THE DEVELOPMENT AND APPLICATION OF NUTRIENT AND CARBONATE SYSTEM PROXIES IN

THE DEEP SEA CORAL Desmophyllum dianthus

by

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ABSTRACT OF THE DISSERTATION

The development and application of nutrient and carbonate system proxies in the deep sea coral Desmophyllum dianthus

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Deep sea corals are a promising paleoceanographic archive because they offer the potential for high temporal resolution and precise absolute dating. This thesis presents the first rigorous development and calibration of geochemical proxies for phosphate, barium, carbonate ion, and pH, recorded as phosphorus to calcium (P/Ca), barium to calcium (Ba/Ca), uranium to calcium (U/Ca) ratios and boron isotopes ($\delta^{11}$B), respectively, in the skeleton of the deep sea coral Desmophyllum dianthus (D. dianthus).

The $\delta^{11}$B proxy was applied for the first time to a modern coral located within the deep mixed layer of the South Chatham Rise (New Zealand), showing a change in ocean pH as a result of anthropogenic CO$_2$ emissions, in approximate agreement with atmospheric and surface ocean CO$_2$ measurements from this region.
The P/Ca, Ba/Ca, and U/Ca proxies were applied to corals dated to 15.4ka and Heinrich 1 (~16.5ka) to reconstruct the history of phosphate, barium, and carbonate ion concentrations at intermediate depths in the northwest Atlantic. The results demonstrate that dissolved phosphate increased and carbonate ion decreased during cold periods, previously characterized by reduced deep water convection and increased meltwater input. This suggests the presence of a nutrient rich and corrosive intermediate southern source water mass (SSW) at 40°N in west Atlantic, in agreement with previous radiocarbon reconstructions. Coral Ba measurements suggest a contemporaneous increase in the North Atlantic dissolved Ba inventory compared to Holocene. Calculations of the mixing ratio between northern and SSW following the 15.4ka event suggest that SSW was the dominant water mass in northwest Atlantic. The 15ka event occurred within ~100y, the life span of the coral.

The initial success of these new geochemical tools is encouraging for the utility of *D. dianthus* as a geochemical paleoceanographic archive. With further development, these proxies could be used to reconstruct aspects of water mass mixing and biogeochemical processes in intermediate-to-deep waters of the Atlantic and Southern Oceans, locations where *D. dianthus* is most abundant.
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CHAPTER 1

THESIS INTRODUCTION
Marine carbonates are among the most successful substrates for chemical paleoceanographic studies. Isotopes and elements substitute into the biogenic carbonate lattice in relation to the chemical and physical properties of the water in which carbonate precipitating organisms live. Therefore, elemental and isotopic calibrations in marine carbonates can be used to reconstruct ocean chemistry and feedbacks within the global climate. Deep sea corals are located at depths that allow the study of variability of intermediate to deep ocean, which is especially important to global climate as the primary store and transporter of heat and CO₂ in the climate system. There is great incentive, therefore, to develop new proxies that could provide high resolution information related to water mass mixing ratios and the biogeochemical processes of nutrient distribution and CO₂ flux to the intermediate and deep ocean.

Desmophyllum dianthus (*D. dianthus*) is an aragonitic scleractinian, azooxanthellate, solitary deep sea coral. It is cosmopolitan in geographic distribution, with a wide depth range of 35-2500m (Cairns, 1994) and thermal tolerance -1°C to 28°C (Stanley and Cairns, 1988). The life span of *D. dianthus* is ~100y and it grows on average 0.5-2 mm/y (Adkins et al., 2004). The relatively large size of these corals provides enough aragonite to allow the study of several geochemical proxies for revealing various aspects of paleoclimate on a single specimen, offering the rare luxury of parallel complementary paleoceanographic records from a single archive. An alternative archive of deep sea paleo reconstructions, benthic foraminifera, does not offer simultaneous measurements and precise dating because of size and often low abundance in marine sediments. Deep sea corals, therefore, offer the potential of subdecadal resolution of century long records of
deep sea variability, and are thus especially suited to test theories of climate change across abrupt transitions including Heinrich 1 (H1, 16.5 ka) and 15.4 ka events during the last deglaciation. When several individual coral reconstructions are combined, continuous records of climate variability is feasible.

