1	2.342	230.0 57 5	30.0 26 4	1.402	02.0 52.0	5.6
r 01	2	Γ-1	2.044	57.5	50.4	1.380	52.0	4.0

Site	Individual Number	Chamber	Mg/Ca	Al/Ca	Mn/Ca	Sr/Ca	Zn/Ca	Ba/Ca
			(mmol/mol)	(µmol/mol)	(µmol/mol)	(mmol/mol)	(µmol/mol)	(µmol/mol)
P81	2	F-2	2.985	129.5	53.1	1.415	45.1	5.6
P81	3	F	4.535	311.8	75.2	1.425	137.2	5.3
P81	3	F-1	4.196	635.9	240.7	1.416	116.3	10.1
P81	3	F-2	4.774	765.4	222.7	1.347	118.5	12.5
P81	5	F	1.994	379.7	118.6	1.332	64.2	8.0
P81	5	F-1	2.485	623.0	144.7	1.364	91.4	12.2
P81	5	F-2	2.214	230.5	159.2	1.346	130.9	10.8
P81	6	F	2.238	73.4	64.4	1.421	36.7	3.1
P81	6	F-1	3.543	68.6	94.0	1.320	19.7	4.3
P81	6	F-2	2.956	36.0	90.5	1.361	36.5	4.0
P81	7	F	3.928	103.4	43.1	1.439	39.4	4.1
P81	7	F-1	4.621	48.0	103.4	1.355	34.5	4.6
P81	7	F-2	4.282	52.4	52.5	1.366	40.4	5.2
P81	8	F	1.796	43.9	26.3	1.437	11.2	1.9
P81	8	F-1	2.439	37.0	34.0	1.365	11.7	2.8
P81	9	F-1	3.533	258.3	240.2	1.301	37.1	1.0
P81	10	F	2.781	34.1	45.0	1.382	29.4	2.8
P81	10	F-1	3.107	43.7	168.0	1.423	36.5	4.7
P81	10	F-2	3.775	90.1	128.6	1.416	272.8	5.6
P81	11	F	2.573	19.9	16.2	1.483	10.4	1.3
P81	11	- F-1	3.924	30.0	70.7	1.403	8.4	1.9
P81	12	F	3.406	71.5	148.3	1.364	115.8	5.7
P81	12	- F-1	3.834	355.3	53.9	1.378	43.1	5.1
P81	12	F-2	4 179	65.0	79.9	1.402	57.3	8.1
P81	13	F_1	4 313	591.6	271.6	1 332	39.5	9.8
P81	13	F-2	3 1 4 6	91.9	118.0	1.352	25.2	53
P81	13	F	1 480	368.0	209.0	1.128	242.0	9.0
P81	14	F-2	2 592	242.0	60.0	1 214	93.0	3.0
P81	14	F_1	3 3 3 7	234.0	44 0	1.211	66.0	3.0
P81	15	F	1 598	311.0	304.0	1.271	140.0	10.0
P81	15	F_2	2 013	219.0	111.0	1.110	46.0	7.0
D81	15	F 1	2.013	400.0	485.0	1.155	72.0	17.0
D81	16	F	1 385	226.0	33.0	1.052	24.0	2.0
D81	16	F 2	2 1 9 4	413.0	166.0	1.134	103.0	6.0
D81	16	F 1	2.104	349.0	121.0	1.071	64.0	5.0
DQ1	10	Г-1 Г	2.405	384.0	22.0	1.140	79.0	3.0
F 01 DQ1	17	Г Г 2	2.038	321.0	22.0	1.240	124.0	3.0
F 01 DQ1	17	Г- <u>-</u> Г 1	2.930	378.0	24.0	1.135	60.0	4.0
F 01 DQ1	17	Г-1 Г	2.334	203.0	24.0	1.235	135.0	3.0
D81	18	F 2	2.460	205.0	83.0	1.007	287.0	4.0
D81	18	F 1	2.400	205.0	55.0	1.051	235.0	5.0
DQ1	10	E 2	2.751	430.0	37.0	1.007	255.0	6.0
P 01 D 01	19	Г- <u>2</u> Г 1	2.477	439.0	37.0 42.0	1.100	117.0	6.0
P 01 D 01	19 20	Г-1 Г	2.371	323.0	43.0 51.0	1.149	121.0	6.0
P 01 D 01	20	г Г 2	1.330	207.0	S1.0	1.139	133.0	0.0
P 01 D 01	20	Г- <u>2</u> Г 1	1.077	296.0	00.0 425.0	1.122	87.0 74.0	0.0 16.0
P01 D01	20	г-1 Г	1.404	184.0	433.0	1.111	74.0	2.0
P81 D01	21	F F 2	1.3//	184.0	65.0	1.192	74.0	5.0
P81	21	F-Z	2.344	231.0	98.0	1.051	325.0	6.0
P81	21	г-1 Г	2.269	528.U	01.0	1.069	1/3.0	/.U E.O
P81	22	Г	1.1/9	363.0	98.0	1.192	191.0	5.0
P81	23	г Г о	2.455	147.0	24.0	1.256	20.0	3.0
P81	23	F-2	3.5/8	440.0	63.0	1.125	106.0	7.0
P81	24	F	2.449	300.0	36.0	1.274	207.0	3.0
P81	24	F-2	2.768	291.0	72.0	1.142	224.0	4.0
P81	25	F	2.380	270.0	44.0	1.233	55.0	4.0
P81	25	F-2	3.663	260.0	48.0	1.304	50.0	7.0
P81	25	F-1	3.153	545.0	33.0	1.207	126.0	6.0
P81	26	F	1.122	167.0	43.0	1.013	159.0	6.0

$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	Site	Individual Number	Chamber	Mg/Ca	Al/Ca	Mn/Ca	Sr/Ca	Zn/Ca	Ba/Ca
P81 26 F-2 1.465 22.0 52.0 0.984 161.0 5.0 P81 27 F 1.925 294.0 54.0 1.005 18.0 3.0 P81 27 F 1.925 294.0 54.0 1.005 18.0 3.0 TAN0706 1 F-1 2.777 420.0 60.0 1.021 5.0 3.0 C4 - - - 1.30 1.3.5 0.9 C4 - - - - 1.31 16.0 1.1 C4 - - - 1.32 7.7 1.331 10.0 1.1 C4 - - - - - - 1.2 1.38 38.1 1.7 C4 7.07 1.4.7 7.6 1.424 50.4 0.9 C4 7.07 1.4.7 5.1 3.0 1.346 9.4 0.7 C4 <				(mmol/mol)	(µmol/mol)	(µmol/mol)	(mmol/mol)	(µmol/mol)	(µmol/mol)
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	P81	26	F-2	1.405	222.0	52.0	0.984	161.0	5.0
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	P81	26	F-1	1.486	308.0	142.0	1.070	221.0	7.0
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	P81	27	F	1.925	294.0	54.0	1.005	18.0	3.0
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	P81	27	F-2	2.727	420.0	60.0	1.021	27.0	5.0
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	TAN0706	1	F	3.573	11.7	6.1	1.340	13.5	0.9
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	C4								
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	TAN0706	1	F-1	4.746	13.2	7.7	1.331	16.9	1.1
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	C4								
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	TAN0706	1	F-2	3.917	10.0	4.7	1.331	10.0	1.1
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	C4	_	_						
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	TAN0706	2	F	4.483	35.2	10.2	1.388	38.1	1.7
$\begin{array}{c c c c c c c c c c c c c c c c c c c $		2	E 4	7407	4.4.7	7 (4 424	50.4	0.0
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	TAN0706	2	F-1	/.10/	14./	/.6	1.424	50.4	0.9
$\begin{array}{c c c c c c c c c c c c c c c c c c c $		2	EA		50.2	()	1 464	10.0	0.0
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	TAN0706	2	F-2	6.5/5	50.3	6.2	1.464	10.9	0.9
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	C4 TANO70C	2	Б	2 474	E 1	2.0	1 246	0.4	0.7
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	C_{A}	5	Г	3.4/4	5.1	3.0	1.340	9.4	0.7
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	C4 TAN0706	3	F 2	5 260	34.4	16.9	1 306	25.7	1 2
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	C4	5	1-2	5.200	54.4	10.9	1.500	23.7	1.2
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	C4 TAN0706	4	F	3 255	28.2	62	1 378	54.4	0.9
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	C4	1	1	5.255	20.2	0.2	1.570	51.1	0.9
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	TAN0706	4	F-2	5.623	22.7	12.9	1.605	23.0	1.2
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	C4			0.000					
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	TAN0706	5	F	1.825	4.8	0.4	1.467	16.4	0.9
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C4								
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	TAN0706	5	F-1	3.699	7.5	4.2	1.387	18.4	0.9
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C4								
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	TAN0706	5	F-2	3.766	7.3	5.7	1.361	38.0	1.1
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C4								
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	TAN0706	6	F	2.498	7.8	1.2	1.403	9.9	0.5
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C4								
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	TAN0706	6	F-1	4.547	6.9	4.0	1.378	21.1	0.8
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C4	,		4.05.4	<i>(</i> 1	2.2	4 400	24.0	0.0
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	TAN0706	6	F-2	4.054	6.1	2.3	1.409	31.2	0.8
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	C4	7	E	2.244	E 2	(1	1 240	(7	0.9
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C_{A}	/	Г	2.200	5.5	0.1	1.349	0.7	0.8
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C4 TAN0706	7	F-1	3.067	22.7	13.8	1 324	37.4	12
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C4	1	1 1	5.007	22.1	15.0	1.521	57.1	1.2
CATANOTOG8F-1 3.631 5.3 6.0 1.326 49.9 0.8 CATAN07068F-2 3.245 3.9 2.4 1.359 40.9 0.7 CATAN07069F 1.903 6.9 3.1 1.357 53.7 0.8 CATAN07069F 1.903 6.9 3.1 1.357 53.7 0.8 CATAN07069F-1 3.186 17.4 8.6 1.362 70.6 1.0 CATAN07069F-2 2.735 11.9 8.2 1.407 45.5 1.0 CATAN070610F 3.401 15.0 5.4 1.351 56.1 0.9 CATAN070610F-1 4.548 12.7 8.0 1.494 20.2 1.2 TAN070610F-2 4.200 13.1 4.8 1.406 18.7 1.0	TAN0706	8	F	2.528	6.5	2.2	1.408	31.2	0.7
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	C4	Ū.	-		0.0				
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	TAN0706	8	F-1	3.631	5.3	6.0	1.326	49.9	0.8
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C4								
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	TAN0706	8	F-2	3.245	3.9	2.4	1.359	40.9	0.7
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C4								
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	TAN0706	9	F	1.903	6.9	3.1	1.357	53.7	0.8
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C4								
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	TAN0706	9	F-1	3.186	17.4	8.6	1.362	70.6	1.0
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C4								
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	TAN0706	9	F-2	2.735	11.9	8.2	1.407	45.5	1.0
TAN0706 10 F 3.401 15.0 5.4 1.351 56.1 0.9 C4 TAN0706 10 F-1 4.548 12.7 8.0 1.494 20.2 1.2 C4 TAN0706 10 F-2 4.200 13.1 4.8 1.406 18.7 1.0	C4		_						
C4 TAN0706 10 F-1 4.548 12.7 8.0 1.494 20.2 1.2 C4 TAN0706 10 F-2 4.200 13.1 4.8 1.406 18.7 1.0	TAN0706	10	F	3.401	15.0	5.4	1.351	56.1	0.9
IAN0706 10 F-1 4.548 12.7 8.0 1.494 20.2 1.2 C4 TAN0706 10 F-2 4.200 13.1 4.8 1.406 18.7 1.0		10	E 4	4 5 40	10 5	0.0	4 40 4	00.0	4.0
TAN0706 10 F-2 4.200 13.1 4.8 1.406 18.7 1.0	1 AIN0 / 06	10	F-1	4.548	12./	8.0	1.494	20.2	1.2
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C4 TAN0706	10	F 2	4 2 00	121	19	1 406	187	1.0
	C4	10	1 -2	7.200	13.1	т.0	1.700	10./	1.0

Site	Individual Number	Chamber	Mg/Ca	Al/Ca	Mn/Ca	Sr/Ca	Zn/Ca	Ba/Ca
		((mmol/mol)	(µmol/mol)	(µmol/mol)	(mmol/mol)	(µmol/mol)	(µmol/mol)
TAN0706	11	F-2	4.420	55.0	7.4	1.408	× /	1.0
C4 TAN0706 C4	11	F	3.019	20.8	8.6	1.479		0.8
TAN0706 C4	11	F-1	4.178	579.0	89.5	1.420		2.2
TAN0706 C4	12	F-2	5.304	58.8	5.4	1.439		1.3
TAN0706 C4	12	F-1	4.542	35.5	13.5	1.417		3.8
TAN0706 C4	12	F	2.882	74.1	18.8	1.311		0.9
TAN0706 C4	13	F	2.617	15.8	4.3	1.297		0.8
TAN0706 C4	13	F-2	2.776	40.6	8.6	1.307		1.0
TAN0706 C4	13	F-1	3.244	80.6	14.3	1.335		1.2
TAN0706 C4	14	F	2.326	23.3	3.1	1.541		0.8
TAN0706 C4	14	F-2	2.410	43.2	12.0	1.461		1.7
TAN0706 C4	14	F-1	2.892	129.7	16.0	1.330		1.0
TAN0706 C4	15	F	2.996	16.6	2.0	1.404		0.7
TAN0706 C4	15	F-1	5.426	65.2	7.1	1.378		1.1
TAN0706 C4	15	F-2	5.251	3/./	13.1	1.429		1.1
TAN0706 C4	16	F	2.473	9.3	1.1	1.344		0.5
TAN0706 C4	16	F-l	2.643	21.1	6.9	1.296		0.6
C4	17	F-1	3./1/ 2.0(E	24.1	2.7	1.347		0.7
C4 TAN0706	17	F-Z	2.572	34.1 249.0	0.4	1.303		12.6
C4 TAN0706	10	г Е 2	2 521	540.9	2 5	1.4/7		1.4
C4 TAN0706	10	Г-2 Б 1	1 754	6.3	9.0	1.412		0.7
C4 TAN0706	18	F	2 985	82	8.6	1.400		0.7
C4 TAN0706	10	F	1.656	38.1	3.2	1 349		0.9
C4 TAN0706	19	г F-2	2 450	31.5	6.6	1 333		1.0
C4 TAN0706	19	F-1	2.200	29.9	19.4	1.306		1.0
C4 TAN0706	20	F	2.396	8.1	1.8	1.463		0.5
C4 TAN0706	20	F-2	3.166	329.4	8.8	1.473		0.9
C4 TAN0706	20	F-1	3.913	355.5	12.3	1.390		3.8
C4								

Site	Individual Numbe r	Chamber	Mg/Ca	Al/Ca	Mn/Ca	Sr/Ca	Zn/Ca	Ba/Ca
		(mmol/mol)	(µmol/mol)	(µmol/mol)	(mmol/mol)	(µmol/mol)	(µmol/mol)
TAN0706	21	F	3.869	13.9	2.2	1.441	× ,	0.6
C4 TAN0706 C4	21	F-1	6.335	16.9	3.9	1.439		1.3
TAN0706 C4	21	F-2	6.588	38.5	7.0	1.459		0.9
TAN0706 C4	22	F	1.666	22.4	2.8	1.330		0.7
TAN0706 C4	22	F-2	2.537	27.2	3.3	1.329		3.2
TAN0706 C4	22	F-1	2.441	36.6	5.8	1.355		0.8
TAN0706 C4	23	F	1.774	6.8	1.6	1.335		0.5
TAN0706 C4	23	F-1	2.462	45.8	10.2	1.261		0.9
TAN0706 C4	23	F-2	2.391	87.0	23.2	1.289		0.8
TAN0706 C4	24	F-1	2.876	36.8	6.5	1.429		1.6
TAN0706 C4	24	F-2	2.606	23.9	18.0	1.516		1.2
TAN0706 C4 TAN0706	24	F E 2	4.263	69.9	38.0	1.386		1.2
C4	25	г-2	1.9(0)	10.2	2.5	1.335		0.5
C4 TAN0706	25	г Е 1	2 271	20.5	5.0 4 1	1.339		2.0
C4 TAN0706	25	F 2	4.008	20.5	3.0	1.314		1.3
C4 TAN0706	20	F	3 235	13.0	1.3	1.274		0.6
C4 TAN0706	26	F-1	3 931	18.9	5.7	1 299		1.1
C4 TAN0706	27	F-2	3.468	37.4	18.0	1.396		0.9
C4 TAN0706	27	F	3.774	38.8	32.7	1.429		1.0
C4 TAN0706	27	F-1	4.213	71.6	38.4	1.384		1.2
C4 TAN0706	28	F-1	2.650	21.5	5.2	1.305		0.8
C4 TAN0706	28	F-2	3.033	30.1	9.4	1.244		0.9
C4 TAN0706	28	F	2.181	159.0	27.4	1.368		1.4
C4 TAN0706	29	F	2.267	15.5	12.8	1.378		0.8
C4 TAN0706	29	F-2	3.077	32.9	42.3	1.347		1.0
C4 TAN0706	29	F-1	3.604	31.4	65.6	1.313		1.2
C4 TAN0706	30	F	2.132	10.1	4.6	1.324		0.7
C4 TAN0706 C4	30	F-2	2.600	71.4	59.5	1.300		0.9

Site	Individual Number	Chamber	Mg/Ca	Al/Ca	Mn/Ca	Sr/Ca	Zn/Ca	Ba/Ca
	rumber		(mmol/mol)	(umol/mol)	(umol/mol)	(mmol/mol)	(umol/mol)	(umol/mol)
U2315	1	F-1	4 095	7 1	9.3	1 577	134.8	1 4
U2315	1	F-2	3 289	20.5	9.1	1.670	153.3	1.1
U2315	2	F _	1.361	-2.3	6.8	1.650	291.4	0.8
U2315	2	F-1	4.064	1.8	4.6	1.564	92.4	0.8
U2315	2	F-2	2.424	-9.7	1.5	1.384	44.4	0.7
U2315	3	F	3.102	-0.9	2.2	1.454	32.3	0.6
U2315	3	F-1	6.082	7.6	4.2	1.521	43.5	1.0
U2315	3	F-2	5.909	1.6	0.9	1.551	35.5	0.9
U2315	4	F	2.497	-6.8	3.8	1.505	268.9	0.7
U2315	4.1	F	3.207	6.2	6.8	1.501	134.8	1.0
U2315	4	F-1	4.680	5.5	7.4	1.529	77.1	1.2
U2315	4	F-2	3.261	5.6	9.6	1.520	63.9	1.3
U2315	5	F	2.178	3.9	5.8	1.466	93.4	0.9
U2315	5	F-1	3.160	0.9	5.9	1.526	69.7	1.2
U2315	5	F-2	2.294	3.7	2.9	1.443	27.2	0.7
U2315	6	F	2.775	12.1	17.5	1.618	300.2	1.8
U2315	6	F-1	3.444	30.2	25.2	1.601	303.0	2.2
U2315	6	F-2	3.673	19.6	25.4	1.609	285.0	1.9
U2315	7	F-1	3.047	2.7	4.1	1.560	70.9	0.8
U2315	7	F-2	4.317	4.4	2.9	1.457	71.2	0.9
U2315	9	F	1.873	25.2	11.0	1.485	190.1	1.5
U2315	9	F-1	2.964	8.1	30.5	1.482	55.3	0.9
U2315	9	F-2	2.624	3.8	7.3	1.496	69.9	0.8
U2315	10	F	3.125	21.0	17.0	1.624	255.0	2.0
U2315	10	F-1	3.514	9.6	8.2	1.529	161.1	1.3
U2315	10	F-2	3.564	14.1	8.2	1.618	146.9	1.5
U2315	11	F	0.913	3.4	2.5	1.531	54.8	0.6
U2315	11	F-1	2.932	0.1	3.1	1.501	27.0	0.8
U2315	11	F-2	2.294	-4.4	2.0	1.427	15.1	0.7
U2315	12	F	2.188	15.1	21.3	1.665	597.0	2.0
U2315	12	F-1	3.929	0.8	14.4	1.604	253.2	1.7
U2315	12	F-2	3.304	-2.5	7.9	1.480	133.8	0.9
U2315	13	F	2.551	1.9	4.7	1.480	88.6	0.9
U2315	13	F-1	2.798	6.2	8.2	1.486	115.7	1.3
U2315	13	F-2	3.364	1.3	13.4	1.481	137.9	1.2
U2315	14	F	1.826	1.3	2.3	1.554	47.3	0.7
U2315	14	F-1	4.241	-1.6	5.3	1.557	62.7	1.0
U2315	14	F-2	2.975	1.0	7.4	1.445	94.6	1.0
U2315	15	F	3.253	36.6	19.1	1.847	638.8	1.8
U2315	15	F-1	3.841	10.5	4.0	1.474	133.7	1.0
U2315	15	F-2	2.090	10.9	5.4	1.552	170.6	0.9
U2315	16	F	2.090	5.8	8.7	1.494	212.6	0.9
U2315	16	F-1	2.845	3.6	5.7	1.514	88.7	0.9
U2315	16	F-2	2.600	5.3	2.6	1.537	70.9	0.7
U2322	1	F	2.695	28.3	10.0	1.469	105.9	0.9
NET6								
U2322	1	F-1	4.602	82.8	8.8	1.448	152.5	1.3
NET6								
U2322	1	F-2	3.934	10.5	8.5	1.472	129.8	1.1
NET6								
U2322	2	F	2.387	16.2	2.7	1.635	16.3	0.8
NET6								
U2322	2	F-2	3.739	26.2	1.5	1.509	25.3	0.6
NET6								
U2322	3	F-1	2.694	24.2	8.3	1.524	369.3	1.0
NET6								
U2322	3	F-2	2.165	6.9	4.0	1.575	300.6	0.8
NET6								