Most research on deep sea scleractinia to date has focused on measurements of Uranium-series nuclides (U/Th) (Cheng et al., 2000; Edwards et al., 2003; Goldstein et al., 2001; Schröder-Ritzrau et al., 2003) and radiocarbon dating (Adkins et al., 2002; Adkins et al., 2004; Frank et al., 2004; Mangini et al., 1998; Robinson et al., 2005). Hence, deep sea corals offer properties unmatched by other deep ocean archives since they can be used to reveal rapid changes in the radiocarbon age of deep ocean water masses (Adkins et al., 1998).

The deep-sea coral *D. dianthus* also has the potential to provide temperature, nutrient, and carbonate system proxies. Coupled with radiocarbon measurements, these proxies will be a useful tool to reconstruct abrupt changes in past circulation rates, and to estimate the chemical/physical properties of water masses. Temperature reconstructions with oxygen isotopes (δ¹⁸O) (Adkins et al., 2003; Emiliani et al., 1978; Lutringer et al., 2005; McConnaughey, 1989; Rollion-Bard et al., 2003; Smith et al., 2002; Smith et al., 2000) are however very complicated due to various disequilibria effects on microstructures of the coral aragonite. The potential of strontium to calcium (Sr/Ca) and magnesium to calcium (Mg/Ca) paleothermometry has been investigated (Cohen et al., 2006; Gagnon et al., 2007; Shirai et al., 2005), but a direct temperature relationship is
complicated by the effects of physiological biomineralization processes. Attempts on developing and assessing nutrient/carbonate system proxies in deep sea scleractinian corals are limited to a phosphorus to calcium (P/Ca) proxy (Montagna et al., 2006), a cadmium to calcium proxy (Cd/Ca) (Adkins et al., 1998; Eltgroth, 2006), and estimates of variations of boron isotopes ($\delta^{11}$B) (Blamart et al., 2007; Rollion-Bard et al.) and barium to calcium ratios (Ba/Ca)(Hart and Cohen, 1996).

Here, high-resolution multi-element measurements are obtained in modern and fossil $D. dianthus$ corals developing a method using laser ablation inductively coupled plasma mass spectrometry (LA ICP-MS), with the goal of precisely measuring P/Ca, Ba/Ca and uranium to calcium (U/Ca) ratios. The Chapter 2 describes this ArF excimer and solid state 193nm LA ICP-MS method development, including discussion of operating conditions and precision, accuracy, and time resolution limits obtainable during LA ICP-MS analyses of $D. dianthus$ sections.

This method was applied to globally distributed $D. dianthus$ with the goal to demonstrate the veracity and utility of nutrient and carbonate ion proxies. Mean element/Ca ratios were obtained for ablation lines along the growth axis of septa sections integrating several decades of growth. The means of each sample were regressed against hydrographic data from nearby locations. The results, as described in Chapter 3, support three new proxy calibrations in the deep-sea coral $D. dianthus$: 1) a revised P/Ca proxy calibration for reconstructing seawater phosphate, 2) a Ba/Ca proxy for tracing variations in the silicate-type element Ba, and 3) a U/Ca proxy for carbonate ion concentration.
This Chapter has been published in Geochimica Cosmochimica Acta (Anagnostou et al., 2011) and constitutes completion of the first steps required to greatly expand the potential utility of *D. dianthus* as a geochemical paleoceanographic archive.

The Chapter 4 explores the first calibration of the $\delta^{11}$B proxy against ambient pH in deep sea corals, specifically in globally distributed modern *D. dianthus* coral specimens. The $\delta^{11}$B proxy in biogenic carbonates has been explored and described in extensive detail (Hemming and Hanson, 1992; Hönisch and Hemming, 2005; Sanyal et al., 1996; Spivack et al., 1993; Zeebe et al., 2001) but has not yet been applied to deep sea corals. Boron is believed to be incorporated into biogenic and inorganic carbonates largely as the borate species (Hemming and Hanson, 1992), and such preferential incorporation results in the $\delta^{11}$B of marine carbonates tracking the $\delta^{11}$B of seawater borate ion and thus being sensitive to pH variations, typically giving a $\sim$1‰ increase in $\delta^{11}$B for every 0.1 unit increase in seawater pH.