Site	Individual Number	Chamber	Mg/Ca	Al/Ca	Mn/Ca	Sr/Ca	Zn/Ca	Ba/Ca
			(mmol/mol)	(µmol/mol)	(µmol/mol)	(mmol/mol)	(µmol/mol)	(µmol/mol)
U2322	3	F	2.083	29.8	7.7	1.588	453.8	0.9
NET6								
U2322	4	F	4.236	3.4	4.1	1.627	49.8	1.0
NET6								
U2322	4	F-1	4.365	-8.9	5.6	1.561	26.6	0.8
NET6								
U2322	4	F-2	2.968	-3.2	3.7	1.504	20.1	0.7
NET6								
U2322	5	F	1.804	8.0	6.5	1.563	158.3	1.2
NET6								
U2322	5	F-1	3.021	20.3	6.0	1.463	123.8	1.3
NET6								
U2322	5	F-2	2.685	53.9	6.7	1.466	127.1	1.3
NET6								
U2322	6	F	2.960	28.2	4.1	1.527	136.7	1.3
NET6								
U2322	6	F-1	3.291	15.0	0.0	1.532	79.2	0.8
NET6								
U2322	6	F-2	3.018	98.0	4.3	1.494	42.4	0.6
NET6								
U2322	7	F	1.842	57.1	2.6	1.539	23.3	0.8
NET6								
U2322	7	F-1	3.549	46.1	6.9	1.522	88.7	1.1
NET6								
U2322	8	F	3.089	4.3	5.9	1.472	39.2	0.8
NET6								
U2322	8	F-1	2.338	-0.2	3.9	1.440	38.1	0.7
NET6								
U2322	8	F-2	3.072	22.9	4.0	1.450	47.4	0.9
NET6								
U2322	9	F	2.522	22.4	3.8	1.454	35.4	0.7
NET6								
U2322	9	F-1	3.335	25.3	5.2	1.542	24.3	0.8
NEI6	0		2 27 4	1011	10	4 400	20 (0.4
U2322	9	F-2	2.3/4	104.4	4.0	1.482	28.6	0.6
NE16	-	E 4	2 250	0.0	40.4	4 554		4.0
U2322	5	F-1	3.250	9.8	10.1	1.556		1.5
NEI/	-	E	2 551	175	12.6	1 45 4		0.0
UZ3ZZ NET7	5	Г	2.551	17.5	12.0	1.454		0.9
INE17 112322	5	БЭ	4.007	21.7	25.0	1 626		1.8
02322 NET7	5	1'-2	4.007	21.7	23.0	1.020		1.0
INE17 112322	6	Б	1 494	18.0	3.2	1 401		0.7
NET7	0	1	1.404	10.0	5.2	1.471		0.7
112322	6	F-2	2 464	9.7	6.4	1 496		1.0
NET7	0	1 -2	2.404	2.1	0.4	1.470		1.0
112322	6	F-1	2 909	6.8	6.6	1 471		0.9
NET7	0	1 1	2.909	0.0	0.0	1.171		0.9
U2322	7	F	2.686	20.6	32	1 546		0.7
NET7	,		2.000	2010	5.2	110 10		0.17
U2322	7	F-2	2.978	7.3	9.1	1.631		1.0
NET7	,							
U2322	7	F-1	3.274	7.4	15.1	1.470		1.2
NET7		-						
U2322	8	F-2	2.509	10.1	2.7	1.483		0.7
NET7	~	-						
U2322	8	F	1.299	19.6	5.4	1.433		0.8
NET7								

Site	Individual Number	Chamber	Mg/Ca	Al/Ca	Mn/Ca	Sr/Ca	Zn/Ca	Ba/Ca
		((mmol/mol)	(µmol/mol)	(µmol/mol)	(mmol/mol)	(µmol/mol)	(µmol/mol)
U2322	8	F-1	2.710	14.5	5.8	1.387		1.0
NET7								
U2322	1	F	2.165	-13.7	1.0	1.499	26.1	0.5
NET7								
U2322	1	F-1	3.054	1.0	3.5	1.559	88.4	2.4
NET7								
U2322	1	F-2	3.368	2.6	2.7	1.565	86.5	1.0
NET7								
U2322	2	F	1.481	124.0	17.3	1.736	484.3	1.6
NET7								
U2322	2	F-1	3.075	26.0	4.4	1.588	120.0	0.9
NET7								
U2322	2	F-2	2.960	-0.4	4.8	1.443	77.1	0.9
NET7								
U2322	3	F	1.858	23.2	5.5	1.588	589.3	0.9
NET7								
U2322	3	F-1	2.207	1.0	1.8	1.566	173.6	0.6
NET7								
U2322	3	F-2	1.782	41.5	5.8	1.565	369.2	0.7
NET7								
U2322	4	F	2.503	6.2	1.8	1.606	57.9	0.6
NET7								
U2322	4	F-1	3.421	9.3	4.8	1.683	91.9	1.1
NET7								
U2322	4	F-2	3.249	109.2	5.8	1.627	98.3	1.2
NET7								
Z/003	1	F	3.326	-27.4	31.4	1.312	1.4	1.0
Z/003	2	F	2.874	145.5	45.7	1.412	11.2	1.1
Z/003	2	F-1	2.822	210.8	40.8	1.446	31.2	2.2
Z/003	2	F-2	1.979	11.1	38.1	1.426	7.1	1.2
Z/003	3	F	3.222	627.5	25.7	1.483	4.1	1.3
Z/003	3	F-1 F	2.692	2/5.0	65.6	1.558	10.3	1./
Z/003	4	F F 2	3.516	1/2.8	19.7	1.580	6.1	0.9
Z/003	4	F-2	2.487	3/./	50.0	1.543	15.8	1./
Z/003	5	F F	2.542	-31.9	38.9	1.429	4.1	1.4
Z/003	5	F-1 F	2.048	195.6	58.2	1.438	10.3	5.5
Z/003	6	F F 1	2.400	336.1	31.4 22.0	1.455	/./	1.4
Z/003	6	F-1 E 2	5.408 2.242	4/4.9	33.0 27.6	1.484	6.5	1.5
Z7003	0 7	г-2 Е 2	2.343	1767.0	37.0	1.400	0.0 7.6	0.9
Z7003	/ Q	г-2 Б	2.621	350.0	56.0	1.321	14.0	1.0
Z7003	8	Г Е 1	0.830	5630.5	0.4	1.422	14.9	1.1
Z7003	0	г-1 Б 2	0.039	-3039.3	52.0	1.313	-19.2	-0.9
Z7003	0	г-2 Б	3.297	2310.5	33.9	1.420	78.5	1.4
Z7003	9	F 1	2.102	-2319.5	33.3 47.4	1.319	3.2	0.9
Z7003	9	F 2	2.557	511.7	31.2	1.420	7.2	1.1
Z7003	10	F	2.020	943.0	10.0	1.420	6.3	1.5
Z7003	10	F_1	3.831	781.9	35.0	1.302	11.6	0.9
Z7003	10	F-2	2 844	-1434.9	28.7	1.372	3.6	0.9
Z7003	10	F-1	3.231	505.8	37.2	1.427	5.0	1.2
Z7003	12	F	3 535	338.0	70.7	1 399	12.0	1.2
Z7003	12	- F-1	3 261	1290.2	18 5	1 488	13.6	2.5
Z7003	13	F	3.382	1523.2	58.4	1.398	21.4	2.5
Z7003	13.1	- F-1	3.638	217.2	37.6	1.495	8.8	1.4
Z7003	13	F-2	3.213	718.9	40.0	1.478	17.5	1.9
Z7003	14	F-1	3.854	730.1	30.0	1.395	8.5	1.0
Z7003	14	F-2	3.068	620.1	26.6	1.492	18.5	2.3
Z7003	15	F	4.175	279.9	37.2	1.478	12.7	3.0

Site	Individual Numbe	r Chamber	Mg/Ca	Al/Ca	Mn/Ca	Sr/Ca	Zn/Ca	Ba/Ca
			(1/ 1)	(1/ 1)	(1 / 1)	(1/ 1)	(1/ 1)	(1/ 1)
		5.4	(mmol/mol)	(µmol/mol)	(µmol/mol)	(mmol/mol)	(µmol/mol)	(µmol/mol)
Z/003	15	F-1	4.100	6/1.6	32.9	1.355	9.8	3.4
Z/003	15	F-2	3.093	704.9	29.4	1.423	6.9	2.6
Z7003	1	F	1.737	37.1	38.7	1.400		0.9
Z7003	1	F-1	2.011	104.3	49.9	1.422		1.0
Z7003	1	F-2	2.490	41.1	57.8	1.514		1.3
Z7003	2	F	1.392	36.4	25.4	1.460		0.9
Z7003	2	F-2	3.343	84.9	35.5	1.311		1.3
Z7003	3	F-1	1.938	17.3	30.8	1.404		1.1
Z7003	3	F	1.369	41.6	35.3	1.561		1.0
Z7003	3	F-2	2.286	18.3	37.9	1.477		1.2
Z7003	4	F-2	2.347	482.7	24.3	1.391		1.9
Z7003	5	F	1.598	37.9	25.7	1.316		0.8
Z7003	5	F-2	2.672	58.2	35.4	1.387		1.0
Z7003	5	F-1	2.798	100.7	47.9	1.281		1.5
Z7003	6	F	2.464	58.0	18.5	1.500		0.8
Z7003	7	F	1.645	12.6	15.7	1.590		0.7
Z7003	7	F-2	3.088	962.9	40.4	1.448		1.2
Z7003	8	F-1	2.867	96.7	25.0	1.310		0.9
Z7003	8	F	1.472	11.2	27.9	1.451		0.8
Z7003	8	F-2	3.088	46.9	34.0	1.323		1.0
Z7003	9	F-2	2.704	83.3	22.5	1.421		0.9
Z7003	9	F	1.802	76.9	34.7	1.411		1.0
Z7003	9	F-1	3.182	144.8	35.3	1.335		1.2
Z7003	10	F	2.225	76.7	35.5	1.525		0.8
Z7003	10	F-2	3.436	123.9	63.1	1.423		1.3
Z7003	10	F-1	4.045	96.5	85.1	1.330		1.4
Z7003	15	F-1	4.100	671.6	32.9	1.355	9.8	3.4

Cells in bold are repeat analyses.

		Paired Samples Test ^a								
			Pair	ed Differe	ences		t	df	t-test (þ)	
					95% C. Diffe	I. of the rence	_		Sig. (2- tailed)	
Site	Chamber Pair (Mg/Ca)	Mean	Std. Deviation	Std. Error Mean	Lower	Upper				
AIMS1361	F-2 - F	1.164	1.211	0.458	0.045	2.284	2.544	6	0.044	
AIMS1361	F-1 - F	0.979	0.921	0.348	0.126	1.831	2.810	6	0.031	
AIMS1631	F-2 - F	0.570	0.323	0.161	0.056	1.084	3.532	3	0.039	
AIMS2078	F-2 - F	1.992	1.468	0.464	0.942	3.042	4.290	9	0.002	
AIMS2078	F-1 - F	2.121	1.389	0.439	1.127	3.115	4.827	9	0.001	
AIMS3703	F-2 - F	0.957	1.163	0.323	0.254	1.660	2.967	12	0.012	
AIMS3703	F-1 - F	1.158	0.971	0.269	0.571	1.744	4.301	12	0.001	
FR1/97/GC12	F-1 - F	1.242	2.030	0.586	-0.048	2.532	2.118	11	0.058*	
ODP Site 1123	F-2 - F	0.372	0.287	0.080	0.198	0.545	4.672	12	0.001	
ODP Site 1123	F-1 - F	0.478	0.384	0.107	0.246	0.710	4.485	12	0.001	
P71	F-2 - F	0.798	0.750	0.172	0.437	1.160	4.641	18	0.000	
P71	F-1 - F	0.613	0.578	0.133	0.334	0.891	4.622	18	0.000	
P81	F-2 - F	0.708	0.331	0.078	0.543	0.872	9.073	17	0.000	
P81	F-1 - F	0.697	0.511	0.121	0.442	0.951	5.779	17	0.000	
TAN0607 C4	F-2 - F	0.944	0.923	0.181	0.571	1.317	5.214	25	0.000	
TAN0607 C4	F-1 - F	1.067	0.872	0.171	0.715	1.420	6.240	25	0.000	
U2315	F-2 - F	0.816	0.876	0.243	0.287	1.345	3.360	12	0.006	
U2315	F-1 - F	1.442	0.937	0.260	0.875	2.008	5.546	12	0.000	
U2322 net 6 &										
7	F-1 - F	0.746	0.724	0.218	0.260	1.232	3.418	10	0.007	
Z7003	F-2 - F	0.607	1.188	0.297	-0.026	1.240	2.045	15	0.059*	
Z7003	F-1 - F	0.665	1.102	0.275	0.078	1.252	2.415	15	0.029	

Table A4: Paired t-test summary for Mg/Ca in *Gs. ruber* from core top and plankton tow sites in the Southwest Pacific Ocean.

^a 2-tailed significance level, p. Only values that are statistically (p<0.05) are shown except those with an asterix which are close to p=0.05. This shows that there is a significant difference (at the 95% level) between Mg/Ca and the specified chamber pairs.

	Independent Samples Test ^a												
	Equa Varia												
Mg/Ca (Chamber)								95% Con Interval Differ	nfidence l of the rence				
s.s. versus s.l.	F	Sig.	t	df	Sig. (2-tailed)	Mean Difference	Std. Error Difference	Lower	Upper				
F-2	1.933	0.167	0.225	140	0.822	0.058	0.259	-0.454	0.571				
F-1	2.709	0.102	-0.091	140	0.927	-0.025	0.269	-0.556	0.507				
F	0.625	0.431	0.789	140	0.432	0.175	0.221	-0.263	0.612				

Table A5: Independent t-test summary for Mg/Ca in different morphotypes of *Gs. ruber* from core top and plankton tow sites in the Southwest Pacific Ocean.

^a 2-tailed significance level, p. Where the significance is <0.05 it shows that there is a significant difference (at the 95% level) of Mg/Ca (per chamber) in the 2 morphotypes (s.s. and s.l).

Appendix B

Appendix B. Chapter 4.

Appendix B

Table B1: Core top, plankton tow and Mg/Ca ratios for individual *Neogloboquadrina incompta* (150 – 300 μ m) from sites in the Southwest Pacific Ocean

Site	Latit ude (degr	Longi tude (degre	Core Type	Dep th (met	Age	Indivi dual Num ber	F-3 Mg/Ca (ICL) (mmol/m	F -3 Mg/Ca (OCL) (mmol/mol	F Mg/Ca (ICL) (mmol	F Mg/Ca (OCL) (mmol/	Ultra- structure	WO A05 SST (0- 100 m)	Sali nity (psu
	ees)	es)		res)	(yr)		ol))	/mol)	mol)		(°C))
271/61/D R05C1	22.13 3	156.7 4	dredg e	1600		1	1.13	0.64	1.75	0.98	crystalline	23.8	35.4 9
271/61/D R05C1	22.13 3 53.63	156.7 4 169.8	dredg e core	1600	Holo	2	1.92	0.72	2.46	0.72	crystalline	23.8	35.4 9 34.3
B32	0	7	top	799	cene	1	2.18		1.68		reticulate	9.1	3
B32	53.63 0 53.63	169.8 7 169.8	top core	799	Holo cene Holo	2	1.00	0.31	1.04	0.60	crystalline	9.1	34.3 3 34.3
B32	0	/	top	/99	cene	3	1.23		1.26		reticulate	9.1	3
B32	53.63 0	169.8 7	top	799	Holo cene	4		1.93	1.28	0.59	crystalline	9.1	34.3 3
B32	53.63 0 53.63	169.8 7 169.8	top	799	Holo cene Holo	5	1.41	0.81	1.25	0.96	crystalline	9.1	34.3 3 34.3
B32	0	7	top	799	cene	6	1.10		0.95		reticulate	9.1	3
B32	53.63 0	169.8 7	top	799	Holo cene	7	1.52		1.42		reticulate	9.1	34.3 3
B32	53.63 0	169.8 7	core top	799	Holo cene	9	1.79	0.90	1.51		crystalline	9.1	34.3 3
B32	53.63 0	169.8 7	core top	799	Holo cene	10		0.29		0.33	crystalline	9.1	34.3 3
B32	53.63 0 53.63	169.8 7 169.8	top core	799	Holo cene Holo	11	1.79	1.15	1.81	1.02	crystalline	9.1	34.3 3 34.3
B32	0 53.63	7 169.8	top core	799	cene Holo	17	0.72		0.97		reticulate	9.1	3 34.3
B32	0 53.63	7 169.8	top core	799	cene Holo	20			1.71		reticulate	9.1	3 34.3
B32	0	7 169.8	top	799	cene Holo	21			1.84		reticulate	9.1	3 34 3
B32	0	7	top	799	cene	22	2.86		2.81		reticulate	9.1	3
B32	0	7	top	799	cene	24	2.43		1.12		reticulate	9.1	3
B32	0 53.63	7 169.8	top core	799	cene Holo	25			1.26		reticulate	9.1	3 34.3
B32	0	7	top	799	cene	26	1.69		1.53		reticulate	9.1	3
D178	51.72 0	167.8 3	core top	629	4835 ±3	4			1.15	0.82	crystalline	10.3	34.4 6

												WO	
												A05	
						Indivi						SST	
						dual	F-3				Ultra-	(0-	
	Latit	Longi	Core	Dept		Num	Mg/Ca	F -3 Mg/Ca	F Mg/Ca	F Mg/Ca	struct	100	Sali
Site	ude	tude	Туре	h	Age	ber	(ICL)	(OCL)	(ICL)	(OCL)	ure	m)	nity
	(degr	(degre		(met			(mmol/mo	(mmol/mol	(mmol/m	(mmol/m		,	(psu
	ees)	es)		res)	(yr)		(I))	ol)	ol)		(°C)	<u>)</u>
	51.72	167.8	core	/	4835		1	/	1	,	crystal	. /	34.4
D178	0	3	top	629	± 3	6		0.60	0.76	0.76	line	10.3	6
	51.72	167.8	core		4835						reticul		34.4
D178	0	3	ton	629	+3	22	1.30		1.20		ate	10.3	6
2110	51 72	167.8	core	02/	4835		1150		1.20		reticul	10.0	34.4
D178	0	3	ton	629	+3	25	1.90		0.87		ate	10.3	6
DITO	51 72	167.8	core	02)	4835	25	1.90		0.07		crystal	10.5	34.4
D178	0	3	ton	629	+3	26			1.98		line	10.3	6
DITO	18.05	174.0	core	02)	6755	20			1.50		raticul	10.5	34.2
F111	40.75	8	ton	704	+36	1	2.84		2.80		ate	10.3	0
1.111	18.05	174.0	top	704	4755	1	2.04		2.00		roticul	10.5	312
E111	40.95	0	ton	704	+26	2	2.06		3 10		ato	10.3	0
1.111	49.05	174.0	top	704	4755	2	2.00		5.10		ate	10.5	24.2
E111	46.95	1/4.9	core	704	+26	2	1 2 2	0.72	1 77	1 16	Crystal	10.2	54.2
ГП	49.05	0	top	704	1.50	3	1.32	0.72	1.//	1.10	line	10.5	24.2
E4.4.4	46.95	1/4.9	core	704	0/33 ±20	4	2.17		1 50		reucui	10.2	54.2
FIII	19.05	8	top	/04	±30 (755	4	2.16		1.58		ate	10.5	24.2
F144	48.95	1/4.9	core	704	6/55	-	0.1.1		1.55		reticui	10.2	34.2
FIII	10.05	8	top	/04	±36	5	2.14		1.55		ate	10.3	9
E 444	48.95	1/4.9	core	7 04	6/55	,	0.05		4 50		reticul	10.2	34.2
F111	0	8	top	/04	±36	6	2.35		1.79		ate	10.3	9
E	48.95	1/4.9	core		6/55	-					reticul		34.2
F111	0	8	top	704	±36	7			1.42		ate	10.3	9
	48.95	174.9	core		6755						crystal		34.2
F111	0	8	top	704	±36	12			1.50	1.50	line	10.3	9
	48.95	174.9	core		6755						crystal		34.2
F111	0	8	top	704	±36	13			2.46	0.98	line	10.3	9
FR97_	23.88	152.6	core								reticul		35.4
GC09	5	4	top	991		2	1.24		2.95		ate	23.5	8
FR97_	23.88	152.6	core								reticul		35.4
GC09	5	4	top	991		3	0.81		2.01		ate	23.5	8
ODP11	41.94	188.5	core								crystal		35.1
23C	2	0	top	3290		1		2.00	1.34	1.18	line	13.5	1
ODP11	41.94	188.5	core								crystal		35.1
23C	2	0	top	3290		2	0.82		0.78		line	13.5	1
ODP11	41.94	188.5	core								reticul		35.1
23C	2	0	top	3290		4	1.40		1.35		ate	13.5	1
ODP11	41.94	188.5	core								reticul		35.1
23C	2	0	top	3290		5	1.18		1.21		ate	13.5	1
ODP11	41.94	188.5	core								crystal		35.1
23C	2	0	top	3290		6		0.80	1.29		line	13.5	1
ODP11	41.94	188.5	core								reticul		35.1
23C	2	0	top	3290		7	0.92		1.28		ate	13.5	1
ODP11	41.94	188.5	core								crystal		35.1
23C	2	0	top	3290		12		0.91	1.09	1.09	line	13.5	1
ODP11	41.94	188.5	core								crystal		35.1
23C	2	0	top	3290		18		1.60		1.25	line	13.5	1
ODP11	41.94	188.5	core								crystal		35.1
23C	2	0	top	3290		21		0.54	0.50	0.50	line	13.5	1
	43.20	186.0	core		6519						reticul		35.0
R623	0	0	top	1128	±35	1			0.91		ate	12.7	1
			1										
	43.20	186.0	core		6519						crystal		35.0
R623	0	0	top	1128	±35	2			1.24	0.89	line	12.7	1
	43.20	186.0	core		6519						crystal		35.0
R623	0	0	top	1128	±35	3			2.05	1.02	line	12.7	1

Sit	Latitu de	Longit ude	Core Type	Dept h	Age	Indivi dual Numb er	F-3 Mg/Ca (ICL)	F -3 Mg/Ca (OCL)	F Mg/Ca (ICL)	F Mg/Ca (OCL)	Ultra- struct ure	WO A05 SST (0- 100m	Salin itv
c	(degr	(degre	Type	(metr	1180		(mmol/mo	(001)	(mmol/m	(mmol/m	ure		(psu
	ees)	es)		es)	(yr)		l)	(mmol/mol)	ol)	ol)		(°C)) 35.0
R6	43.20	186.00	core	1128	6519 +35	3			2.05	1.02	crystal	127	1
R6	43.20	100.00	core	1120	6519	5			2.05	1.02	reticul	12./	35.0
23	0	186.00	top	1128	±35	4	1.21		1.64		ate	12.7	1
R6	43.20		core		6519						reticul		35.0
23	0	186.00	top	1128	±35	5	1.61		1.01		ate	12.7	1
R6	43.20		core		6519						crystal		- 35.0 1
23 D	0	186.00	top	1128	±35	7	1.17	1.57	1.44	1.72	line	12.7	25.0
23	45.20	186.00	ton	1128	+35	8	1 73		1.96		ate	12.7	35.0 1
R6	43.20	100.00	core	1120	6519	0	1.75		1.90		reticul	12.7	35.0
23	0	186.00	top	1128	±35	9			2.58		ate	12.7	1
R6	43.20	104.00	core	1100	6519	10	1.00		1.00		reticul	107	35.0
23	0	186.00	top	1128	±35	12	1.88		1.29		ate	12./	35.0
R6	43.20	107.00	core	1120	6519	24	1.05	0.70	1.07	0.02	crystal	107	1
23	0	186.00	top	1128	±35	31	1.25	0.72	1.36	0.93	line	12./	35.0
R6	43.20	104.00	core	1100	6519						crystal	105	1
23 R6	0 43 20	186.00	top	1128	±35 6519	32				0.77	line	12.7	35.0
23	45.20	186.00	top	1128	±35	33	1.57		1.65		ate	12.7	1
R6	43.20		core		6510						crustal		35.0
23	45.20	186.00	top	1128	±35	34				0.87	line	12.7	1
R6	43.20		core		6519						reticul		35.0
23	0	186.00	top	1128	±35	35	1.24		1.07		ate	12.7	1
R6 22	43.20	186.00	core	1120	6519 +25	36	1 27		1 47		reticul	127	35.0
2.5 R6	43.20	100.00	core	1120	<u>-</u> 35 6519	50	1.57		1.47		reticul	12./	35.0
23	0	186.00	top	1128	±35	37	2.02		1.40		ate	12.7	1
R6	43.20		core		6519						crystal		35.0
23	0	186.00	top	1128	±35	40		0.84		1.16	line	12.7	1
R6	43.20		core		6519						crystal		35.0
23	0	186.00	top	1128	±35	41		0.81		1.00	line	12.7	1
R6	43.20	196.00	core	1120	6519	12	1.00		1.67		reticul	107	35.0
23	0	186.00	top	1128	±35	42	1.90		1.07		ate	12./	35.0
R6	43.20	196.00	core	1120	6519	42	0.02	0.65	1 47	0.04	crystal	107	1
23 R6	43.20	186.00	top core	1128	±35 6519	43	0.98	0.65	1.47	0.94	reticul	12./	35.0
23	0	186.00	top	1128	±35	45	1.47		1.10		ate	12.7	1
R6	43.20		core		6519						reticul		35.0
23	0	186.00	top	1128	±35	46			1.51		ate	12.7	1
R6	43.20		core		6519						crystal		35.0
23	0	186.00	top	1128	±35	48	1.48	0.95	1.81	0.95	line	12.7	25.0
R6	43.20		core		6519						crystal		35.0
23	0	186.00	top	1128	±35	50	1.03	0.70	1.47	0.64	line	12.7	25.0
R6	43.20		core		6519						crystal		35.0
23	0	186.00	top	1128	±35	52		1.19	1.79	1.79	line	12.7	35.0
R6	43.20	10100	core		6519						crystal		1
23	0	186.00	top	1128	±35	53	1.38	0.86	1.45	0.82	line	12.7	35.3
S9	40.33	1	core		843±						reticul		4
38	0	1/9.99	top	3003	35	4	0.69		0.74		ate	14.9	35.2
S9	40.33	170.00	core	2002	843±	-	1.22	0.01	1.00	0.07	crystal	140	4
38	0	1/9.99	top	3003	35	5	1.33	0.91	1.28	0.97	line	14.9	35.3
S9	40.33	170.00	core	2002	843±	/	1.79		1 10		reticul	14.0	4
50	0	1/9.99	top	5003	22	0	1.08		1.19		ate	14.9	35 3
S9 29	40.33	170.00	core	2002	843±	0	1 40		1 22		reticul	14.0	4
50	0	1/9.99	top	5005	55	0	1.40		1.33		ate	14.9	35.3
59 38	40.33	179.99	core	3003	843± 35	0	1.04		1.24		reticul	14.0	4
	0	11/.//	ωp	5005	55	,	1.04		1.47		au	17./	

						Indiv	Ε 2		F		Ultra	WO A05 SST	
Site	Latit ude	Longi tude	Core Type	Dep th	Age	ıdual Num ber	F-3 Mg/Ca (ICL)	F -3 Mg/Ca (OCL)	F Mg/Ca (ICL)	F Mg/Ca (OCL)	- struct ure	(0- 100 m)	Sali nity
	(degr ees)	(degr ees)		(met res)	(yr)		(mmol/m ol)	(mmol/mo l)	(mmol/ mol)	(mmol/ mol)		(°C)	(ps u)
S938	40.3 30	179.9 9	core top	300 3	843± 35	10	1.57		1.90		reticu late	14.9	35.3 4
S938	40.3 30	179.9 9	core top	300 3	843± 35	11	1.40	0.91	1.17	0.82	crysta lline	14.9	35.3 4
S938	40.3 30	179.9 9	core top	300 3	843± 35	12			1.29	0.90	crysta lline	14.9	35.3 4
S938	40.3 30	179.9 9	core top	300 3	843± 35	14	1.16		1.27		reticu late	14.9	35.3 4
TAN0103 U2309 NET 5	46.6 78	178.5 1	plankto n tow	100	April 2001	1	1.74		1.36		reticu late	7.9	34.3 7
TAN0103 U2309 NET 5	46.6 78	178.5 1	plankto n tow	100	April 2001	2	1.59		2.21		reticu late	7.9	34.3 7
TAN0103 U2309 NET 5	46.6 78	178.5 1	plankto n tow	100	April 2001	3	1.33		1.59		reticu late	7.9	34.3 7
TAN0103 U2309 NET 5	46.6 78	178.5 1	plankto n tow	100	April 2001	4	1.73		1.42		reticu late	7.9	34.3 7
TAN0103 U2315	38.5 09	179.0 2	plankto n tow	125	April 2001	1	1.47		5.25		reticu late	20.3	35.6 5
TAN0103 U2315	38.5 09	179.0 2	plankto n tow	125	April 2001	2	1.71		2.88		reticu late	20.3	35.6 5
TAN0103 U2322 net 6	41.6 01	178.0 5	plankto n tow	100	April 2001	1	2.52		1.44		reticu late	18.3	35.6 1
R623	43.2 00	186.0 0	core top	112 8	6519 ±35	52		1.19	1.79	1.79	crysta lline	12.7	35.0 1
R623	43.2 00	186.0 0	core top	112 8	6519 ±35	53	1.38	0.86	1.45	0.82	crysta lline	12.7	35.0 1
S938	40.3 30	179.9 9	core top	300 3	843± 35	4	0.69		0.74		reticu late	14.9	35.3 4
S938	40.3 30	179.9 9	core top	300 3	843± 35	5	1.33	0.91	1.28	0.97	crysta lline	14.9	35.3 4
S938	40.3 30	179.9 9	core top	300 3	843± 35	6	1.68		1.19		reticu late	14.9	35.3 4
S938	40.3 30	179.9 9	core top	300 3	843± 35	8	1.40		1.33		reticu late	14.9	35.3 4
S938	40.3 30	179.9 9	core top	300 3	843± 35	9	1.04		1.24		reticu late	14.9	35.3 4
S938	40.3 30	179.9 9	core top	300 3	843± 35	10	1.57		1.90		reticu late	14.9	35.3 4
S938	40.3 30	179.9 9	core top	300 3	843± 35	11	1.40	0.91	1.17	0.82	crysta lline	14.9	35.3 4
S938	40.3 30	179.9 9	core top	300 3	843± 35	12			1.29	0.90	crysta lline	14.9	35.3 4
S938	40.3 30	179.9 9	core top	300 3	843± 35	14	1.16		1.27		reticu late	14.9	35.3 4
TAN0103 U2309 NET 5	46.6 78	178.5 1	plankto n tow	100	April 2001	1	1.74		1.36		reticu late	7.9	34.3 7
TAN0103 U2309 NET 5	46.6 78	178.5 1	plankto n tow	100	April 2001	2	1.59		2.21		reticu late	7.9	34.3 7
TAN0103 U2309 NET 5	46.6 78	178.5 1	plankto n tow	100	April 2001	3	1.33		1.59		reticu late	7.9	34.3 7
TAN0103 U2309 NET 5	46.6 78	178.5 1	plankto n tow	100	April 2001	4	1.73		1.42		reticu late	7.9	34.3 7
TAN0103 U2315	38.5 09	179.0 2	plankto n tow	125	April 2001	1	1.47		5.25		reticu late	20.3	35.6 5

Site	Latit	Longi	Core	Dep	4	Indivi dual Num	F-3 Mg/Ca	F -3 Mg/Ca	F Mg/Ca	F Mg/Ca	Ultra - struct	WO A05 SST (0- 100	Sali nity
Site	(degr ees)	(degr ees)	Type	(met res)	(vr)	ber	(mmol/m ol)	(mmol/mo l)	(mmol/ mol)	(mmol/ mol)	ure	(°C)	(ps u)
TAN0103 U2315	38.5 09	179.0 2	plankto n tow	125	April 2001	2	1.71	,	2.88	,	reticu late	20.3	35.6 5
TAN0103 U2322 net 6 TAN0103 U2322 net 6	41.6 01 41.6 01	178.0 5 178.0 5	plankto n tow plankto n tow	100 100	April 2001 April 2001	2 6	2.63 1.37		2.49 1.64		reticu late reticu late	18.3 18.3	35.6 1 35.6 1
TAN0103 U2322 net 6	41.6 01	178.0 5	plankto n tow	100	April 2001	7	3.09		1.69		reticu late	18.3	35.6 1
Z7003	36.6 93	176.2 4	core top	430	4650 ±35	1	1.30		1.10		reticu late	16.9	35.4 6
Z7003	36.6 93	176.2 4	core top	430	4650 ±35	2	2.37		2.24		reticu late	16.9	35.4 6
Z7003	36.6 93	176.2 4	core top	430	4650 ±35	3	2.72		2.22		reticu late	16.9	35.4 6
Z7003	36.6 93	176.2 4	core top	430	4650 ±35	7	1.40			1.45	crysta lline	16.9	35.4 6
Z7003	36.6 93	176.2 4	core top	430	4650 ±35	9			1.13		reticu late	16.9	35.4 6
Z7003	36.6 93	176.2 4	core top	430	4650 ±35	10			2.65		reticu late	16.9	35.4 6
Z7003	36.6 93	176.2 4	core top	430	4650 ±35	11	1.53		2.27		reticu late	16.9	35.4 6
Z7003	36.6 93	176.2 4	core top	430	4650 ±35	12	2.11	1.93	2.50	1.97	crysta lline	16.9	35.4 6
Z7003	36.6 93	176.2 4	core top	430	4650 ±35	13	2.07		2.21		reticu late	16.9	35.4 6
Z7003	36.6 93	176.2 4	core top	430	4650 ±35	14	2.07	0.72	1.83	0.88	crysta lline	16.9	35.4 6
Z7003	36.6 93	176.2 4	core top	430	4650 ±35	16			1.09		reticu late	16.9	35.4 6
Z7003	36.6 93	176.2 4	core top	430	4650 ±35	18	0.74		1.67		reticu late	16.9	35.4 6
Z7003	36.6 93	176.2 4	core top	430	4650 ±35	19	1.32		1.22		reticu late	16.9	35.4 6
Z7003	36.6 93	176.2 4	core top	430	4650 ±35	20	1.57		1.28		reticu late	16.9	35.4 6
Z7003	36.6 93	176.2 4	core top	430	4650 ±35	21		1.38	1.20	0.69	crysta lline	16.9	35.4 6
Z7003	36.6 93	176.2 4	core top	430	4650 ±35	23	2.46		1.90		reticu late	16.9	35.4 6
Z7003	36.6 93	176.2 4	core top	430	4650 ±35	30	2.09		1.65		reticu late	16.9	35.4 6
Z7003	36.6 93	176.2 4	core top	430	4650 ±35	32	1.53		1.00		reticu late	16.9	35.4 6

Appendix B

					Individual				Size-
Site	Latitude	Longitude	Core Type	Denth	Number	x	Y	Weight	Weight
bite	(degrees)	(degrees)	cole Type	(metres)	rumber	(um)	(um)	(ug)	(ug/um)
	(degrees)	(degrees)		(interret)		(paris)	(perir)	(~8/	(48) (411)
271/61/DR05C1	22.133	156.74	dredge	1600	1	301	345		
271/61/DR05C1	22.133	156.74	dredge	1600	2	251	356		
B32	53.630	169.87	core top	799	1	155	198	3.7	2.39
B32	53.630	169.87	core top	799	2	264	283	14.9	5.64
B32	53.630	169.87	core top	799	3	156	202	3.6	2.31
B32	53.630	169.87	core top	799	4	156	201	5.5	3.53
B32	53.630	169.87	core top	799	5	153	169	2.8	1.83
B32	53.630	169.87	core top	799	6	258	347	17.6	6.82
B32	53.630	169.87	core top	799	7	158	198	3.6	2.28
B32	53.630	169.87	core top	799	9	160	205	14.5	9.06
B32	53.630	169.87	core top	799	10	266	292	4.0	1.50
B32	53.630	169.87	core top	799	11	161	207	2.9	1.80
B32	53.630	169.87	core top	799	17	199	247	5.5	2.76
B32	53.630	169.87	core top	799	20	179	193	3.3	1.84
B32	53.630	169.87	core top	799	21	141	151	2.4	1.70
B32	53.630	169.87	core top	799	22	151	185	2.5	1.66
B32	53.630	169.87	core top	799	24	145	176	2.1	1.45
B32	53.630	169.87	core top	799	25	148	198	2.0	1.35
B32	53.630	169.87	core top	799	26	145	158	0.9	0.62
D178	51.720	167.83	core top	629	4	168	177	3.7	2.20
D178	51.720	167.83	core top	629	6	187	219	5.0	2.67
D178	51.720	167.83	core top	629	22	152	187	14.7	9.67
D178	51.720	167.83	core top	629	25	196	234	5.0	2.55
D178	51.720	167.83	core top	629	26	175	202	1.7	0.97
F111	48.950	174.98	core top	704	1	167	221	3.4	2.04
F111	48.950	174.98	core top	704	2	180	238	4.5	2.50
F111	48.950	174.98	core top	704	3	195	224	5.6	2.87
F111	48.950	174.98	core top	704	4	174	209	2.8	1.61
F111	48.950	174.98	core top	704	5	171	228	2.2	1.29
F111	48.950	174.98	core top	704	6	183	217	3.2	1.75
F111	48.950	174.98	core top	704	7	171	207	3.7	2.16
F111	48 950	174 98	core top	704	12	152	184	18	1 1 8
	10.750	1 / f.70	core top		12	1.52	107	1.0	1.10
F111	48.950	174.98	core top	704	13	143	186	2.1	1.47
FR97_GC09	23.885	152.64	core top	991	2	314	296	16.3	5.19
FR97_GC09	23.885	152.64	core top	991	3	299	229	17.8	5.95

Table B2: Size and weight data for *Neogloboquadrina incompta* (150 – 350 μ m) for core top and plankton tow sites in the Southwest Pacific Ocean
Site	Latitude	Longitude	Core Type	Depth	Individual Number	Х	Y	Weight	Size-normalised Weight
	(degrees)	(degrees)		(metres)		(µm)	(µm)	(µg)	(µg/µm)
ODP1123C	41.942	188.50	core top	3290	1	193	223	6.0	3.11
000044020	11.0.12	100 50		2200	2	200	105	5.0	2.20
ODPI123C	41.942	188.50	core top	3290 3200	2	209	185	5.0	2.39
ODP1123C	41.942	188.50	core top	3290	4	215	206	3.0	1.41
00111290	11.912	100.50	core top	5270	5		200	5.2	1.11
ODP1123C	41.942	188.50	core top	3290	6	213	197	2.6	1.22
ODP1123C	41.942	188.50	core top	3290	7	248	228	3.9	1.57
ODP1123C	41.942	188.50	core top	3290	12	197	136	2.7	1.37
ODP1123C	41.942	188.50	core top	3290	18	202	175	8.0	3.96
ODD1122C	41.042	100 50		2200	21	1(2	122	2.2	2.04
R623	43 200	186.00	core top	1128	1	246	291	9.5	3.98
1025	15.200	100.00	core top	1120	1	210	271	2.0	5.20
R623	43.200	186.00	core top	1128	2	231	286	8.7	3.77
			•						
R623	43.200	186.00	core top	1128	3	204	232	4.0	1.96
R623	43.200	186.00	core top	1128	4	174	212	4.0	2.30
R623	43.200	186.00	core top	1128	5	184	221	5.8	3.15
D (22	12 200	104.00		1100	_	450	224		2.02
R623	43.200	186.00	core top	1128	/	179	231	5.4	3.02
R623	43.200	186.00	core top	1120	0	167	100	3.4	2.04
R623	43 200	186.00	core top	1120	12	150	203	5.4	3.93
1025	151200	100.00	core top	1120	12	100	200	517	5000
R623	43.200	186.00	core top	1128	31		339	10.5	
R623	43.200	186.00	core top	1128	32	220	267	7.6	3.45
R623	43.200	186.00	core top	1128	33	274	346	6.8	2.48
D (22	12 200	104.00		1100	2.4			-	
R623	43.200	186.00	core top	1128	34	250	245	7.9 8.0	3 14
R623	43.200	186.00	core top	1120	36	239	545	7.6	5.44
R623	43.200	186.00	core top	1120	37	262	247	15.1	5.76
			tott top						
R623	43.200	186.00	core top	1128	40	214	206	9.3	4.35
R623	43.200	186.00	core top	1128	41	217	198		0.00
R623	43.200	186.00	core top	1128	42	241	195	7.7	3.20
D (22	12 200	104.00		1100	12	244	250		1.20
R623	43.200	186.00	core top	1128	43	264	250	11.1	4.20
R623	43.200	186.00	core top	1120	45	258	263	13.2	5.12
1025	15.200	100.00	core top	1120	10	200	205	15.2	5.12
R623	43.200	186.00	core top	1128	48	257	221	9.4	3.66
			1						
R623	43.200	186.00	core top	1128	50	211	216	5.7	2.70
R623	43.200	186.00	core top	1128	51	245	235	8.2	3.35
D. (40.555			- -			0.7	• * *
R623	43.200	186.00	core top	1128	52	257	245	9.8	3.81
R623	43 200	186.00	core top	1179	53	278	232	11.0	3.96
S938	40.330	179.99	core top	3003	4	228	264	4.0	1.75
			r					-	