Boron isotope measurements in foraminiferal calcite and tropical coral aragonite have been used as a proxy of surface oceanic pH (Hönisch and Hemming, 2005; Hönisch et al., 2009; Palmer and Pearson, 2003; Pelejero et al., 2005; Sanyal and Bijma, 1999). However, low benthic foraminifera abundance has been an obstacle to studies of the evolution of intermediate to deep ocean pH using this proxy (Hönisch et al., 2008; Sanyal et al., 1995; Yu et al., 2010). The *D. dianthus* pH proxy could provide a powerful alternative that could complement intermediate to deep water pH reconstructions. To test the *D. dianthus* $\delta^{11}$B-pH calibration, it was further applied to a coral collected alive on
the South Chatham Rise (NZ). The measured $\delta^{11}$B decrease over the century long lifespan of this coral is viewed within the context of anthropogenic CO$_2$ emissions, and provides the first evidence of 20$^{th}$ century subsurface acidification from deep sea coral reconstructions.

Chapter 5 explores the application of the P/Ca, Ba/Ca, and U/Ca proxies in fossil $D. dianthus$ corals from the Northwest Atlantic during the 15.4 ky event, a century long transition of intermediate to deep water mass geometry, studies of which require the high resolution and precise dating that deep sea corals offer (Adkins et al., 1998; Robinson et al., 2005). This extremely abrupt event, that is often considered part of the H1 event (Thornalley et al., 2011), was characterized by significantly reduced intermediate water mass ventilation (Adkins et al., 1998; Robinson et al., 2005).

Similar events are observed throughout deglacial periods in the North Atlantic (Sarnthein, 2011) with the formation of a shallower Glacial North Atlantic Intermediate Water (GNAIW) instead of NADW, resulting from changes in the northward flux of heat through the return surface warm waters. Additionally, changes in the input of freshwater may have triggered changes in deep water convection for example the Younger Dryas (YD) and H1 events (Broecker et al., 1989; Marchitto et al., 1998). Additionally, several pieces of evidence support increased influence of Antarctic Intermediate Water (AAIW) to the North Atlantic during periods of weak Atlantic overturning circulation during the last deglaciation (e.g. Boyle and Keigwin, 1987; Curry and Oppo, 2005; Pahnke et al., 2008; Rickaby and Elderfield, 2005). Such events require shoaling of convection and
intrusion of a radiocarbon depleted and nutrient rich southern source water mass, possibly linked to enhance vertical mixing of the Southern Ocean Polar Front zone (Anderson et al., 2009; Sigman et al., 2007; Skinner et al., 2010).

The P/Ca, U/Ca, and Ba/Ca in *D. dianthus* provide an independent way to test changes in circulation at precisely dated times in the past, and infer end member properties, assuming no production or consumption of nutrients and carbonate ion along the flow path of each water mass. To achieve this 15.4ky old fossil solitary deep sea corals *Desmophyllum dianthus* (*D. dianthus*) were analyzed and compared to corals dated within the preceding Heinrich 1 event. Here, therefore, the first paleoreconstructions based on established coral P/Ca, U/Ca, and Ba/Ca proxies are presented, suggesting changes in water mass chemistry of the northwest Atlantic which are in agreement with records from sedimentary and foraminifera records. This thesis also suggests potential inventory changes in Ba concentrations of the North Atlantic as a result of freshwater discharges. Finally it provides estimates of changes in rate of transport of southern origin intermediate water masses during the 15.4 ky event which are in agreement with previously reported radiocarbon measurements, encouraging the utility of *D. dianthus* as a geochemical paleoceanographic archive.