Site	Latitude	Longitude	Core Type	Depth	Individual Number	Х	Y	Weight	Size-normalised Weight
	(degrees)	(degrees)		(metres)		(µm)	(µm)	(µg)	(µg/µm)
S938	40.330	179.99	core top	3003	5	191	242	4.8	2.49
S938	40.330	179.99	core top	3003	6	164	213	2.0	1.22
S938	40.330	179.99	core top	3003	8	206	242	1.9	0.92
S938	40.330	179.99	core top	3003	9	161	206	3.8	2.36
S938	40.330	179.99	core top	3003	10	203	255	1.4	0.69
S938	40.330	179.99	core top	3003	11	157	180	3.1	1.97
S938	40.330	179.99	core top	3003	12	199	232	2.7	1.36
S938	40.330	179.99	core top	3003	14	188	212		0.00
TAN0103 U2309 NET 5	46.678	178.51	plankton tow	100	1				
TAN0103 U2309 NET 5	46.678	178.51	plankton tow	100	2	206	292	5.5	2.67
TAN0103 U2309 NET 5	46.678	178.51	plankton tow	100	3	202	257	4.5	2.23
TAN0103 U2309 NET 5	46.678	178.51	plankton tow	100	4	188	250	4.5	2.39
TAN0103 U2315	38.509	179.02	plankton tow	125	1	214	275		0.00
TAN0103 U2315	38.509	179.02	plankton tow	125	2	214	275		0.00
TAN0103 U2322 net 6	41.601	178.05	plankton tow	100	1			5.7	
TAN0103 U2322 net 6	41.601	178.05	plankton tow	100	2			4.4	
TAN0103 U2322 net 6	41.601	178.05	plankton tow	100	6			8.2	
TAN0103 U2322 net 6	41.601	178.05	plankton tow	100	7			2.2	
Z7003	36.693	176.24	core top	430	1	182	209	8.4	4.62
Z7003	36.693	176.24	core top	430	2	192	233	9.1	4.74
Z7003	36.693	176.24	core top	430	3	223	292	9.5	4.26
			1						
Z7003	36.693	176.24	core top	430	7	198	231	7.8	3.94
Z7003	36.693	176.24	core top	430	9	198	253	7.9	3.99
Z7003	36.693	176.24	core top	430	10	194	221	4.6	2.37
Z7003	36.693	176.24	core top	430	11	212	272	6.7	3.16
			1						
Z7003	36.693	176.24	core top	430	12	201	256	7.4	3.68
Z7003	36.693	176.24	core top	430	13	209	271	3.9	1.87
			•						
Z7003	36.693	176.24	core top	430	14			7.4	
Z7003	36.693	176.24	core top	430	16	202	249	1.5	0.72
Z7003	36.693	176.24	core top	430	18	225	285	5.8	2.58
Z7003	36.693	176.24	core top	430	19	186	244	5.5	2.93
Z7003	36.693	176.24	core top	430	20	194	257	3.3	1.70
Z7003	36.693	176.24	core top	430	21	210	241	5.7	2.71
Z7003	36.693	176.24	core top	430	23	162	233	4.4	2.72
Z7003	36.693	176.24	core top	430	30			4.5	
Z7003	36.693	176.24	core top	430	32	257	289	9.0	3.50

	Individu				PD					
Site	al Number	Chamb er	Ultra- structure	Kummer- form	intergrad e	Quadrat e	Al/Ca	Mn/Ca	Sr/Ca	Ba/Ca
							(µmol/mo	(µmol/mo	(mmol/mo	(µmol/mo
271/61/DR05	1	E	crystallin		1	1	-7	29.4	2 2 4 6	7.0
271/61/DR05	1	Г	e crystallin		1	1	48.4	28.4	2.340	/.8
C1 271/61/DR05	1	F-3	e crystallin		1	1	118.0	17.7	2.462	2.2
C1 271/61/DR05	2	F	e crystallin		1	1	107.6	7.2	1.642	4.1
C1	2	F-3	e		1	1	150.4	14.0	1.571	8.9
B32	1	F	e e		1	2	7.8	34.6	1.314	3.2
B32	1	F-3	e		1	2	14.2	26.3	1.291	3.0
B32	2	F	crystallin e		1	1	22.8	4.2	1.494	1.2
B32	2	F-3	crystallin e		1	1	24.5	1.4	1.533	0.7
B32	3	F	reticulat		1	1	24 3	15.8	1 309	15
B32	2	Г 2	reticulat		1	1	45.5	11.0	1 200	1.4
D32	5	P-5	crystallin		1	1	45.5	11.0	1.399	1.4
B32	4	F	e crystallin		1	1	16.6	26.8	1.490	3.1
B32	4	F-3	e crystallin		1	1	63.3	72.7	1.383	9.1
B32	5	F	e		1	1	12.4	7.5	1.386	2.2
B32	5	F-3	e		1	1	54.7	11.7	1.345	3.1
B32	6	F	e	1	1	2	41.0	5.1	1.234	2.1
B32	6	F-3	reticulat e		1	2	44.1	1.7	1.268	1.4
B32	7	F	reticulat e		1	1	30.8	21.2	1.428	3.8
B32	7	F-3	reticulat e		1	1	52.0	21.6	1.348	3.3
B32	9	F	crystallin		1	1	13.4	43.1	1 635	42
B32	0	г Е 2	crystallin		1	1	20.1	47.6	1.655	10.2
D32	9	г-э	crystallin		1	1	32.1	47.0	1.505	10.5
B32	10	F	e crystallin		1	1	8.4	2.2	1.384	0.8
B32	10	F-3	e crystallin		1	1	22.3	0.8	1.428	0.8
B32	11	F	e		2	1	14.5	18.3	1.514	5.5
B32	11	F-3	e		2	1	31.5	15.4	1.457	4.5
B32	17	F	e		2	2	36.0	13.6	1.473	12.0
B32	17	F-3	reticulat e		2	2	101.1	11.2	1.401	4.8
B32	20	F	reticulat e		2	2	105.9	26.2	1.352	16.7
B32	20	F-1	reticulat e		2	2	12.8	14.1	1.520	3.6
B32	21	F	reticulat	1	2	1	35.2	25.2	1 456	34
D22	21	• E 1	reticulat	1	2	1	15.0	15 4	1.429	э.т 1.0
1532	21	F-1	e reticulat		2	1	15.9	15.4	1.428	1.8
B32	22	F	e reticulat		2	1	36.9	24.0	1.471	6.2
B32	22	F-3	e		2	1	26.7	22.5	1.405	2.9

Table B3: Other trace element data for *Neogloboquadrina incompta* (150 – 350 μ m) for core top and plankton tow sites in the Southwest Pacific Ocean

	Individu				PD					
	al	Chambe	Ultra-	Kummer-	intergrad	Quadrat		26.42	2 (2	D (0
Site	Number	r	structure	form	e	e	Al/Ca	Mn/Ca	Sr/Ca	Ba/Ca
							(µmoi/mo l)	(µmoi/mo l)	(mmor/mo l)	(µmoi/mo l)
B32	24	F	reticulate		1	1	61.1	17.9	1.393	4.9
B32	24	F-3	reticulate		1	1	43.4	33.2	1.366	3.0
B32	25	F	reticulate		1	2	22.4	17.0	1.382	3.4
B32	25	F-1	reticulate		1	2	60.9	20.8	1.432	1.8
B32	26	F	reticulate		1	1	74.5	31.4	1.448	10.5
B32	26	F-3	reticulate crystallin		1	1	94.3	21.0	1.485	2.4
D178	4	F	e crystallin		2	2	12.9	1.5	1.756	1.7
D178	4	F-1	e crystallin		1	1	8.7	0.1	1.652	0.9
D178	6	F	e crystallin	1	1	1	14.8	3.5	1.606	4.9
D178	6	F-3	e		1	1	30.2	1.4	1.554	3.2
D178	22	F	reticulate	1	2	1	31.0	4.3	1.503	3.4
D178	22	F-3	reticulate		2	1	11.7	5.6	1.615	2.5
D178	25	F	reticulate		1	1	24.0	3.9	1.619	50.9
D178	25	F-3	reticulate crystallin		1	1	130.4	6.2	1.517	216.9
D178	26	F	e crystallin	1	1	2	31.5	9.4	1.559	2.8
D178	26	F-2	e		1	2	11.9	10.3	1.558	3.8
F111	1	F	reticulate		2	2	26.4	15.8	1.451	15.3
F111	1	F-3	reticulate		2	2	58.9	20.6	1.460	18.4
F111	2	F	reticulate crystallin		2	2	83.2	6.8	1.518	6.7
F111 FR97_GC0	13	F-1	e		1	2	30.4	29.6	1.284	51.0
9 FR97_GC0	2	F	reticulate		2	1	806.3	23.3	1.563	1.9
9 FR97_GC0	2	F-3	reticulate		2	1	1487.9	2.9	1.448	0.6
9 FR97_GC0	3	F	reticulate	1	2	1	908.9	3.0	1.326	0.6
9	3	F-3	reticulate crystallin		2	1	291.4	2.1	1.375	0.4
ODP1123C	1	F	e crystallin		1	1	12.9	67.8	1.407	2.5
ODP1123C	1	F-3	e crystallin		1	1	1898.8	106.2	1.352	4.6
ODP1123C	2	F	e crystallin	1	1	1	370.0	34.6	1.492	7.8
ODP1123C	2	F-3	e		1	1	329.6	19.3	1.427	4.0
ODP1123C	4	F	reticulate		1	2	116.3	69.2	1.296	10.9
ODP1123C	4	F-3	reticulate		1	2	1685.8	68.3	1.365	8.4
ODP1123C	5	F	reticulate	1	1	1	125.1	16.5	1.502	2.7
ODP1123C	5	F-3	reticulate crystallin		1	1	38.2	5.5	1.471	1.2
ODP1123C	6	F	e crystallin	1	1	1	1399.9	98.4	1.461	12.5
ODP1123C	6	F-3	e		1	1	580.2	23.7	1.370	5.9
ODP1123C	7	F	reticulate		1		103.8	324.2	1.468	7.4

	Individu				PD					
	al	Chambe	Ultra-	Kummer-	intergrad	Quadrat				
Site	Number	r	structure	form	e	e	Al/Ca	Mn/Ca	Sr/Ca	Ba/Ca
							(µmol/mol	(µmol/mol	(mmol/mo	(µmol/mol
ODP1123))	1))
C ODP1123	7	F-3	reticulate		1		1007.1	185.9	1.543	5.4
C	12	F	e		1	1	113.5	244.6	1.518	6.0
ODP1123	12	Е 2	crystallin		1	1	02.1	1227	1 20 2	2.2
ODP1123	12	1-5	crystallin		1	1	75.1	155.7	1.572	5.2
C ODP1123	18	F	e	1	1	1	678.3	196.2	1.310	14.4
C C	18	F-3	e		1	1	959.9	145.3	1.380	32.8
ODP1123	21	F	crystallin		1		17.6	147	1 452	3.6
ODP1123	21	1	crystallin		1		17.0	11.7	1.152	5.0
С	21	F-3	e		1		139.7	14.4	1.327	4.5
R623	1	F	reticulate	1	1	1	601.4	15.9	1.408	2.9
R623	1	F-1	reticulate		1	1	54.3	35.7	1.447	4.3
R623	2	F	e	1	1	1	631.3	12.7	1.333	2.7
R623	2	F-1	e crystallin		1	1	31.1	13.5	1.505	2.5
R623	3	F	e crystallin	1	1	1	199.8	12.1	1.434	2.7
R623	3	F-1	e		1	1	71.6	23.9	1.490	5.8
R623	4	F	reticulate		1	1	60.2	37.3	1.470	5.2
R623	4	F-3	reticulate		1	1	851.2	15.1	1.411	3.5
R623	5	F	reticulate		1	2	92.7	10.8	1.406	2.4
R623	5	F-3	reticulate		1	2	1150.0	14.9	1.324	6.1
R623	7	F	e crystallin		1	1	190.6	47.1	1.401	2.0
R623	7	F-3	e		1	1	1171.9	9.8	1.437	17.8
R623	8	F	reticulate	1	1	2	27.1	107.1	1.470	1.6
R623	8	F-3	reticulate		1	2	323.5	93.8	1.384	18.8
R623	9	F	reticulate	1	1	1	194.9	28.4	1.425	7.2
R623	9	F-1	reticulate		1	1	55.6	32.5	1.493	7.1
R623	12	F	reticulate		1	2	173.6	44.5	1.400	2.5
R623	12	F-3	reticulate		1	2	297.3	56.0	1.403	5.5
R623	31	F	e crystallin		2	2	17.0	55.7	1.361	69.6
R623	31	F-3	e crystallin		2	2	80.7	83.9	1.349	36.8
R623	32	F	e crystallin		1	2	328.7	7.8	1.385	3.3
R623	32	F-1	e		1	2	187.3	15.5	1.337	4.8
R623	33	F	reticulate		2	2	35.9	57.2	1.238	82.8
R623	33	F-3	reticulate		2	2	331.4	58.7	1.256	66.0
R623	34	F	e crystallin		1	2	62.9	23.7	1.483	2.6
R623	34	F-1	e		1	2	257.6	45.4	1.394	4.0
R623	35	F	reticulate		1	2	67.4	52.4	1.333	5.2
R623	35	F-3	reticulate		1	2	386.2	44.1	1.274	4.5

Site	Individua l Number	Chambe r	Ultra- structure	Kummerfor m	PD intergrad e	Quadrat e	Al/Ca	Mn/Ca	Sr/Ca	Ba/Ca
							(µmol/mol)	(µmol/mol)	(mmol/mol)	(µmol/mol)
R62	25	E 2			4	2	20(2		1.07.1	15
3 R62	35	F-3	reticulate		1	2	386.2	44.1	1.2/4	4.5
3 R62	35	F-3	reticulate		1	2	386.2	44.1	1.274	4.5
3 R62	36	F	reticulate		1		9.0	55.3	1.415	4.8
3 R62	36	F-3	reticulate		1		596.6	20.3	1.344	3.6
3 B(2	37	F	reticulate		1	2	317.0	4.0	1.582	3.0
3	37	F-1	reticulate		1	2	515.0	14.0	1.488	12.0
R62 3	37	F-2	reticulate		1	2	302.0	6.0	1.534	4.0
R62	37	F-3	reticulate		1	2	468.0	15.0	1.444	29.0
R62 3	40	F	crystallin e		1	2	219.0	4.0	1.534	4.0
R62 3	40	F-1	crystallin e		1	2	148.0	3.0	1.382	3.0
R62 3	40	F-2	crystallin e		1	2	339.0	-7.0	1.562	1.0
R62 3	40	F-3	crystallin e		1	2	565.0	-5.0	1.533	1.0
R62 3	41	F	crystallin e		1	1	42.0	1.0	1.483	4.0
R62 3	41	F-1	crystallin e		1	1	91.0	10.0	1.408	4.0
R62 3	41	F-2	crystallin		1	1	106.0	7.0	1 551	2.0
R62	41	F_3	crystallin		1	1	91.0	3.0	1 536	2.0
R62	42	Г- <u></u>	roticulato		1	2	120.0	6.0	1 245	4.0
R62	42	F 1	reticulate		1	2	220.0	2.0	1.040	4.0
3 R62	42	F-1	reticulate		1	2	320.0	5.0	1.288	5.0
3 R62	42	F-2	reticulate		1	2	616.0	7.0	1.348	3.0
3 R62	42	F-3	reticulate crystallin		1	2	1056.0	8.0	1.531	5.0
3 R62	43	F	e crystallin		1	2	37.0	3.0	1.498	1.0
3 R62	43	F-1	e crystallin		1	2	276.0	8.0	1.411	5.0
3 R62	43	F-2	e crystallin		1	2	146.0	2.0	1.434	2.0
3 R62	43	F-3	e		1	2	127.0	-1.0	1.467	1.0
3 R62	45	F	reticulate		1	2	105.0	6.0	1.518	2.0
3 B62	45	F-1	reticulate		1	2	54.0	4.0	1.459	4.0
3 B(2	45	F-2	reticulate		1	2	157.0	0.0	1.514	5.0
3 D(2	45	F-3	reticulate	2	1	2	228.0	6.0	1.534	6.0
3 3	46	F	reticulate		1	2	37.0	1.0	1.606	15.0
R62 3	46	F-1	reticulate		1	2	62.0	6.0	1.454	27.0
R62 3	46	F-2	reticulate		1	2	581.0	2.0	1.502	16.0
K62 3	48	F	crystallin e		1	1	-71.0	6.0	1.405	2.0
R62 3	48	F-1	crystallin e		1	1	56.0	13.0	1.223	3.0
R62 3	48	F-2	crystallin e		1	1	155.0	2.0	1.337	1.0
R62 3	48	F-3	crystallin e		1	1	261.0	4.0	1.351	2.0

Site	Individua l Number	Chambe r	Ultra- structure	Kummerfor m	PD intergrad e	Quadrat e	Al/Ca	Mn/Ca	Sr/Ca	Ba/Ca
							(µmol/mol	(µmol/mol	(mmol/mol	(µmol/mol
R62			crystallin))))
3 D(2	50	F	e		1	2	71.0	7.0	1.581	4.0
K62 3	50	F	e		1	2	28.0	5.0	1.582	2.0
R62	50	E 1	crystallin		1	2	40.0	10.0	1 401	7.0
R62	50	1'-1	crystallin		1	2	40.0	10.0	1.491	7.0
3 R62	50	F-1	e		1	2	176.0	5.0	1.455	4.0
3	50	F-2	e		1	2	336.0	0.0	1.523	3.0
R62	50	F-2	crystallin		1	2	93.0	-1.0	1 468	2.0
R62			crystallin		-	_				
3 R62	50	F-3	e crystallin		1	2	138.0	0.0	1.552	4.0
3	50	F-3	e		1	2	825.0	4.0	1.468	6.0
R62 3	51	F	reticulate		1	1	153.0	13.0	1.496	43.0
R62	51	F	and the		1	1	247.0	14.0	1 4/7	20.0
3 R62	51	Г	reticulate		1	1	347.0	14.0	1.407	38.0
3 R62	51	F-1	reticulate		1	1	340.0	11.0	1.526	32.0
3	51	F-1	reticulate		1	1	403.0	9.0	1.402	35.0
R62	51	F-2	reticulate		1	1	1303.0	18.0	1 417	22.0
R62					-		100010			
3 R62	51	F-2	reticulate		1	1	1123.0	15.0	1.393	19.0
3	51	F-3	reticulate		1	1	940.0	9.0	1.464	11.0
R62 3	51	F-3	reticulate		1	1	946.0	14.0	1.391	14.0
R62	50	F	crystallin		1	1	45.0	2.0	1 461	6.0
R62	52	1,	crystallin		1	1	-45.0	5.0	1.401	0.0
3 R62	52	F-1	e		1	1	-6.0	11.0	1.390	6.0
3	52	F-2	e		1	1	470.0	1.0	1.440	3.0
R62 3	52	F-3	crystallin		1	1	419.0	5.0	1 440	2.0
S938	4	F	reticulate		1	2	82.9	96.3	1.700	7.6
R62	52	F	crystallin		1	1	6.0	2.0	1 612	4.0
R62	55	1,	crystallin		1	1	-0.0	5.0	1.012	4.0
3 R62	53	F-1	e		1	1	34.0	3.0	1.434	7.0
3	53	F-2	e		1	1	44.0	2.0	1.634	2.0
R62	53	F-3	crystallin		1	1	167.0	2.0	1 538	6.0
S938	4	F-3	reticulate		1	2	265.9	31.0	1.696	2.5
\$029	5	F	crystallin		1	2	00 2	250.5	1 577	4.6
3930	5	Г	crystallin		1	2	00.3	230.5	1.577	4.0
S938	5	F-3	e		1	2	326.9	177.1	1.486	5.8
S938	6	F E 2	reticulate		1	1	14.9	91.8	1.596	2.7
5938	0 8	F-5	reticulate	1	2	1	15.6	102.5	1.405	4.0
S938	8	F-3	reticulate		2	1	118.2	74.5	1.530	4.6
S938	9	F	reticulate		1	2	29.1	79.3	1.510	7.7
S938	9	F-3	reticulate		1	2	785.2	31.0	1.486	4.3
S938	10	F	reticulate		1	2	3.2	81.9	1.377	3.8

Site	Individu al Number	Chamb er	Ultra- structur e	Kummerfo rm	PD intergra de	Quadra te	Al/Ca (umol/m	Mn/Ca (umol/m	Sr/Ca (mmol/m	Ba/Ca
							ol)	ol)	ol)	ol)
S938	10	F-3	reticulat e		1	2	433.2	165.4	1.396	7.8
\$938	11	F	crystalli ne		1	1	28.4	68.9	1.501	3.8
S938	11	F-3	ne		1	1	73.3	46.9	1.562	3.1
S938	12	F	ne	1	1	1	47.7	75.7	1.579	8.2
S938	12	F-1	ne		1	1	622.1	35.2	1.448	10.4
S938	14	F	e e		1	1	38.7	52.1	1.614	4.6
S938	14	F-3	e e		1	1	105.6	22.6	1.541	1.7
NET 5	1	F	e e		1	1	16.5	2.0	2.576	2.8
NET 5	1	F-3	e		1	1	9.2	8.5	2.605	5.7
NET 5	2	F	e		1	2	7.1	4.0	2.698	2.6
NET 5	2	F-3	reticulat e		1	2	22.3	10.0	2.492	3.5
TAN0103 U2309 NET 5	3	F	reticulat e		1	2	6.8	4.6	2.643	3.0
TAN0103 U2309 NET 5	3	F-3	reticulat e		1	2	11.8	6.8	2.476	4.4
TAN0103 U2309 NET 5	4	F	reticulat e		1	2	9.5	6.4	2.719	2.7
TAN0103 U2309 NET 5	4	F-3	reticulat e		1	2	104.8	25.9	2.444	5.4
TAN0103 U2315	1	F	reticulat e		1	1	17.7	6.5	1.582	7.0
TAN0103 U2315	1	F-1	reticulat e		1	1	4.2	1.1	1.466	1.7
TAN0103 U2315	1	F-2	reticulat e		1	1	6.1	1.6	1.518	1.1
TAN0103 U2315	1	F-3	reticulat e		1	1	1.1	1.7	1.418	1.5
TAN0103 U2315	2	F	reticulat e		1	1	46.4	3.4	1.527	2.5
TAN0103 U2315	2	F-1	reticulat e		1	1	47.4	4.3	1.441	2.1
TAN0103 U2315	2	F-2	reticulat e		1	1	1.6	2.5	1.362	1.3
TAN0103 U2315	2	F-3	reticulat e		1	1	1.9	1.7	1.373	2.1
1AN0103 U2322 net 6	1	F	reticulat e		2	2	19.3	95.6	1.399	4.8
TAN0103 U2322 net 6	1	F-3	reticulat e		2	2	15.2	48.4	1.429	27.2
1AN0103 U2322 net 6	2	F	reticulat e		2	2	6.9	40.8	1.293	3.7
TAN0103 U2322 net 6	2	F-3	reticulat e		2	2	8.3	10.2	1.307	4.6
TAN0103 U2322 net 6	6	F	reticulat e		1	2	6.8	7.4	1.308	19.3
TAN0103 U2322 net 6	6	F-3	reticulat e		1	2	12.8	15.5	1.360	3.5
TAN0103 U2322 net 6	7	F	reticulat e		1		24.4	17.9	1.329	1.9
1AN0103 U2322 net 6	7	F-3	reticulat e		1		44.2	19.7	1.391	3.5
Z7003	1	F	reticulat e	1	2	1	113.6	14.3	1.486	1.5
Z7003	1	F-3	reticulat e		2	1	2821.5	5.5	1.430	2.1
Z7003	2	F	reticulat e	1	1	2	55.2	34.1	1.503	5.3
Z7003	2	F-3	reticulat e		1	2	1420.3	37.9	1.384	13.7

	Individua	Chambe	Ultra-	Kummerfor	PD intergrad	Quadrat		26.40	a (a	D /0
Site	l Number	r	structure	m	e	e	AI/Ca (umol/mol	Mn/Ca (umol/mol	Sr/Ca (mmol/mol	Ba/Ca (umol/mol
)	(unioi/ inoi))	(umoi/ moi)
Z700 3 Z700	3	F	reticulate	1	1	2	1333.8	18.7	1.426	49.2
2700 3 7700	3	F-3	reticulate		1	2	2646.4	38.4	1.409	37.2
3 Z700	7	F	e crystallin		2	2	1774.3	12.3	1.353	12.9
3 Z700	7	F-1	e		2	2	102.6	2.7	1.455	1.8
3 Z700	9	F	reticulate	1	1	1	43.4	17.0	1.730	3.9
3 Z700	9	F-3	reticulate		1	1	178.4	33.0	1.581	23.9
3 Z700	10	F	reticulate		1	1	380.0	27.6	1.405	5.5
3 Z700	10	F-1	reticulate		1	1	37.9	22.7	1.574	1.3
3 Z700	11	F	reticulate	1	2	2	573.1	40.5	1.519	34.6
3 Z700	11	F-3	reticulate		2	2	588.2	16.4	1.428	16.2
3 Z700	12	F	e		1	2	19.0	3.2	1.538	6.0
3 Z700	12	F-3	e		1	2	90.8	2.1	1.466	3.3
3 Z700	13	F	reticulate	1	1	2	401.5	47.2	1.399	1.1
3 Z700	13	F-3	reticulate		1	2	125.0	56.4	1.413	1.0
3 Z700	14	F	e crystallin	1	1	1	701.2	17.2	1.355	6.7
3 Z700	14	F-3	e		1	1	644.7	3.6	1.386	0.7
3 Z700	16	F	reticulate		1	1	80.0	3.8	1.519	1.6
3 Z700	18	F	reticulate	1	2	2	23.6	24.6	1.444	2.7
3 Z700	18	F-3	reticulate		2	2	474.0	5.7	1.420	1.3
3 Z700	19	F	reticulate	1	1	2	21.4	26.8	1.369	1.0
3 Z700	19	F-3	reticulate		1	2	726.3	19.2	1.327	2.5
3 Z700	20	F	reticulate		1	2	80.7	21.4	1.369	4.4
3 Z700	20	F-3	reticulate crystallin		1	2	1810.5	16.3	1.409	4.8
3 Z700	21	F	e crystallin	1	1	2	27.0	11.0	1.491	17.2
3 Z700	21	F-3	e		1	2	3205.8	8.1	1.477	11.9
3 Z700	23	F	reticulate		1	2	70.6	32.3	1.383	2.6
3 Z700	23	F-3	reticulate		1	2	458.8	3.1	1.511	0.6
3 Z700	30	F	reticulate		1	1	94.7	37.5	1.517	3.8
3 7700	30	F-3	reticulate		1	1	2378.9	34.0	1.616	3.3
2700 3 7700	32	F	reticulate	1	1	1	16.3	16.8	1.358	0.9
3	32	F-3	reticulate		1	1	730.6	16.4	1.278	1.5

Table B4: Independent t-test summary for size normalised weight versus ultrastructure (reticulate or crystalline) in *N. incompta* from core top and plankton tow sites in the Southwest Pacific Ocean.

				Indep	pendent Sam	ples Testª			
	Equa Vari	lity of ances			t-1	test for Equalit	y of Means		
Size- normalised weight								95% Con Interva Diffe	nfidence l of the rence
Reticulate vs. crystalline.	F	Sig.	t	df	Sig. (2- tailed)	Mean Difference	Std. Error Difference	Lower	Upper
Equal variance assumed*	0.154	0.696	-0.401	92	0.690	-0.000148	0.00034	-0.00081	0.00054

^a 2-tailed significance level, p. * Equal variances tested using a Levene's test.

Appendix C

Appendix C. Chapter 5.

Table C1: Mean trace element/Ca data for *Globigerinoides ruber* ($250 - 350 \mu m$) from ODP Site 1123, ~ 1140 to 1000 Kyr.

ODP 1	123C L	eg 181 Core	e 005H								
Cor	e, sectio	n, interval ((cm)				Gs. 1	ruber			
Section	Top	Bottom	Depth	Age	Mg/Ca	Sr/Ca	Al/Ca	Mn/Ca	Zn/Ca	Ba/Ca	n
	(cm)	(cm)	(mbsf)	(Kyr)	(mmol/mol)	(mmol/mol)	(mmol/mol)	(mmol/mol)	(µmol/mol)	(µmol/mol)	-
2	00	01	20.0	1017 (0	2 207	1 20 4	0.544	0.257	45	2	1
2	90	91	39.9	1017.60	3.296	1.294	0.544	0.256	45	2	1
2	94	95	39.94	1010.70	2 100	1.300	0.212	0.075	15	4	8
2	102	103	40.02	1019.90	2.100	1.304	0.200	0.112	25	4	12
2	102	105	40.02	1020.00	2.200	1 392	0.303	0.087	25	6	4
2	110	111	40.1	1022.32	2.077	1 344	0.086	0.180	32	2	4
2	114	115	40.14	1024.68	2.943	1.372	0.378	0.116	43	42	3
2	118	119	40.18	1025.86	2.875	1.408	0.337	0.080	9	3	3
2	122	123	40.22	1027.04							
2	126	127	40.26	1029.39							
2	130	131	40.3	1029.43	2.886	1.415	0.619	0.070	21	37	2
2	134	135	40.34	1029.47	2.504	1.340	0.173	0.089	77	1	2
2	138	139	40.38	1031.75	1.867	1.366	0.060	0.113	23	1	2
2	142	143	40.42	1032.93	1.798	1.338	0.164	0.054	16	10	2
2	146	147	40.46	1034.11	3.179	1.374	0.908	0.044	16	5	1
2	149	150	40.49	1035.00	2.130	1.364	0.298	0.042	13	2	6
3	4	5	40.54	1036.47	2.111	1.408	0.212	0.063	10	2	7
3	8	9	40.58	1036.50	1.398	1.445	0.299	0.046	20	1	1
3	12	13	40.62	1038.83							
3	16	17	40.66	1038.86	1.896	1.385	0.060	0.030	26	1	2
3	20	21	40.7	1038.90	2.184	1.323	0.167	0.157	179	4	6
3	24	25	40.74	1038.93	1.970	1.459	0.103	0.062	44	1	5
3	28	29	40.78	1043.54							
3	32	33	40.82	1043.58	2.444	1.309	0.073	0.195	15	3	2
3	36	3/	40.86	1043.62	3.330	1.406	0.462	0.205	59	3	1
3	40	41	40.9	1043.66	2.667	1.293	1.590	0.124	97	10	1
2	44	45	40.94	1048.20	2.322	1.560	1.259	0.120	39	30	1
2	40	49	40.96	1046.50	2.951	1 2 2 7	0.266	0.245	20	2	1
2	52	55	41.02	1046.54	2.651	1.557	0.300	0.545	20	5	1
3	60	61	41.00	1051.80							
3	64	65	41.1	1051.84							
3	68	69	41.14	1051.00							
3	72	73	41.22	1056 51							
3	76	77	41.26	1056.55							
3	80	81	41.3	1058.84	2.266	1.291	0.085	0.101	26	4	1
3	82	83	41.32	1058.88	1.677	1.366	0.062	0.142	15	3	1
3	84	85	41.34	1060.01	2.624	1.283	0.235	0.429	342	5	3
3	86	87	41.36	1060.04							
3	88	89	41.38	1060.08							
3	90	91	41.4	1061.75							
3	92	93	41.42	1061.79							
3	94	95	41.44	1062.92							
3	96	97	41.46	1063.50							
3	98	99	41.48	1063.53	2 0 5 7	4 400	0 7 40	0.454	10	-	
3	100	101	41.5	1064.66	3.057	1.433	0.740	0.1/1	40	5	1
3	102	103	41.52	1065.24	0.755	1 201	1 520	0.015	20	24	4
3	104	105	41.54	1065.82	2.755	1.291	1.530	0.215	20	24	I
3	100	107	41.50	1066.00	1 9 4 7	1 265	0.172	0.024	20	2	2
3	108	109	41.56	1067.57	1.04/	1.505	0.175	0.024	20	2	2
3	112	111	41.62	1068.15	2 345	1 378	0.146	0.171	11	3	3
3	112	115	41.62	1068.73	2.045	1.375	0.140	0.165	13	2	3
3	116	117	41.66	1068.77	2.614	1 334	0.079	0.152	8	1	1
3	118	119	41.68	1069.90	2.187	1.345	0.299	0.141	18	3	6
3	120	121	41.7	1070.45	2.961	1.306	0.573	0.305	66	3	6
3	122	123	41.72	1070.96	2.797	1.341	0.213	0.211	81	2	6
3	124	125	41.74	1071.00	2.461	1.302	0.282	0.258	57	3	4
3	126	127	41.76	1072.00	2.913	1.345	0.367	0.119	28	5	2
3	128	129	41.78	1072.04	2.325	1.307	0.248	0.150	58	3	7
3	130	131	41.8	1073.03	2.893	1.297	0.177	0.197	160	3	6
3	132	133	41.82	1073.55	2.707	1.293	0.270	0.243	30	0	3
3	134	135	41.84	1074.07	2.681	1.290	0.283	0.128	56	4	8

ODP 1	123C L	eg 181 Core	e 005H								
Cor	e, section	n, interval (cm)				Gs. 1	ruber			
Section	Top	Bottom	Depth	Age	Mg/Ca	Sr/Ca	Al/Ca	Mn/Ca	Zn/Ca	Ba/Ca	n
	(cm)	(cm)	(mbsf)	(Kyr)	(mmol/mol)	(mmol/mol)	(mmol/mol)	(mmol/mol)	(µmol/mol)	(µmol/mol)	
3	136	137	41.86	1074.59	2.553	1.343	0.108	0.097	16	0	13
3	138	139	41.88	1075.11	2.753	1.337	0.252	0.198	13	2	9
3	140	141	41.9	1075.62	2.501	1.341	0.321	0.120	16	22	10
3	142	143	41.92	1075.66	2.693	1.362	0.493	0.156	9	3	12
3	144	145	41.94	1076.66	2.842	1.371	0.340	0.141	10	2	18
3	146	147	41.96	1077.18	2.514	1.361	0.430	0.205	12	2	4
3	148	149	41.98	1077.22	2.820	1.361	0.193	0.182	11	14	11
4	4	5	42.04	1079.25	2.729	1.343	0.412	0.208	10	2	13
4	8	9	42.08	1079.29	2.818	1.382	0.328	0.246	9	14	19
4	10	11	42.1	1080.80	2.653	1.340	0.298	0.274	11	19	14
4	12	13	42.12	1080.84	2.704	1.348	0.423	0.252	17	5	16
4	14	15	42.14	1081.84	2.807	1.372	0.203	0.219	10	1	16
4	16	17	42.16	1081.88	2.887	1.397	0.154	0.222	13	2	15
4	18	19	42.18	1082.87	2.719	1.384	0.210	0.296	12	22	15
4	20	21	42.2	1082.91	2.970	1.356	0.382	0.244	22	2	13
4	22	23	42.22	1082.95	2.697	1.369	0.266	0.273	9	6	28
4	24	25	42.24	1084.43	2.780	1.376	0.175	0.293	8	2	13
4	26	27	42.26	1084.46	2.796	1.343	0.346	0.265	10	8	13
4	28	29	42.28	1084.49	2.673	1.333	0.356	0.304	11	5	13
4	30	31	42.3	1086.31	2.741	1.326	0.410	0.225	14	2	12
4	32	33	42.32	1086.34	2.444	1.351	0.308	0.199	15	3	8
4	34	35	42.34	1087.63	2.195	1.347	0.395	0.217	10	19	9
4	38	39	42.38	1087.66	2.313	1.339	0.371	0.200	9	2	7
4	42	43	42.42	1090.26	3.251	1.276	0.797	0.328	16	5	2
4	46	47	42.46	1090.29	2.180	1.274	0.265	0.174	22	3	2
4	50	51	42.5	1092.90	2.886	1.367	0.395	0.195	8	3	2
4	54	55	42.54	1092.93	2.078	1.360	0.339	0.206	12	5	6
4	58	59	42.58	1092.96	3.143	1.278	0.124	0.316	77	2	1
4	62	63	42.62	1096.85	2.262	1.302	0.236	0.150	7	3	4
4	66	67	42.66	1096.88							
4	70	71	42.7	1096.91							
4	74	75	42.74	1100.81	2.705	1.235	0.161	0.390	16	4	1
4	78	79	42.78	1102.12							
4	82	83	42.82	1102.15							
4	86	87	42.86	1104.76							
4	90	91	42.9	1104.79	2.519	1.365	0.282	0.148	7	2	6
4	94	95	42.94	1107.40	2.869	1.334	0.177	0.090	7	1	4
4	98	99	42.98	1108.84	2.363	1.305	0.241	0.150	13	2	9
4	102	103	43.02	1110.89	2.224	1.336	0.171	0.117	11	1	22
4	106	107	43.06	1110.91	2.673	1.326	0.464	0.150	6	2	12
4	110	111	43.1	1114.99	2.414	1.340	0.464	0.195	17	4	12
4	114	115	43.14	1115.01	2.517	1.316	0.258	0.288	15	5	7
4	118	119	43.18	1119.10	2.495	1.330	0.455	0.370	23	7	2
4	122	123	43.22	1121.15	2.252	1.320	0.417	0.236	50	6	2
4	126	127	43.26	1121.17	2.532	1.287	0.674	0.234	12	10	2
4	130	131	43.3	1125.26	2.625	1.338	0.346	0.240	13	3	1
4	134	135	43.34	1127.31	2.995	1.426	0.932	0.241	25	3	1

Table C2: Mean trace element/Ca data for *Globigerina bulloides* ($250 - 350 \mu m$) from ODP Site 1123, ~ 1140 to 1000 Kyr.