**References**


CHAPTER 2

LASER ABLATION INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY:

DEVELOPMENT OF A METHOD FOR ELEMENTAL RATIO ANALYSIS OF DEEP SEA CORAL SKELETON

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M. PAUL FIELD

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2.1. Introduction

Deep sea corals hold great potential as recorders of intermediate to deep oceanic variability, thus recently there has been an effort to develop novel methods for deep sea coral skeleton elemental and isotopic analysis (Adkins et al., 1998; Blamart et al., 2007; Gagnon et al., 2007; Montagna et al., 2006; Sinclair et al., 2006; van der Flierdt et al., 2006). Here a laser ablation (LA) Inductively Coupled Plasma Mass Spectrometry (ICP-MS) method was explored, which can be used to measure multiple elements in a single sample. This technique allows sampling at the micron scale, and is extremely powerful for exploring novel paleo-proxies. So far this method provides sub-annual resolution records in the skeleton of the deep sea coral *Desmophyllum dianthus* (*D. dianthus*), although higher resolution data are possible at compromised reproducibility by sample heterogeneity.

2.2. Coral Sampling

Samples were obtained from the National Museum of Natural History (Smithsonian Institution, Washington, D.C.), the National Institute for Water and Atmosphere (NIWA, Greta Point, Wellington, NZ), and Dr. Jess Adkins (Caltech). The corals were treated with the ultrasonic-cleaning protocol of Cheng et al. (2000), and then septa were removed, cut longitudinally, mounted in epoxy and prepared as polished thick sections (300µm) to ~1µm roughness ensuring a flat surface for maintaining laser focus and signal stability. The thick sections were subsequently rinsed with isopropyl alcohol.
(99.9% purity) in an ultrasonic bath for several seconds and dried. The sections were oriented along the growth axis, to enable sampling of the fibrous (acicular) aragonite portion of the septa, while visualizing the central band, septal exterior, and bioeroded features, all within the ~1mm width of a typical septum. The sampling strategy was to ablate lines along the growth axis of the corals, either integrating several years of growth to obtain mean elemental composition for the specimen, or interpreting the finer resolution records for time series analyses.

2.3. Sample Set-up

Samples and standards were mounted on a micrometer X-Y sample stage (52x52 mm travel; 0.25μm resolution). A CCD video camera enables direct viewing of the sample during ablation, and image capturing when the laser is not firing. Samples were line scanned at 15-25 μm/s beneath the laser. Ablation occurred in a sealed sample chamber under a helium (He) atmosphere (Eggins et al., 1998; Günther and Heinrich, 1999), increasing sensitivity by minimizing aerosol losses and enhancing sample transfer. The ablated material was then entrained in an argon (Ar) gas stream for transport into the ICP-MS (Figure 2.1). Argon flow was ~600 μL min⁻¹, and helium flow ~ 400 μL min⁻¹.

2.4. Instrumentation

2.4.1. Description of lasers

The samples were ablated using both a 193 nm ArF excimer laser (UP193HE, New Wave Research Fremont, CA) and a 193 nm solid state laser (UP193SS, New Wave Research
Fremont, CA). Pulse length is nominally around 20 ± 5 ns (Excimer) and <3 ns (solid state), and the drill-rate for both is approximately 0.1 µm per pulse when drilling into NIST 612 glass. The final energy density on the sample for a 100 µm laser spot size was approximately 4-7 J/cm² at 10-15 Hz shot frequency.

One of the significant advantages of the ArF excimer over solid state laser systems is that the output beam is large, 4 mm x 15 mm, with a relatively uniform energy density. The beam can therefore be masked to produce final beam shapes that are not limited to circular spots. On the contrary, the beam size of solid state lasers is smaller (round, <5 mm) masked for the flat portion of Gaussian energy distribution profile. As a result, ablation with solid state lasers increase the risk of a non-smooth crater floor, cracks

Figure 2.1. The laser ablation system (modified from Russo et al. 2002).
surrounding the crater rim, and particle spattering. For 193nm solid state lasers (Nd-YAG), though, even when beam homogenization is not implemented, the structure of crater is comparable to the excimer lasers, suggesting that wavelength has larger influence on ablation behavior than beam energy structure (Horn et al., 2003). Therefore both lasers used in this study are expected to ablate with comparable quality.

2.4.2. ICP-MS

<table>
<thead>
<tr>
<th>Table 2.1. ICP-MS Acquisition parameters</th>
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<tbody>
<tr>
<td>Isotope</td>
</tr>
<tr>
<td>11B</td>
</tr>
<tr>
<td>25Mg</td>
</tr>
<tr>
<td>31P</td>
</tr>
<tr>
<td>43Ca</td>
</tr>
<tr>
<td>55Mn</td>
</tr>
<tr>
<td>56Fe</td>
</tr>
<tr>
<td>138Ba</td>
</tr>
<tr>
<td>238U</td>
</tr>
</tbody>
</table>

Resolution m/Δm: 4000
Mass window: 40%
Search window: 10%
Integration window: 15%
Samples per peak: 40
Scan type: E-scan
Total duty cycle: 73%

Analyses were carried out using Element XR sector field inductively coupled plasma mass spectrometer (SF-ICP-MS) (ThermoFinnigan, Bremen, Germany) using a combination of magnet jumps and electrostatic peak scanning (E-scan). Elements were selected to monitor crust and oxide materials, centers of calcification, and desirable
proxies on deep sea corals (Chapter 3). All elements (Table 2.1) were analyzed in medium resolution (MR = 4000M/ΔM) to eliminate resolution switching and obtain interference free phosphorus (e.g. NO and NOH) and iron (e.g. ArO and CaO).

### 2.5. Operating Parameters

#### 2.5.1. Laser-ICP-MS

**2.5.1.1. Ablation process**

The ablation process could be summarized as follows: First, the laser encounters the solid and then is absorbed by the electrons within the solid sample. Within picoseconds, the excited electrons and atoms equilibrate within the solid which leads to heating. Then, the material from the heated volume is ejected from the solid continuing to absorb energy from the laser. At this stage, a thin layer of 10-100 μm thickness of ionized vapor is formed on the surface of the sample. Following the laser pulse termination, the plume expands adiabatically as if it is occurring in vacuum but after several μs the expansion is determined by the interaction of the plume atoms with the atoms and molecules of the background gas (Schou et al., 2007). Expansion results in cooling and condensation of the plume into aerosol that is transported to the ICP.

**2.5.1.2. Tuning**

The tuning of the ICP-MS for laser analyses differs significantly from the settings for solution analyses, mostly due to the analyte ion distribution characteristics in a dry plasma compared to wet plasma (Hasegawa et al., 1992) (Table 2.2, Table 2.3). Additionally, under dry sample aerosol, all solvent-based interferences (e.g. oxides) are
removed, reducing background for several isotopes of interest. Sensitivities for the laser typically range from 1-2.5 \times 10^6 \text{cps} for both $^{139}$La and $^{232}$Th in NIST 612 glass standard (~40 ppm La and Th) using 100 $\mu$m diameter laser spot ablating at a rate of 10-15 Hz.

Considering that the laser under these conditions ablates ~0.06-0.09g material per second (see below), the yield is equivalent to 1-2.5 million counts per ~3.6 \times 10^{-6} \mu g La (0.03 \times 10^{-6} \mu mol La) using laser ablation. This is comparable to the sensitivity obtained for solution analysis (typically 1 \times 10^6 \text{cps per} 1 \mu g/kg In using ~100\muL min^{-1} nebulizer flow rates results in 1.6 \times 10^{-6} \mu g $^{115}$In or 0.02 \times 10^{-6} \mu mol In).

<table>
<thead>
<tr>
<th>Table 2.2. Tuning parameters for LA-ICP-MS</th>
</tr>
</thead>
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<tr>
<td>TORCH POSITION (mm)</td>
</tr>
<tr>
<td>X-POSITION</td>
</tr>
<tr>
<td>Y-POSITION</td>
</tr>
<tr>
<td>Z-POSITION</td>
</tr>
<tr>
<td>GAS FLOWS (L min^{-1})</td>
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<td>COOL</td>
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<td>AUX</td>
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<td>SAMPLE</td>
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<tr>
<td>Y-DEFLECTION</td>
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<tr>
<td>SHAPE</td>
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<tr>
<td>GUARD ELECTRODE</td>
</tr>
<tr>
<td>OTHER (V)</td>
</tr>
<tr>
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</tr>
<tr>
<td>ROTATION QUAD2</td>
</tr>
<tr>
<td>FOCUS QUAD1</td>
</tr>
<tr>
<td>FOCUS QUAD2</td>
</tr>
<tr>
<td>SENSITIVITY (x10^6 cps)</td>
</tr>
<tr>
<td>La</td>
</tr>
<tr>
<td>Th</td>
</tr>
<tr>
<td>ThO/Th (%)</td>
</tr>
</tbody>
</table>
2.5.1.3. Internal standard