ODP 1	123C L	eg 181 Core	005H								
Core	e, section	n, interval (cm)				G. bul	loides			
Section	Top	Bottom	Depth	Age	Mg/Ca	Sr/Ca	Al/Ca	Mn/Ca	Zn/Ca	Ba/Ca	n
	(cm)	(cm)	(mbsf)	(Kyr)	(mmol/mol)	(mmol/mol)	(mmol/mol)	(mmol/mol)	(µmol/mol)	(µmol/mol)	
2	90	91	39.9	1017.60	2.471	1.244	0.450	0.228	69	5	6
2	94	95	39.94	1018.78	2.276	1.282	0.332	0.188	20	14	10
2	98	99	39.98	1019.96	2.476	1.336	0.157	0.196	39	5	6
2	102	103	40.02	1020.00	2.240	1.330	0.206	0.172	47	5	9
2	106	107	40.06	1022.32	2.131	1.282	0.274	0.163	46	13	8
2	110	111	40.1	1022.36	2.446	1.302	0.330	0.148	44	8	7
2	114	115	40.14	1024.68	2.341	1.301	0.235	0.180	41	4	6
2	118	119	40.18	1025.86	2.118	1.318	0.484	0.146	30	14	6
2	122	123	40.22	1027.04	2.12/	1.310	0.721	0.134	28	11	9
2	126	12/	40.26	1029.39	1.908	1.320	0.243	0.155	63	27	5
2	130	131	40.5	1029.45	2.505	1.324	0.291	0.179	4/	15	7
2	1.34	133	40.34	1029.47	2.111	1.200	0.241	0.170	20	70	12
2	1.30	1/3	40.38	1031.73	2.024	1.332	0.304	0.203	47	10	13
2	146	145	40.46	1034 11	2.210	1.322	0.652	0.151	62	6	8
2	140	150	40.49	1035.00	1 923	1.308	0.345	0.131	54	62	10
3	4	5	40.54	1036.47	1.657	1.292	0.295	0.100	26	18	14
3	8	9	40.58	1036 50	1.682	1 338	0.189	0.078	17	2	11
3	12	13	40.62	1038.83	1.759	1.286	0.257	0.099	74	10	10
3	16	17	40.66	1038.86	2.126	1.298	0.839	0.145	47	5	13
3	20	21	40.7	1038.90	2.188	1.320	0.158	0.153	156	16	13
3	24	25	40.74	1038.93	1.795	1.301	0.240	0.125	96	34	12
3	28	29	40.78	1043.54	1.942	1.309	0.292	0.095	46	1	9
3	32	33	40.82	1043.58	1.791	1.288	0.411	0.122	51	3	10
3	36	37	40.86	1043.62	2.108	1.297	0.251	0.131	59	4	13
3	40	41	40.9	1043.66	1.966	1.326	0.261	0.119	105	5	10
3	44	45	40.94	1048.26	2.376	1.268	0.343	0.224	188	5	11
3	48	49	40.98	1048.30	2.173	1.269	0.568	0.198	97	6	11
3	52	53	41.02	1048.34	2.192	1.272	0.316	0.180	135	4	7
3	56	57	41.06	1051.80	1.743	1.339	0.289	0.123	16	5	3
3	60	61	41.1	1051.84	1.917	1.292	0.426	0.142	95	5	14
3	64	65	41.14	1051.88	2.278	1.316	0.568	0.176	232	39	10
3	68	69	41.18	1051.92	2./9/	1.345	0.332	0.224	112	1/	9
3	/2	/3	41.22	1056.51	2.979	1.341	0.150	0.1/8	129	6	5
2	70	01	41.20	1050.55	2.505	1.301	0.370	0.205	70	5	2
3	82	01 83	41.5	1058.88	2.411	1.250	0.239	0.256	70	7	5
3	84	85	41.32	1050.00	2 201	1.302	0.140	0.405	147	6	13
3	86	87	41.34	1060.01	2.501	1.275	0.358	0.222	85	8	11
3	88	89	41 38	1060.08	2.006	1 345	0.081	0.205	12	3	17
3	90	91	41.4	1061.75	3.035	1.290	0.195	0.299	15	23	15
3	92	93	41.42	1061.79	2.449	1.306	0.182	0.265	51	3	7
3	94	95	41.44	1062.92	1.967	1.334	0.147	0.186	13	8	20
3	96	97	41.46	1063.50	1.691	1.283	0.168	0.119	16	3	4
3	98	99	41.48	1063.53	2.912	1.349	0.233	0.338	119	5	4
3	100	101	41.5	1064.66	2.464	1.275	0.430	0.298	117	42	10
3	102	103	41.52	1065.24	2.560	1.280	0.257	0.299	272	29	7
3	104	105	41.54	1065.82	1.777	1.257	0.129	0.150	172	6	7
3	106	107	41.56	1066.41	1.996	1.257	0.227	0.224	121	16	9
3	108	109	41.58	1066.99	1.836	1.249	0.082	0.247	74	30	3
3	110	111	41.6	1067.57	2.464	1.298	0.420	0.216	25	10	6
3	112	113	41.62	1068.15	2.087	1.309	0.134	0.231	160	37	9
3	114	115	41.64	1068./3	2.112	1.28/	0.166	0.211	58	6	22
3	116	11/	41.66	1068.//	2.4/2	1.2/2	0.395	0.232	46	21	1/
3	118	119	41.08	1009.90	2.201	1.2/9	0.331	0.21/	∠/ 52	2 21	14
2	120	121	41.7	1070.45	2.494	1.313	0.371	0.230	55 90	∠1 ∧	14
3	124	125	41 74	1070.90	2.029	1.295	0.302	0.210	68	+	10
3	124	125	41 76	1072.00	1 893	1 205	0.707	0.255	20	5	2
3	128	129	41 78	1072.00	1.956	1.205	0.403	0.125	38	6	7
3	130	131	41.8	1073.03	2,481	1.281	0.350	0.199	308	125	ģ
3	132	133	41.82	1073.55	2.276	1.347	0.425	0.173	21	72	7
3	134	135	41.84	1074.07	1.535	1.247	0.290	0.053	18	8	2
3	136	137	41.86	1074.59	2.307	1.280	0.620	0.198	36	18	9

ODP 1	123C L	eg 181 Core	005H								
Core	e, sectio	n, interval (cm)				G. bul	loides			
Section	Тор	Bottom	Depth	Age	Mg/Ca	Sr/Ca	Al/Ca	Mn/Ca	Zn/Ca	Ba/Ca	n
	(cm)	(cm)	(mbsf)	(Kyr)	(mmol/mol)	(mmol/mol)	(mmol/mol)	(mmol/mol)	(µmol/mol)	(µmol/mol)	
3	138	139	41.88	1075.11	2.674	1.296	0.301	0.239	30	2	10
3	140	141	41.9	1075.62	2.198	1.256	0.277	0.180	35	2	3
3	142	143	41.92	1075.66	3.201	1.280	0.876	0.274	30	3	8
3	144	145	41.94	1076.66	2.632	1.248	0.682	0.181	22	12	14
3	146	147	41.96	1077.18	2.363	1.272	0.644	0.201	27	18	11
3	148	149	41.98	1077.22	2.753	1.250	0.271	0.211	26	17	13
4	4	5	42.04	1079.25	2.562	1.252	0.376	0.181	10	23	14
4	8	9	42.08	1079.29	3.406	1.275	0.497	0.234	22	15	13
4	10	11	42.1	1080.80	3.033	1.307	1.055	0.310	28	51	15
4	12	13	42.12	1080.84	3.167	1.341	1.226	0.273	18	135	18
4	14	15	42.14	1081.84	3.039	1.284	0.256	0.232	21	2	16
4	16	17	42.16	1081.88	2.986	1.292	0.339	0.202	13	2	18
4	18	19	42.18	1082.87	3.130	1.283	0.297	0.220	22	2	17
4	20	21	42.2	1082.91	2.930	1.293	0.248	0.234	22	6	17
4	22	23	42.22	1082.95	3.010	1.293	0.272	0.241	30	5	17
4	24	25	42.24	1084.43	2.974	1.300	0.242	0.247	26	6	14
4	26	27	42.26	1084.46	3.502	1.308	0.495	0.242	30	5	14
4	28	29	42.28	1084 49	2.611	1 304	0.468	0.216	15	6	17
4	30	31	42.3	1086.31	2.834	1.289	0.391	0.207	11	6	19
4	32	33	42.32	1086.34	2.908	1 333	0.851	0.201	13	38	22
4	34	35	42.34	1087.63	3 327	1 291	0.922	0.210	11	4	9
4	38	39	42.38	1087.66	3.025	1 306	0.886	0.240	13	2	22
4	42	43	42.42	1090.26	2 530	1 324	1 300	0.190	11	19	17
4	46	47	42.46	1090.20	3.007	1 315	1 340	0.214	11	26	17
4	50	51	42.5	1092.90	3 283	1 302	1.047	0.241	16	22	17
4	54	55	42 54	1092.93	2 708	1 319	1.017	0.191	13	11	15
4	58	59	42.58	1092.96	2 551	1 315	0.534	0.179	12	3	9
4	62	63	42.62	1096.85	2.892	1 323	0.573	0.195	8	18	17
4	66	67	42.66	1096.88	2.652	1 313	0.491	0.235	20	5	7
4	70	71	42.00	1096.00	1.815	1.515	0.283	0.173	20	4	2
4	74	75	42.7	1100.91	2 4 3 9	1.275	0.205	0.222	16	5	11
4	78	79	42.74	1102.01	2.455	1.223	0.751	0.124	10	4	3
4	82	83	42.70	1102.12	2.000	1 3/3	0.240	0.353	18	4	7
4	86	87	42.02	1102.15	2.979	1.345	2 580	0.355	10	13	5
4	90	91	42.00	1104.70	2.670	1.271	1 385	0.203	12	3	10
4	04	05	42.7	1107.40	2.007	1.207	0.087	0.157	12	26	14
4	94	95	42.94	1107.40	2.019	1.299	0.586	0.209	0	20	14
4	102	103	42.00	1110.04	2.040	1.300	0.500	0.130	12	4	14
4	102	105	43.02	1110.69	2.062	1.297	0.809	0.179	12	4	14
4	110	107	43.00	1114.00	2.309	1.324	0.760	0.195	20	25	1.0
4	110	111	43.1	1114.99	2.704	1.334	0.745	0.210	20 11	33 22	11
4	114	110	43.14	1110.01	2.704	1.294	0.017	0.197	11	5	14
4	110	119	43.10	1121.10	2.270	1.209	0.526	0.100	0	25	13
4	122	123	43.22	1121.13	2.213	1.2/0	0.554	0.101	0	20	14
4	120	127	43.20	1121.1/	2.220	1.297	0.022	0.140	10	∠1 F	17
4	130	131	43.3	1125.20	2.550	1.294	0.982	0.131	10	5	10
4	1.04	1.35	45.54	112/.31	∠.401	1.281	1.4/0	0.120	15	ð	11

Table C3: Mean stable oxygen and carbon isotope data for *Uvigerina spp., Globigerinoides ruber* and *Globerina bulloides* from ODP Site 1123, ~ 1140 to 1000 Kyr. Grey shaded cells indicate replicate analysis on the same sample.

Adjusted Depth Urigerina spp. G. ruber <th colsp<="" th=""><th colspan="5">ODP 1123C Leg 181 Core 005H</th><th></th><th></th><th></th><th></th><th></th><th></th><th></th></th>	<th colspan="5">ODP 1123C Leg 181 Core 005H</th> <th></th> <th></th> <th></th> <th></th> <th></th> <th></th> <th></th>	ODP 1123C Leg 181 Core 005H											
Core, section, interval (cm) Depth Lingerna dp. C. interval (cm) C. indicates 2 90 91 39.90 39.90 1,017.60 -0.884 3.868 6.90	_				Adjusted				~		~ .		
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	Core	, section	n, interval	(cm)	Depth ¹		Uvigeri	na spp.	Gs.	ruber	G. bu	lloides	
$ \begin{array}{c cmc} (cm) (cm) (mbst) (p) (%) (%) (%) (%) (%) (%) (%) (%) (%) (%$	Section	Тор	Bottom	Depth	Uvigerina spp.	Age	$\delta^{13}C$	$\delta^{18}O$	$\delta^{13}C$	$\delta^{18}O$	$\delta^{13}C$	$\delta^{18}O$	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		(cm)	(cm)	(mbsf)	(mbsf)	(Kyr)	(‰)	(‰)	(‰)	(‰)	(‰)	(‰)	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	2	90	91	39.90	39.90	1,017.60	-0.884	3.860		. ,		. ,	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	2	94	95	39.94	39.94	1,018.78	-0.973	3.858			0.073	1.243	
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	2	98	99	39.98	40.00	1,019.96	-0.671	3.890			-0.178	1.317	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$							-0.706	3.789					
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	2	102	103	40.02		1,020.00			0.77	0.97	-0.496	0.885	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	2	106	107	40.06	40.08	1,022.32	-0.872	3.769			-0.105	1.232	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	2	110	111	40.10		1,022.36					-1.263	0.563	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	2	114	115	40.14	40.16	1,024.68	-1.123	4.095					
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	2	118	119	40.18	40.18	1,025.86	-1.001	4.108			-0.536	1.148	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	2	122	123	40.22	40.24	1,027.04	-1.101	4.399					
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$,	-1.139	4.246					
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	2	126	127	40.26		1,029.39							
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	2	130	131	40.30	40.32	1,029.43	-1.248	4.083					
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	2	134	135	40.34		1,029.47					-0.173	1.788	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2	138	139	40.38	40.38	1.031.75	-1.102	4.586			-0.670	1.209	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2	142	143	40.42	40.42	1.032.93	-1.445	4.648			-0.355	1.928	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	2	146	147	40.46	40.46	1.034.11	-1.259	4.484			-0.015	1.620	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	2	149	150	40.49	40.49	1,035.00	-1.392	4.821			0.059	2.374	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	3	4	5	40.54	40.56	1,036,47	-1 316	4 620			-0.571	1 824	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	5		5	10.51	10.50	1,050.17	1.510	1.020			0.185	2 378	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	3	8	9	40.58		1 036 50					0.105	2.570	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	3	12	13	40.62	40.68	1,038,83	-1 371	4 793			0.196	2 528	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	3	16	17	40.66	10.00	1,038.86	1.571	1.725			-0.389	1 922	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3	20	21	40.70		1,038,90					0.088	2 1 5 3	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3	20	25	40.74		1,038,93					-0.095	1.892	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3	28	29	40.78	40.84	1,030.55	-1 477	4 637			0.124	1.837	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3	32	33	40.82	40.04	1,043.54	-1.7//	1.0 57			0.124	2 213	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3	36	37	40.86		1,043.62					0.244	2.036	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3	36	37	40.86		1,015.02					0.187	1.966	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3	40	41	40.90		1 043 66					0.203	2 166	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3	44	45	40.90	40.98	1,049.00	-1 355	4 419			-1.167	2.100	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3	48	40	40.94	40.20	1,048.30	-1.555	7.717			-1.107	-0.296	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3	-10 52	53	41.02		1,048.34					-0.193	1 720	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3	56	57	41.02	41.12	1,040.94	1 /35	1 123			-0.175	1.720	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3	60	61	41.00	41.12	1,051.80	-1.433	4.423			0 211	2 001	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3	64	65	41.10		1,051.84					0.211	1.850	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3	68	60	41.14		1,051.00					0.558	1.650	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3	72	73	41.10	41.24	1,051.92	1 3 2 2	4 557			-0.556	1.575	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2	76	75	41.22	41.24	1,050.51	-1.322	4.557			0.764	1.005	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2	70	01	41.20	41 21	1,050.55	1 5 4 0	4 445			-0.704	1.095	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3	80	61	41.30	41.31	1,058.84	-1.549	4.445			-0.104	1.370	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2	00	02	41.20		1 050 00	-1.422	4.323			0.050	1 705	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2 2	02 04	0 <i>3</i> 05	41.32	41.26	1,000.00	1 157	4 15 4			-0.039	1./00	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3	04	00	41.34	41.30	1,000.01	-1.13/	4.134			-0.000	1.555	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2	07	07	11.26		1.0(0.04	-1.180	4.1/5			0 1 2 2	1 740	
5 66 69 41.58 1,000.08 -0.001 2.308	2	00	0/ 00	41.30		1,000.04					-0.123	1./48	
	3	00	69	41.38		1,000.08					-0.001	2.308	

Core	, section	n, interval	(cm)	Depth ¹		Uvigeri	na spp.	Gs.	ruber	G. hu	lloides
Section	Ton	Bottom	Depth	Luigaring spp	Age	813C	<u>8180</u>		8180	813C	818O
3	<u>90</u>	91	41 40	41 41	1.061.75	-1 427	4 342	0.0	0.0	-0.406	1 239
5	20	<i>,</i> 1	11.10	11.11	1,001.75	-1.256	4.394			0.100	1.200
3	92	93	41.42		1,061.79					-1.063	-0.110
3	94	95	41.44	41.44	1,062.92	-1.148	4.344			0.344	2.612
3	96	97	41.46	41.47	1,063.50	-1.194	4.132				
3	98	99	41.48		1,063.53					0.021	2.068
3	100	101	41.50	41.50	1,064.66	-0.908	3.981			-0.154	1.449
3	102	103	41.52	41.52	1,065.24	-0.763	4.090			-0.068	0.760
3	104	105	41.54	41.54	1,065.82	-0.737	3.774				
						-0.821	3.614				
3	106	107	41.56	41.56	1,066.41	-0.816	3.593			0.230	1.657
2	100	4.00	44 50	44.50	4.044.00	-0.828	3.927			0.055	1 207
3	108	109	41.58	41.58	1,066.99	-0.733	4.022			0.255	1.287
3	110	111	41.60	41.60	1,067.57	-0.834	3.986			0.1.11	1 1 7 5
3	112	115	41.62	41.62	1,068.15	-0.//6	3.792			-0.141	1.1/5
3 2	114	115	41.64	41.65	1,068.75	-0./51	3.647			0.339	1.382
3	110	11/	41.00	11 68	1,008.77	0.560	3 176			0.051	0.911
3	110	119	41.00	41.00	1,009.90	-0.309	3.470			0.155	0.011
3	120	121	41.70	41.70	1,070.45	-0.780	3.702			0.013	0.797
3	122	125	41.72	41.75	1,070.90	-0.758	5.702			0.058	1.085
3	124	123	41.74	41 77	1,071.00	-0 591	3 570			0.510	1.005
3	120	127	41.70	71.77	1,072.00	-0.571	5.570			0.417	1.051
3	130	131	41.80	41.80	1,073.03	-0.857	3 700			0.466	1 311
3	132	133	41.82	41.82	1,073,55	-0.806	3 491			0.100	0.895
5	152	155	11.02	11.02	1,075.55	-0.874	3 270			0.205	0.075
3	134	135	41.84	41.84	1.074.07	-0.861	3.838				
Č,					-,	-0.894	3.818				
3	136	137	41.86	41.86	1.074.59	-0.652	3.602			0.105	1.119
3	138	139	41.88	41.88	1,075.11	-0.709	3.498			-0.622	0.777
3	140	141	41.90	41.91	1,075.62	-0.641	3.614	1.23	0.98	0.303	1.494
3	142	143	41.92		1,075.66			1.39	1.03		
2	144	145	41.04	41.04	1.076.66	0.650	2 620	1.25	0.66	0.001	1.052
3	144	145	41.94	41.94	1,070.00	-0.659	5.629	1.25	0.66	0.001	1.055
								1.12	0.68		
								1.16	0.56		
3	146	147	41.96	41.97	1,077.18	-0.706	3.462			0.257	1.401
						-0.625	3.395				
3	148	149	41.98		1,077.22					-0.384	0.889
4	4	5	42.04	42.04	1,079.25	-0.659	3.385			0.402	1.655
4	8	9	42.08		1,079.29			1.16	0.39	0.461	1.453
4	10	4.4	10 10	10.10	1 000 00	0 (02	2 ((2	1.14	$\frac{0.72}{0.02}$	0.027	1 405
4	10	11	42.10	42.12	1,080.80	-0.683	3.663	1.20	0.92	-0.03/	1.485
4	10	12	12 1 2		1 000 04			1 10	0.08	0 211	1 467
4	12	15	42.12		1,080.84			1.19	0.98	0.311	1.407
4	14	15	12 14	42.15	1 081 84	0.724	3 / 3 1			0.525	1.240
4	16	17	42.14	42.15	1,001.04	-0.724	5.451	1 36	0.71	0.007	1 409
т	10	1 /	72.10		1,001.00			1.50	0.67	0.230	1.407
4	18	19	42.18	42 20	1 082 87	-0 538	3 917	1.58	0.70	0 2 3 9	1 682
	10	.,	.2.10	12.20	-,002.07	-0.695	3.946	1.50	0.10	0.207	1.002
4	20	21	42.20		1,082.91	0.070		1.47	0.62	0.001	1.372
4	22	23	42.22		1,082.95			1.66	0.85	-0.171	1.629
		-			, .			1.27	0.50		

	ODP	1123C Le	g 181 Core	e 005H Adjusted							
Core	, sectio	n, inte r val	(cm)	Depth ¹		Uvigeri	na spp.	Gs.	ruber	G. bu	lloides
Section	Тор	Bottom	Depth	Uvigerina spp.	Age	$\delta^{13}C$	$\delta^{18}O$	δ ¹³ C	$\delta^{18}O$	$\delta^{13}C$	$\delta^{18}O$
4	24	25	42.24	42.26	1,084.43	-0.675	3.929 4.020			0.270	1.392
4	26	27	42.26		1,084.46			1.18	0.50	-0.012	1.345
4	28	29	42.28		1,084.49			1.29	0.70	-0.179 0.141	1.512 1.325
4	30	31	42.30	42.31	1,086.31	-0.725	4.376	1.15	0.90	0.096	1.720
4	32	33	42.32		1,086.34						
4	34	35	42.34	42.36	1,087.63	-0.890	4.135			-0.277	1.686
4	38	39	42.38	10.11	1,087.66	0.040		0.98	1.31	-0.274	1.676
4	42	43	42.42	42.44	1,090.26	-0.918	4.494			-0.527	1.620
4	46	47	42.46	10.54	1,090.29	1 1 2 5	4 70 4			-0.536	1.259
4	50	51	42.50	42.54	1,092.90	-1.135	4.736			-0.804	1.015
4	54	55	42.54		1,092.93					-0.640	1.187
4	58	59	42.58		1,092.96					-0.392	1.506
4	62	63	42.62	42.66	1,096.85	-1.323 -1.175	4.636 4.436			-0.911	1.079
4	66	67	42.66		1,096.88						
4	70	71	42.70		1,096.91						
4	74	75	42.74	42.74	1,100.81	-1.252	4.486			-0.329	1.967
4	78	79	42.78	42.80	1,102.12	-1.358	4.539				
4	82	83	42.82		1,102.15					0.507	2.017
4	86	87	42.86	42.88	1,104.76	-0.918	4.101				
						-0.757	4.076				
4	90	91	42.90		1,104.79						
4	94	95	42.94	42.94	1,107.40	-0.867	4.178			-0.548	0.959
4	98	99	42.98	42.98	1,108.84	-0.730	4.019			-0.432	1.273
4	102	103	43.02	43.04	1,110.89	-0.956	4.042	1.07	1.13 0.99		
4	106	107	43.06		1,110.91			1.10 1.00 0.84	0.98 1.18 1.27	-0.541	1.190
4	110	111	43.10	43.13	1,114.99	-0.752	4.089	1.12	1.05	-0.532	1.367
4	114	115	43.14		1,115.01					-0.800	1.174
4	118	119	43.18	43.18	1,119.10	-1.010	4.417			-0.642	1.449
4	122	123	43.22	43.24	1,121.15	-1.159	4.537			-0.683	1.490
4	126	127	43.26		1,121.17					-0.678	1.546
4	130	131	43.30	43.30	1,125.26	-1.238	4.616				
4	134	135	43.34	43.34	1,127.31	-0.937	4.126			-0.052	2.293

¹Represents the linear interpolation where more than one sample was analysed to provide minimum weights for stable isotope analysis.

Age	$\delta^{18} O$	Mg/Ca	SST	$\delta^{18}O_{seawater}$	Salinity
(Kyr)	(‰)	(mmol/mol)	(°C)	(‰)	(psu)
1017.60	-	2.471	13.75	-	-
1018.78	1.24	2.276	12.53	0.69	35.01
1019.96	1.32	2.476	13.79	1.02	35.50
1020.00	0.88	2.240	12.30	0.28	34.41
1022.32	1.23	2.131	11.55	0.47	34.69
1022.36	0.56	2.446	13.60	0.23	34.34
1024.68	-	2.341	12.95	-	-
1025.86	1.15	2.118	11.45	0.37	34.54
1027.04	-	2.127	11.52	-	-
1029.39	-	1.908	9.90	-	-
1029.43	-	2.505	13.96	-	-
1029.47	1.79	2.111	11.40	1.00	35.46
1031.75	1.21	2.624	14.66	1.10	35.60
1032.93	1.93	2.210	12.09	1.28	35.87
1034.11	1.62	2.382	13.21	1.20	35.76
1035.00	2.37	1.923	10.02	1.29	35.89
1036.47	2.10	1.657	7.79	0.56	34.82
1036.50	-	1.682	8.02	-	-
1038.83	2.53	1.759	8.68	1.17	35.71
1038.86	1.92	2.126	11.51	1.15	35.69
1038.90	2.15	2.188	11.95	1.47	36.16
1038.93	1.89	1.795	8.99	0.60	34.88
1043.54	1.84	1.942	10.17	0.79	35.15
1043.58	2.21	1.791	8.96	0.91	35.34
1043.62	2.00	2.108	11.39	1.21	35.77
1043.66	2.17	1.966	10.34	1.15	35.69
1048.26	1.11	2.376	13.17	0.69	35.01
1048.30	-0.30	2.173	11.84	-1.00	32.54
1048.34	1.72	2.192	11.97	1.05	35.53
1051.80	-	1.743	8.55	-	-
1051.84	2.09	1.917	9.97	1.00	35.47
1051.88	1.85	2.278	12.54	1.30	35.90
1051.92	1.58	2.797	15.61	1.66	36.43
1056.51	-	2.979	16.55	-	-
1056.55	1.10	2.563	14.30	0.91	35.33
1058.84	1.37	2.411	13.39	0.99	35.45
1058.88	1.78	3.053	16.91	2.14	37.14
1060.01	1.53	2.201	12.03	0.87	35.28
1060.04	1.75	2.501	13.94	1.48	36.17

Table C4: Calculated δ^{18} O, Mg/Ca and SST used to estimate δ^{18} O_{sw} in *Globerina* bulloides from ODP Site 1123, ~ 1140 to 1000 Kyr.

	2180		000	2180	0.1.
Age	δ ¹⁰ O	Mg/Ca	SST	δ ¹⁰ O _{seawater}	Salinity
(Kyr)	(‰)	(mmol/mol)	(°C)	(%0)	(psu)
1060.08	2.36	2.006	10.64	1.41	36.07
1061.75	1.24	3.035	16.83	1.58	36.31
1061.79	-0.11	2.449	13.62	-0.44	33.36
1062.92	2.61	1.967	10.35	1.60	36.35
1063.50	-	1.691	8.10	-	-
1063.53	2.07	2.912	16.21	2.28	37.34
1064.66	1.45	2.464	13.72	1.14	35.67
1065.24	0.76	2.560	14.29	0.57	34.83
1065.82	-	1.777	8.84	-	-
1066.41	1.66	1.996	10.57	0.69	35.01
1066.99	1.29	1.836	9.32	0.06	34.09
1067.57	-	2.464	13.71	-	-
1068.15	1.17	2.087	11.24	0.35	34.51
1068.73	1.38	2.112	11.42	0.59	34.87
1068.77	1.07	2.472	13.76	0.77	35.12
1069.90	0.81	2.201	12.03	0.15	34.22
1070.45	0.80	2.494	13.90	0.52	34.77
1070.96	0.65	2.629	14.68	0.54	34.80
1071.00	1.08	2.340	12.94	0.61	34.90
1072.00	1.83	1.893	9.78	0.70	35.03
1072.04	1.17	1.956	10.27	0.14	34.21
1073.03	1.31	2.481	13.82	1.02	35.50
1073.55	0.89	2.276	12.53	0.34	34.49
1074.07	-	1.535	6.65	-	-
1074.59	1.12	2.307	12.73	0.60	34.88
1075.11	0.78	2.674	14.94	0.72	35.06
1075.62	1.49	2.198	12.01	0.83	35.21
1075.66	-	3.201	17.62	-	-
1076.66	1.05	2.632	14.70	0.95	35.39
1077.18	1.40	2.363	13.09	0.96	35.41
1077.22	0.89	2.753	15.37	0.92	35.35
1079.25	1.66	2.562	14.30	1.47	36.15
1079.29	1.45	3.406	18.55	2.15	37.15
1080.80	1.48	3.033	16.82	1.82	36.67
1080.84	1.35	3.167	17.46	1.82	36.67
1081.84	1.40	3.039	16.84	1.75	36.56
1081.88	1.41	2.986	16.58	1.70	36.49
1082.87	1.68	3.130	17.28	2.12	37.10
1082.91	1.37	2.930	16.30	1.60	36.34
1082.95	1.63	3.010	16.70	1.94	36.84
1084.43	1.39	2.974	16.52	1.67	36.44
1084.46	1.34	3.502	18.96	2.13	37.12

Age	$\delta^{18} O$	Mg/Ca	SST	$\delta^{18}O_{seawater}$	Salinity
(Kyr)	(‰)	(mmol/mol)	(°C)	(‰)	(psu)
1084.49	1.42	2.611	14.58	1.29	35.89
1086.31	1.72	2.834	15.80	1.85	36.70
1086.34	-	2.908	16.19	-	-
1087.63	1.69	3.327	18.20	2.31	37.38
1087.66	1.68	3.025	16.78	2.00	36.94
1090.26	1.62	2.530	14.11	1.39	36.04
1090.29	1.26	3.007	16.69	1.57	36.30
1092.90	1.02	3.283	18.00	1.60	36.34
1092.93	1.19	2.708	15.12	1.17	35.71
1092.96	1.51	2.551	14.23	1.30	35.91
1096.85	1.08	2.892	16.11	1.27	35.86
1096.88	-	2.460	13.69	-	-
1096.91	-	1.815	9.16	-	-
1100.81	1.97	2.439	13.56	1.63	36.38
1102.12	-	2.086	11.23	-	-
1102.15	2.02	2.979	16.55	2.30	37.36
1104.76	-	2.870	15.99	-	-
1104.79	-	2.667	14.90	-	-
1107.40	0.96	2.819	15.73	1.07	35.56
1108.84	1.27	2.048	10.96	0.39	34.57
1110.89	-	2.682	14.98	-	-
1110.91	1.19	2.569	14.34	1.01	35.48
1114.99	1.37	2.764	15.43	1.41	36.07
1115.01	1.17	2.704	15.10	1.15	35.69
1119.10	1.45	2.270	12.49	0.88	35.30
1121.15	1.49	2.273	12.51	0.93	35.36
1121.17	1.55	2.228	12.21	0.92	35.35
1125.26	-	2.556	14.26	-	-
1127.31	2.29	2.461	13.70	1.98	36.90

Age	$\delta^{18} \mathrm{O}$	Mg/Ca	SST	$\delta^{18}O_{seawater}$	Salinity
(Kyr)	(‰)	(mmol/mol)	(°C)	(‰)	(psu)
1017.60		3.296	20.26		
1018.78		1.891	12.32		
1019.96		2.100	13.82		
1020.00	0.97	2.266	14.91	1.24	35.82
1022.32		2.402	15.74		
1022.36		2.077	13.66		
1024.68		2.943	18.64		
1025.86		2.875	18.31		
1027.04					
1029.39					
1029.43		2.886	18.36		
1029.47		2.504	16.34		
1031.75		1.867	12.14		
1032.93		1.798	11.60		
1034.11		3.179	19.75		
1035.00		2.130	14.02		
1036.47		2.111	13.90		
1036.50		1.398	8.01		
1038.83					
1038.86		1.896	12.36		
1038.90		2.184	14.38		
1038.93		1.970	12.91		
1043.54					
1043.58		2.444	15.99		
1043.62		3.330	20.41		
1043.66		2.667	17.24		
1048.26		2.322	15.26		
1048.30					
1048.34		2.851	18.19		
1051.80					
1051.84					
1051.88					
1051.92					
1056.51					
1056.55					
1058.84		2.266	14.91		
1058.88		1.677	10.61		
1060.01		2.624	17.00		

Table C5: Calculated δ^{18} O, Mg/Ca and SST used to estimate δ^{18} O_{sw} in *Globigerinoides ruber* from ODP Site 1123, ~ 1140 to 1000 Kyr.

Appendix C

Age	$\delta^{18} O$	Mg/Ca	SST	$\delta^{18}O_{seawater}$	Salinity
(Kyr)	(‰)	(mmol/mol)	(°C)	(‰)	(psu)
1060.04					
1060.08					
1061.75					
1061.79					
1062.92					
1063.50					
1063.53					
1064.66		3.057	19.19		
1065.24					
1065.82		2.755	17.70		
1066.41					
1066.99		1.847	11.99		
1067.57					
1068.15		2.345	15.40		
1068.73		2.091	13.76		
1068.77		2.614	16.95		
1069.90		2.187	14.40		
1070.45		2.961	18.73		
1070.96		2.797	17.92		
1071.00		2.461	16.09		
1072.00		2.913	18.50		
1072.04		2.325	15.28		
1073.03		2.893	18.40		
1073.55		2.707	17.45		
1074.07		2.681	17.31		
1074.59		2.553	16.61		
1075.11		2.753	17.69		
1075.62	0.98	2.501	16.32	1.55	36.27
1075.66	1.03	2.693	17.38	1.82	36.66
1076.66	0.63	2.842	18.15	1.58	36.31
1077.18		2.514	16.39		
1077.22		2.820	18.04		
1079.25		2.729	17.57		
1079.29	0.55	2.818	18.02	1.48	36.16
1080.80	0.92	2.653	17.16	1.66	36.43
1080.84	0.98	2.704	17.44	1.78	36.60
1081.84		2.807	17.97		
1081.88	0.69	2.887	18.37	1.68	36.47
1082.87	0.70	2.719	17.51	1.51	36.22
1082.91	0.62	2.970	18.77	1.69	36.48
1082.95	0.68	2.697	17.40	1.47	36.15
1084.43		2.780	17.83		

Age	$\delta^{18} O$	Mg/Ca	SST	$\delta^{18}O_{seawater}$	Salinity
(Kyr)	(‰)	(mmol/mol)	(°C)	(‰)	(psu)
1084.46	0.53	2.796	17.91	1.42	36.09
1084.49	0.70	2.673	17.27	1.46	36.14
1086.31	0.90	2.741	17.63	1.73	36.54
1086.34		2.444	15.99		
1087.63		2.195	14.45		
1087.66	1.31	2.313	15.20	1.64	36.40
1090.26		3.251	20.06		
1090.29		2.180	14.36		
1092.90		2.886	18.37		
1092.93		2.078	13.67		
1092.96		3.143	19.58		
1096.85		2.262	14.88		
1096.88					
1096.91					
1100.81		2.705	17.44		
1102.12					
1102.15					
1104.76					
1104.79		2.519	16.42		
1107.40		2.869	18.28		
1108.84		2.363	15.51		
1110.89	1.04	2.224	14.64	1.25	35.84
1110.91	1.23	2.673	17.27	1.99	36.91
1114.99	1.05	2.414	15.81	1.50	36.20
1115.01		2.517	16.41		
1119.10		2.495	16.28		
1121.15		2.252	14.82		
1121.17		2.532	16.49		
1125.26		2.625	17.01		
1127.31		2.995	18.90		

Table C6: Mean weight, width, height, size-normalised weight and predicted weight data for *Globigerinoides ruber* and *Globigerina bulloides* ($250 - 350 \mu m$) from ODP Site 1123, ~ 1140 to 1000 Kyr.

C	DDP 112	23C Leg 181	l Core 005	БH								
Core	e, sectio	n, interval (cm)			Gs. ruber				G. bulloides	r	
											Size	
					Mean			Mean			normalised	Predicted
Section	Тор	Bottom	Depth	Age	Weight	Width (x)	Height (y)	Weight	Width (x)	Height (y)	weight	Weight
	(cm)	(cm)	(mbsf)	(Kyr)	(µg)	(µm)	(µm)	(µg)	(µm)	(µm)	(µg/µm)	(µg)
2	90	91	39.90	1017.60	9	315	307	15	305	370	5.05	8.38
2	94	95	39.94	1018.78	11	306	279	10	332	379	2.98	8.65
2	98	99	39.98	1019.96	10	313	309	10	330	373	3.09	8.37
2	102	103	40.02	1020.00	12	315	302	8	328	395	2.57	8.70
2	106	107	40.06	1022.32	10	317	300	11	339	391	3.13	8.86
2	110	111	40.10	1022.36	9	289	270	10	359	422	2.85	8.41
2	114	115	40.14	1024.68	8	293	269	9	352	410	2.61	8.55
2	118	119	40.18	1025.86	10	322	310	10	316	381	3.02	8.88
2	122	123	40.22	1027.04				11	330	378	3.43	8.87
2	126	127	40.26	1029.39				11	308	362	3.53	9.22
2	130	131	40.30	1029.43	16	305	304	12	333	400	3.64	8.33
2	134	135	40.34	1029.47	14	325	300	14	340	415	4.06	8.89
2	138	139	40.38	1031./5	14	326	333	8	328	388	2.34	8.18
2	142	145	40.42	1032.93	10	222	293	12	332	407	3.73	8.74
2	140	14/	40.46	1034.11	12	225	292	11	346	390	5.14	8.50
2	149	150	40.49	1035.00	11	312	301	17	324	429	5.14	9.20
2	4	0	40.54	1036.47	15	322	305	16	332	421	4.09	9.69
3	0 12	13	40.58	1030.50	10	304	350	10	384	457	4.50	9.04
3	16	17	40.62	1038.86	17	351	344	12	327	387	3.82	8.87
3	20	21	40.00	1038.00	1/	327	207	14	357	418	4.02	8 77
3	20	25	40.70	1038.93	10	303	283	16	336	392	4.02	9.42
3	24	29	40.74	1043 54	10	505	205	15	337	395	4 31	9.17
3	32	33	40.70	1043.54	12	308	315	16	375	438	4 23	9.43
3	36	37	40.86	1043.62	12	315	288	15	357	419	4 22	8 90
3	40	41	40.90	1043.66	16	384	364	14	362	422	4.00	9.13
3	44	45	40.94	1048.26	17			10	329	402	2.94	8.50
3	48	49	40.98	1048.30				9	317	376	2.88	8.80
3	52	53	41.02	1048.34	10	239	312	13	353	425	3.82	8.77
3	56	57	41.06	1051.80				19	388	473	5.00	9.52
3	60	61	41.10	1051.84				12	362	413	3.39	9.21
3	64	65	41.14	1051.88				11	328	389	3.36	8.64
3	68	69	41.18	1051.92				10	332	378	2.93	7.97
3	72	73	41.22	1056.51				8	336	389	2.51	7.76
3	76	77	41.26	1056.55				8	349	405	2.32	8.26
3	80	81	41.30	1058.84	11	278	269	16	427	461	3.80	8.46
3	82	83	41.32	1058.88	9			12	326	389	3.66	7.68
3	84	85	41.34	1060.01	9	316	293	9	313	361	2.73	8.76
3	86	87	41.36	1060.04				10	331	401	3.16	8.34
3	88	89	41.38	1060.08				13	343	418	3.86	9.06
3	90	91	41.40	1061.75				9	343	406	2.69	7.70
3	92	93	41.42	1061.79				11	344	387	3.32	8.41
3	94	95	41.44	1062.92				15			1.07	0.42
3	96	97	41.46	1063.50				15	333	414	4.36	9.62
3	98	99	41.48	1063.53	7	075	2(0	13	330	397	3.94	/.84
3	100	101	41.50	1064.66	/	275	269	10	359	426	3.16	8.39
3	102	105	41.52	1065.24	0	207	269	10	340 217	399	2.85	8.20
3	104	105	41.54	1065.82	ð	28/	208	δ 12	31/ 345	305	2.54	9.40
2	100	107	41.50	1066.00	12	200	201	12	345	420	3.44	9.08
3	100	109	41.50	1067.57	15	306	201	13	324	407 306	5.55 2.81	9.55
3	110	111	41.00	1069.157	11	300	271	9 12	351	300	2.01	0.37
2	114	115	41.02	1068 72	7	276	265	10	378	301	2.05	8.25
3	116	117	41.66	1068 77	10	305	259	10	340	305	2.90	8 38
3	118	110	41.68	1069.90	13	305	293	0	332	382	2.55	876
3	120	121	41 70	1070.45	12	291	303	9	345	396	2.53	8 35
3	122	123	41 72	1070.96	10	297	279	10	345	390	2.83	8.17
3	124	125	41 74	1071.00	9	305	305	10	353	397	2.00	8 56

C	DDP 112	23C Leg 181	Core 005	ΞH								
Cor	e, sectio	n, interval (cm)			Gs. ruber				G. bulloide	5	
Section	Top	Bottom	Depth	Age	Mean Weight	Width (x)	Height (v)	Mean Weight	Width (x)	Height (v)	Size normalised weight	Predicted Weight
	(cm)	(cm)	(mhsf)	(Kvr)	(110)	(um)	(um)	(110)	(um)	(um)	(ug/um)	(119)
3	126	127	41.76	1072.00	9	292	284	10	339	379	2.89	9.25
3	128	129	41.78	1072.04	8	294	284	13	335	402	3.89	9.14
3	130	131	41.80	1073.03	12	309	317	13	356	418	3.66	8.36
3	132	133	41.82	1073.55	11	344	343	11	342	395	3.12	8.65
3	134	135	41.84	1074.07	10	311	296	13	303	362	4.20	9.94
3	136	137	41.86	1074.59	12	327	306	14	359	411	3.99	8.60
3	138	139	41.88	1075.11	11	328	301	10	325	379	3.16	8.12
3	140	141	41.90	1075.62	11	314	302	16	371	418	4.21	8.76
3	142	143	41.92	1075.66	11	308	296	14	356	426	3.86	7.53
3	144	145	41.94	1076.66	11	316	311	19	334	377	5.72	8.17
3	146	147	41.96	1077.18	10	324	315	14	328	397	4.34	8.52
3	148	149	41.98	1077.22	6	342	304	9	323	376	2.79	8.02
4	4	5	42.04	1079.25	14	330	319	14	344	404	3.93	8.26
4	8	9	42.08	1079.29	12	314	293	16	348	399	4.53	7.32
4	10	11	42.10	1080.80	9	295	295	10	332	390	3.11	7.70
4	12	13	42.12	1080.84	9	317	308	13	336	391	3.98	7.56
4	14	15	42.14	1081.84	11	327	303	12	339	412	3.57	7.70
4	16	1/	42.16	1081.88	11	319	292	13	345	415	3.80	/./6
4	18	19	42.18	1082.87	12	338	314	15	354	425	4.15	7.60
4	20	21	42.20	1082.91	12	335	312	15	355	409	3.5/	7.82
4	24	25	42.22	1084.43	11	214	290	11	271	391	5.45 2.70	7.75
4	24	23	42.24	1084.45	10	307	297	14	327	387	3.76	7.23
4	20	20	42.20	1084.40	8	304	280	12	336	308	3.73	8 20
4	30	31	42.20	1086 31	12	301	285	13	354	414	3.60	7.93
4	32	33	42.32	1086.34	15	324	203	13	361	420	3.72	7.84
4	34	35	42.32	1087.63	11	300	306	14	362	440	3.81	7.04
4	38	39	42.38	1087.66	10	293	299	11	342	390	3.31	7.71
4	42	43	42.42	1090.26	10	268	275	11	347	394	3.25	8.30
4	46	47	42.46	1090.29	12	357	302	11	329	386	3.26	7.73
4	50	51	42.50	1092.90	19	327	365	11	355	413	2.96	7.44
4	54	55	42.54	1092.93	8	291	269	10	341	403	3.04	8.08
4	58	59	42.58	1092.96	6	311	284	10	353	420	2.95	8.27
4	62	63	42.62	1096.85	12	320	295	10	340	392	2.85	7.86
4	66	67	42.66	1096.88				7	332	360	2.12	8.39
4	70	71	42.70	1096.91				11	396	460	2.82	9.39
4	74	75	42.74	1100.81	5	328	295	13	367	437	3.52	8.42
4	78	79	42.78	1102.12				17	386	421	4.51	8.93
4	82	83	42.82	1102.15				11	343	426	3.33	7.76
4	86	87	42.86	1104.76				15	359	421	4.09	7.89
4	90	91	42.90	1104.79	11	316	301	11	341	393	3.32	8.13
4	94	95	42.94	1107.40	12	311	296	11	348	402	3.14	7.94
4	98	99	42.98	1108.84	13	320	303	11	352	417	3.13	8.99
4	102	103	43.02	1110.89	13	315	301	10	332	395	3.05	8.11
4	106	107	43.06	1110.91	11	319	298	12	343	406	3.38	8.25
4	110	111	43.10	1114.99	14	319	297	10	308	371	3.26	8.01
4	114	115	43.14	1115.01	11	310	275	13	352	426	3.71	8.08
4	118	119	43.18	1119.10	9	304	270	12	345	405	3.34	8.65
4	122	123	43.22	1121.15	8	309	2/4	14	350	415	4.13	8.65
4	120	12/	43.20	1121.1/	/	331	296	13	545 247	409	3.8/	8./2 8.27
4	130	101	43.30	1125.20	ð 10	292	200	1.5	270	418	3.83	0.27
4	134	135	43.34	1127.31	10	311	264	14	370	438	3./4	8.39

Table C7: Mean Trace element/Ca, data from Chambers F-2 and F measured in *Globigerinoides ruber* from ODP Site 1123, at various depth intervals. Analyses in bold refer to anomalous data that was excluded from further analysis.