Deep sea corals skeletons have denser structures than do surface corals (Sinclair et al., 1998). However small variations on the scale of 10% of $^{43}$Ca in coral sample signal are typical and are associated with variation in the ablation yield. Possible causes may be a: pulsed nature of the laser, b: coral structural variability, and c: uneven surface of the coral analyzed. These variations can largely be removed by normalizing the signal to a major element of constant concentration in aragonite, Ca. This element plays the role of an internal standard correcting not only for variations in ablation yield and sample density but also for instrumental drift (Craig et al., 2000; Hathorne et al., 2003; Longerich et al., 1996b). The $^{43}$Ca was chosen because it is traditionally used in laser ablation since it is measurable in both NIST 612 standard and coral samples by ICP-MS, and it does not have the isobaric interference of $^{48}$Ti on $^{48}$Ca, an element abundant in NIST standards. During routine analyses, $^{43}$Ca count rates are around 20 x 10$^6$ cps.

2.5.1.4. Elemental fractionation

Fractionation is defined as the non stoichiometric ablation (Fryer et al., 1995), resulting in element ratios in aerosol exiting the ablation chamber that do not match element ratios in the sample solid. In theory, standards that are perfectly matrix-matched both in bulk composition and physical structure should be able to correct for it. Such standards are rare in laser ablation, therefore it is necessary to ensure that ablation produces stoichiometric vapor (Russo et al., 2000). A measure of fractionation is the fractionation index, which is defined as the change in elemental ratio with time as a crater is developed.
at a single sample location using a pulsed laser. The laser is fired continuously for 4 min, the time signal is normalized to the Ca signal, and the second half of the time signal is divided by the first half (Fryer et al., 1995). Fractionation index >1 implies enrichment in a specific element with depth of ablation.

Considering the various parameters related to differences in the set-up and operation of a LA ICP-MS (wavelength, pulse length, beam homogenization, optics, fluence/irradiance, spot size, material analyzed, forward power, tuning, cones, introduction systems, and others), it is difficult to directly compare individual fractionation results from different systems and thus derive general conclusions on which are the most important factors controlling fractionation in laser ablation (Günther and Hattendorf, 2001). The selected laser parameters result in minimized fractionation for P/Ca, U/Ca, and Ba/Ca elemental ratios based on findings in the literature and this work.
The size of aerosol particles entering the plasma is considered the key candidate for fractionation effects in laser ablation, because of variable degrees of vaporization and ionization within the ICP as a function of particle size (Guillong and Gónther, 2002).

The size of particles that can be transported into the ICP has been calculated to be 2 nm to 5 μm in diameter (Arrowsmith and Hughes, 1988). Of this size range only <150 nm size particles are completely ionized in the plasma (Kuhn et al., 2004). The production of larger particles is potentially due to imperfect coupling of the laser beam with different materials (Figure 2.2), and this is related to laser wavelength. For example, fractionation is agreed to be insignificant for 193 nm excimer lasers compared to Nd/YAG lasers of higher wavelength, but it is still unclear if this advantage is related to higher photon