Core, section, interval					Gs. ruber	Gs. ruber											
Secti	(c To D	em) Bott om	Dep th	Age	Mg	/Ca	Sr/	′Ca	Al	/Ca	Mn/Ca		Zn/Ca		Ba/Ca		
011	P	0111	ţ.		Chambe r F-2	Chambe r F											
	(c	(cm)	(mb	(Ma)	(mmol/	(mmol/	(µmol/	(µmol/									
3	m) 8	9	40.5	1036.	1.40	1.85	1.45	1.28	0.30	0.05	0.05	0.06	0.02	0.02	1.45	0.90	
3	16	17	8 40.6	50 1038.	1.40	1.56	1.34	1.36	0.08	0.54	0.03	0.13	0.01	0.08	1.22	2.10	
3	16	17	6 40.6	86 1038.	2.83	2.67	1.33	1.47	1.72	0.63	0.08	0.13	0.08	0.14	30.25	3.78	
3	16	17	40.6	1038. 86	2.40	1.55	1.42	1.43	0.04	0.39	0.03	0.14	0.04	0.05	1.01	2.29	
3	20	21	40.7	1038. 90	2.73	1.65	1.33	1.44	0.07	0.00	0.29	0.10	0.23	0.01	5.65	0.60	
3	20	21	40.7	1038. 90	1.57	2.09	1.40	1.47	0.04	0.00	0.07	0.25	0.10	0.29	1.00	2.20	
3	20	21	40.7	1038. 90	3.79	1.17	1.33	1.58	0.06	0.01	0.19	0.07	0.43	0.14	4.11	1.36	
3	20	21	40.7	1038. 90	1.87	3.62	1.29	1.40	0.65	0.14	0.11	0.23	0.13	0.56	9.97	8.29	
3	20	21	40.7	1038. 90	35.24	1.40	1.55	1.43	17.82	0.06	7.65	0.06	0.50	0.14	13308.8 5	2.02	
3	20	21	40.7	1038. 90	3.38	2.67	1.33	1.43	2.59		1.02	0.41	0.35	0.37	3242.84	3.28	
3	20	21	40.7	1038. 90	3.56	1.52	1.49	1.42	5.60	0.20	0.22	0.15	0.06	0.17	760.68	0.90	
3	20	21	40.7	1038. 90	1.84	1.59	1.16	1.36	0.01		0.25	0.13	0.17	0.08	3.09	1.04	
3	24	25	40.7 4	1038. 93	1.97	1.46	1.52	1.37	0.19	0.02	0.04	0.17	0.04	0.15	1.76	1.29	
3	24	25	40.7 4	1038. 93	2.24	1.39	1.57	1.42	0.06	0.90	0.05	0.09	0.01	0.11	0.89	3.36	
3	24	25	40.7 4	1038. 93	2.27	1.73	1.44	1.48	0.13	0.03	0.05	0.06	0.08	0.06	1.63	2.41	
3	24	25	40.7 4	1038. 93	1.28	2.42	1.45	2.40	0.04	0.05	0.03	0.08	0.01	0.06	0.82	1.87	
3	24	25	40.7 4	1038. 93	3.33	3.04	1.35	2.77	6.42		0.27	0.08	0.01	0.20	10.90	1.76	
3	24	25	40.7 4	1038. 93	2.10	1.04	1.31	1.41	0.10	0.05	0.15	0.06	0.08	0.01	1.36	0.77	
3	32	33	40.8 2	1043. 58	2.83	2.30	1.34	1.37	0.14	2.74	0.28	0.30	0.02	0.06	4.00	4.46	
3	32	33	40.8 2	1043. 58	2.06	2.07	1.28	1.25	0.01	0.85	0.12	0.30	0.01	0.03	1.23	4.35	
3	14 8	149	41.9 8	1077. 22	2.85	1.97	1.44	1.45	0.10	0.20	0.17	0.17	0.01	0.01	1.32	1.31	
3	14 8	149	41.9 8	1077. 22	2.22	2.29	1.29	1.35	0.02	0.03	0.20	0.21	0.01	0.01	1.24	1.19	
3	14 8	149	41.9 8	1077. 22	3.01	1.77	1.34	1.37	0.09	0.38	0.38	0.25	0.01	0.01	1.87	1.50	
3	14 8	149	41.9 8	1077. 22	3.07	1.96	1.37	1.44	0.20	0.02	0.22	0.36	0.03	0.01	1.74	1.60	
3	14 8	149	41.9 8	1077. 22	3.06	2.39	1.43	1.39	0.16	0.06	0.24	0.42	0.01	0.02	1.73	1.57	
3	14 8	149	41.9 8	1077. 22	2.63	2.98	1.41	1.42	0.36	0.44	0.13	0.30	0.00	0.03	2.94	2.20	
3	14 8	149	41.9 8	1077. 22	2.33	2.93	1.36	1.42	0.53	1.26	0.18	0.19	0.01	0.01	1.59	0.96	
3	14 8	149	41.9 8	1077. 22	2.89	1.95	1.42	1.41	0.14	0.03	0.06	0.13	0.00	0.01	0.70	0.94	

Core,	sect	ion, in	iterval		Gs. ruber	Gs. ruber												
Secti	To	Bott	Dep th	Age	Mg	/Ca	Sr,	/Ca	Al,	/Ca	Mn	/Ca	Zn	/Ca	Ba/Ca			
011	P	OIII	tii		Chambe													
					r F-2	r F	f F-Z	r F										
	(c m)	(cm)	(mb sf)	(Ma)	(mmol/ mol)	(µmol/ mol)	(µmol/ mol)											
3	14	149	41.9	1077.	3.89	2.66	1.38	1.36	3.88	0.25	0.41	0.15	0.01	0.01	9.34	3.66		
	8		8	22														
3	14 8	149	41.9 8	1077.	1.98	2.43	1.42	1.35	0.17	0.21	0.12	0.32	0.01	0.02	1.51	1.73		
3	0 14 0	149	41.9	1077.	2.84	2.01	1.27	1.40	0.38	0.49	0.23	0.17	0.01	0.02	132.12	2.03		
3	0 14 8	149	41.9 8	1077. 22	3.00	2.68	1.27	1.40	0.37	0.67	0.12	0.28	0.01	0.04	3.99	1.67		
3	14 8	149	41.9 8	1077. 22	2.26	2.36	1.39	1.33	0.94	0.33	0.18	0.08	0.02	0.01	119.70	1.27		
3	14 8	149	41.9 8	1077. 22	2.67	2.63	1.33	1.46	0.79	1.10	0.26	0.14	0.02	0.02	2.78	2.32		
3	14 8	149	41.9 8	1077. 22	3.48	3.06	1.31	1.38	0.14	0.58	0.13	0.31	0.01	0.02	1.13	2.66		
4	4	5	42.0 4	1079. 25	2.23	2.12	1.37	1.06	0.97	0.33	0.18	0.38	0.01	0.01	1.58	0.56		
4	4	5	42.0 4	1079. 25	3.38	2.20	1.31	1.06	0.15	0.35	0.22	0.32	0.01	0.00	1.54	4.10		
4	4	5	42.0 4	1079. 25	3.13	2.35	1.30	1.10	0.26	1.11	0.17	0.29	0.01	0.02	1.23	1.28		
4	4	5	42.0 4	1079. 25	2.71	3.39	1.42	1.11	0.24	1.00	0.24	0.32	0.01	0.02	1.67	0.80		
4	4	5	42.0 4	1079. 25	3.49	2.05	1.38	1.02	0.17	0.19	0.21	0.20	0.01	0.00	1.06	2.01		
4	4	5	42.0 4	1079. 25	2.96	1.97	1.26	1.13	0.55		0.33	0.21	0.03	0.00	2.25	0.05		
4	4	5	42.0 4	1079. 25	2.98	2.31	1.41	1.04	0.56	0.44	0.17	0.45	0.01	0.02	4.84	0.87		
4	4	5	42.0 4	1079. 25	2.21	1.99	1.39	1.00	0.90		0.23	0.14	0.01	0.00	1.46			
4	4	5	42.0 4	1079. 25	2.17	1.44	1.23	1.03	0.17	0.46	0.14	0.17	0.00	0.00	1.03	0.06		
4	4	5	42.0 4	1079. 25	1.86	1.65	1.32	1.09	0.52	0.01	0.16	0.20	0.01	0.00	1.29	0.28		
4	4	5	42.0 4	1079. 25	2.78	2.61	1.37	1.11	0.06	0.30	0.19	0.23	0.02	0.01	2.53	1.26		
4	4	5	42.0 4	1079. 25	2.85	2.02	1.37	1.09	0.38		0.26	0.30	0.01	0.01	1.88	0.65		
4	4	5	42.0 4	1079. 25	3.69	3.07	1.23	1.15	4.43	0.36	0.51	0.37	0.01	0.01	3.84	1.09		
4	14	15	42.1 4	1081. 84	3.18	2.07	1.40	1.33	0.03	0.00	0.14	0.40	0.01	0.01	1.70	1.66		
4	14	15	42.1 4	1081. 84	3.24	2.79	1.22	1.37	0.41	0.10	0.26	0.31	0.02	0.01	1.91	1.88		
4	14	15	42.1 4	1081. 84	2.53	2.29	1.43	1.39	0.07	0.24	0.05	0.06	0.00	0.01	1.21	1.11		
4	14	15	42.1 4	1081. 84	2.72	1.89	1.53	1.44	0.21	0.00	0.06	0.12	0.00	0.00	0.61	0.82		
4	14	15	42.1 4	1081. 84	2.83	2.00	1.24	1.40	0.30	0.26	0.17	0.24	0.01	0.01	1.84	2.64		
4	14	15	42.1 4	1081. 84	3.24	2.25	1.39	1.47	0.29	0.06	0.23	0.17	0.01	0.01	1.37	0.81		
4	14	15	42.1 4	1081. 84	2.89	2.01	1.32	1.47	1.26	0.29	0.09	0.11	0.00	0.01	2.57	1.47		
4	14	15	42.1 4	1081. 84	2.82	1.56	1.33	1.39	0.34	0.35	0.23	0.14	0.01	0.01	1.47	2.03		
4	14	15	42.1 4	1081. 84	2.81	2.35	1.33	1.48	0.04	0.03	0.32	0.29	0.01	0.05	1.01	1.50		
4	14	15	42.1 4	1081. 84	2.36	2.55	1.42	1.47	0.07	0.08	0.21	0.36	0.01	0.01	1.88	2.13		
4	14	15	42.1 4	1081. 84	2.81	2.09	1.34	1.69	0.04	0.34	0.04	0.22	0.00	0.02	0.52	1.66		
4	14	15	42.1 4	1081. 84	3.52	1.40	1.28	1.42	0.05	0.06	0.39	0.26	0.02	0.04	1.37	1.34		

Core,	sect	ion, in	terval		Gs. ruber											
	(0	cm)														
Secti	То	Bott	Dep	Age	Mg	/Ca	Sr/Ca		Al/Ca		Mn/Ca		Zn/Ca		Ba/Ca	
on	р	om	th	_	0,											
					Chambe	Chambe	Chambe	Chambe	Chambe	Chambe	Chambe	Chambe	Chambe	Chambe	Chambe	Chambe
					r	r	r	r	r	r	r	r	r	r	r F-2	r
					F-2	F	F-2	F	F-2	F	F-2	F	F-2	F		F
	(c	(cm)	(mb	(Ma)	(mmol/	(mmol/	(mmol/	(mmol/	(mmol/	(mmol/	(mmol/	(mmol/	(mmol/	(mmol/	(µmol/	(µmol/
	m)		sf)		mol)	mol)	mol)	mol)	mol)	mol)	mol)	mol)	mol)	mol)	mol)	mol)
4	14	15	42.1	1081.	1.90	1.61	1.41	1.56	0.07	0.15	0.18	0.18	0.00	0.05	1.23	1.06
			4	84												
4	14	15	42.1	1081.	3.21	2.23	1.46	1.34	0.55	0.10	0.58	0.18	0.01	0.00	2.71	2.22
			4	84												

Table C8: Mean Trace element/Ca, data from Chambers F-2 and F measured in *Globigerina bulloides* from ODP Site 1123, at various depth intervals. Analyses in bold refer to anomalous data that was excluded from further analysis.

Core, section, interval				<i>G</i> .												
	(c	:m)			bulloides											
Secti	То	Bott	Dep	Age	Mg	/Ca	Sr/	'Ca	Al,	'Ca	Mn	/Ca	Zn/Ca		Ba/Ca	
on	р	om	th													
					Chambe	Chambe	Chambe	Chambe	Chambe	Chambe	Chambe	Chambe	Chambe	Chambe	Chambe	Chambe
					r F-2	r F	r F-2	r F	r F-2	r F	r F-2	r F	r F-2	rF	r F-2	rF
	(c	(cm)	(mb	(Ma)	(mmol/	(mmol/	(mmol/	(mmol/	(mmol/	(mmol/	(mmol/	(mmol/	(mmol/	(mmol/	(µmol/	(µmol/
	m)		st)	1000	mol)	mol)	mol)	mol)	mol)	mol)	mol)	mol)	mol)	mol)	mol)	mol)
2	00	00	39.9	1029.	1.64	1 70	1.07	1.24	0.02	0.45	0.07	0.45	0.00	0.12	5.02	10.50
2	98	99	8	39	1.64	1./2	1.37	1.34	0.03	0.15	0.07	0.15	0.08	0.13	5.03	12.59
2	00	00	39.9	20	1 17	1 42	1 2 2	1 22	0.07	0.24	0.05	0.13	0.06	0.21	1 36	0.61
2	20	22	30.0	1020	1.1/	1.45	1.52	1.2.3	0.07	0.24	0.05	0.15	0.00	0.21	4.50	9.01
2	98	99	8	39	1 4 3	1 22	1 25	1 26	0.08	0.02	0.12	0 10	0.06	0.08	8 75	10 74
4	20	,,	39.9	1029	1.45	1,22	1.25	1.20	0.00	0.02	0.12	0.10	0.00	0.00	0.75	10.74
2	98	99	8	39	1.39	1.21	1.36	1.29	0.09	0.08	0.10	0.14	0.26	0.36	7.41	12.63
			39.9	1029.												
2	98	99	8	39	2.12	1.38	1.26	1.31	0.11	0.05	0.21	0.12	0.21	0.17	6.48	5.84
	10		40.0	1029.												
2	2	103	2	43	3.38	1.73	1.49	1.47	0.62	0.03	0.27	0.15	0.19	0.10	16.69	11.69
	10		40.0	1029.												
2	2	103	2	43	2.78	1.95	1.52	1.59	0.11	0.05	0.05	0.12	0.02	0.06	8.11	7.95
_	10		40.0	1029.												
2	2	103	2	43	2.27	1.67	1.54	1.40	0.12	0.09	0.15	0.15	0.02	0.07	3.71	8.29
2	10	102	40.0	1029.	0.00	1.02	1 40	1.24	0.04	0.10	0.20	0.16	0.04	0.12	24.20	2 (1
2	2	105	40.0	4.5	2.60	1.85	1.40	1.34	0.04	0.18	0.30	0.16	0.24	0.15	24.30	3.61
2	2	103	40.0	1029.	2 03	1 58	1 30	1 58	0.27	0.04	0.21	0.13	0.08	0.05	5 47	2 75
4	10	105	40.0	1029	2.95	1.50	1.57	1.50	0.27	0.04	0.21	0.15	0.00	0.05	5.47	2.15
2	2	103	2	43	2.35	2.61	1.27	1.33	0.14	0.14	0.14	0.14	0.09	0.13	3.52	5.07
_	10		40.0	1029.												
2	2	103	2	43	1.89	1.50	1.32	1.37	0.23	0.14	0.13	0.18	0.07	0.10	4.15	5.60
			42.3	1086.												
4	32	33	2	34	1.64	1.72	1.37	1.34	0.03	0.15	0.07	0.15	0.08	0.13	5.03	12.59
			42.3	1086.												
4	32	33	2	34	1.17	1.43	1.32	1.23	0.07	0.24	0.05	0.13	0.06	0.21	4.36	9.61
			42.3	1086.												
4	32	33	2	34	1.43	1.22	1.25	1.26	0.08	0.02	0.12	0.10	0.06	0.08	8.75	10.74
4	22	22	42.5	1086.	1 20	1.01	1.20	1.20	0.00	0.00	0.10	0.1.4	0.24	0.26	7 44	12 (2
4	32	33	12.2	34 1096	1.39	1.21	1.30	1.29	0.09	0.08	0.10	0.14	0.26	0.56	/.41	12.65
4	32	33	42.5	34	2 12	1 38	1 26	1 31	0 11	0.05	0.21	0.12	0.21	0 17	6.48	5.84
4	54	55	42.3	1086	2.12	1.50	1.20	1.51	0.11	0.05	0.21	0.12	0.21	0.17	0.40	5.04
4	32	33	2	34	3.38	1.73	1.49	1.47	0.62	0.03	0.27	0.15	0.19	0.10	16.69	11.69
		~~	42.3	1086.							····					
4	32	33	2	34	2.78	1.95	1.52	1.59	0.11	0.05	0.05	0.12	0.02	0.06	8.11	7.95
			42.3	1086.												
4	32	33	2	34	2.27	1.67	1.54	1.40	0.12	0.09	0.15	0.15	0.02	0.07	3.71	8.29

Core, section, interval					G.											
(cm)				bulloides												
Secti	То	Bott	Dep	Age	Mg	/Ca	Sr/Ca		Al/Ca		Mn/Ca		Zn	/Ca	Ba/Ca	
on	р	om	th													
					Chambe											
					r F-2	r F										
	(c	(cm)	(mb	(Ma)	(mmol/	(µmol/	(µmol/									
	m)		sf)		mol)											
			42.3	1086.												
4	32	33	2	34	2.60	1.83	1.40	1.34	0.04	0.18	0.30	0.16	0.24	0.13	24.30	3.61
			42.3	1086.												
4	32	33	2	34	2.93	1.58	1.39	1.58	0.27	0.04	0.21	0.13	0.08	0.05	5.47	2.75
			42.3	1086.												
4	32	33	2	34	2.35	2.61	1.27	1.33	0.14	0.14	0.14	0.14	0.09	0.13	3.52	5.07
			42.3	1086.												
4	32	33	2	34	1.89	1.50	1.32	1.37	0.23	0.14	0.13	0.18	0.07	0.10	4.15	5.60

Appendix C

DVD Contents

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- 01 Gs. ruber LA-ICP-MS depth profiles
- 02 Gs. ruber photographs
- 03 Gs. ruber SEM images
- 04 Gs. ruber Analysis Summary
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