<table>
<thead>
<tr>
<th>Laser 193nm</th>
<th>Material</th>
<th>Spot (μm)</th>
<th>Hz</th>
<th>Fluence (J/cm²)</th>
<th>B/Ca</th>
<th>Mg/Ca</th>
<th>P/Ca</th>
<th>Ba/Ca</th>
<th>U/Ca</th>
</tr>
</thead>
<tbody>
<tr>
<td>Excimer</td>
<td>NIST612</td>
<td>100</td>
<td>15</td>
<td>7</td>
<td>1.08</td>
<td>1.08</td>
<td>1.09</td>
<td>0.96</td>
<td>0.92</td>
</tr>
<tr>
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<td>6</td>
<td>1.00</td>
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<td>0.98</td>
<td>0.99</td>
</tr>
<tr>
<td>SS</td>
<td>coral pellet 1</td>
<td>100</td>
<td>10</td>
<td>5</td>
<td>1.02</td>
<td>1.00</td>
<td>1.06</td>
<td>0.96</td>
<td>0.97</td>
</tr>
<tr>
<td>SS</td>
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<td>10</td>
<td>6</td>
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<td>1.01</td>
<td>1.03</td>
<td>1.00</td>
<td>0.97</td>
</tr>
<tr>
<td>SS</td>
<td>MACS3</td>
<td>100</td>
<td>15</td>
<td>7</td>
<td>1.01</td>
<td>0.98</td>
<td>1.07</td>
<td>0.92</td>
<td>1.03</td>
</tr>
<tr>
<td>AVERAGE</td>
<td>SS NIST612</td>
<td>100-120</td>
<td>10</td>
<td>5-6</td>
<td>1.01 ± 0.04</td>
<td>1.08 ± 0.17</td>
<td>1.07 ± 0.05</td>
<td>0.98 ± 0.01</td>
<td>0.98 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>SS coral</td>
<td>100-120</td>
<td>10</td>
<td>5-6</td>
<td>1.00 ± 0.06</td>
<td>1.23 ± 0.19</td>
<td>1.26 ± 0.08</td>
<td>1.04 ± 0.05</td>
<td>1.02 ± 0.03</td>
</tr>
<tr>
<td></td>
<td>Excimer NIST612</td>
<td>100</td>
<td>15</td>
<td>7</td>
<td>1.08</td>
<td>1.08</td>
<td>1.09</td>
<td>0.96</td>
<td>0.92</td>
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<tr>
<td></td>
<td>Excimer coral</td>
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<td>0.98</td>
<td>1.07</td>
<td>0.92</td>
<td>1.03</td>
</tr>
</tbody>
</table>
energy or differences in beam homogenization and focusing conditions. Nevertheless, shorter wavelengths offer higher photon energies for bond breaking and ionization (Russo et al., 2000). Therefore a 266 nm laser couples less completely with carbonate material compared to a 193nm laser (Figure 2.2) producing a larger quantity of micron size particles formed by photomechanical fracturing along lines of cleavage or weakness, which are less completely vaporized within the ICP than smaller particles (Guillong et al., 2003). Both 193nm and 213 nm lasers were, however, suggested to cause negligible chemical fractionation of carbonates during the ablation process and transport to the plasma (Hathorne et al., 2008). The use of 193nm lasers in this study ensures minimal fractionation effects due to the wavelength selection.

Fractionation is also a function laser irradiance and pulse length (Russo et al. 2002 and references therein). To simplify, longer pulse length and lower irradiance can lead to laser energy loss through thermal dissipation. When irradiance of > 0.2 GW/cm$^2$ is used however, fractionation is minimal (Liu et al., 2000). For this study, irradiance was always $\geq 0.5$ GW/cm$^2$ ensuring minimal fractionation associated with thermal dissipation.

Another cause of large particles in the plasma is molten material that gives rise to hydrodynamic sputtering, producing micron sized, and smooth rounded particles. Additionally, vapor pressure, atomic/ionic radius, charge, and speciation could potentially all have an effect to non stoichiometric ablation (Russo et al., 2002). In an effort to group elements according to their fractionation behavior, Fryer et al.(1995) and Longerich et al. (1996a) observed that elements behave similarly not clearly based on
their ionization potential, electronegativity or other atomic properties, but most likely related to how they distribute themselves among different phases (for example chalcophile, lithophile, and siderophile grouping). Therefore, fractionation effects and calcium carbonate versus silicate matrix effects will be corrected if elements within the lithophile group, which contains Ca, U and Ba (Longerich et al. 1996), are normalized to Ca as an internal standard.

Figure 2.2. Calcite absorbance spectrum (1 cm thickness) showing increase in energy absorption as wavelength decreases (Jeffries et al., 1998).

Additionally, the crater geometry could affect fractionation. For example, Eggins et al. (1998) observed that repetitive static ablation on NIST glass standards resulted in craters that changed from flat-bottom to cone-shape. Fractionation during this drilling experiment was described as laser plume enrichment in more volatile elements at shallower crater depths evolving to enrichment in refractory elements at greater depths, with an observed condensation of mostly refractory elements from the expanding plasma.
The exact mechanism that describes crater-related fractionation is not established yet. One hypothesis is that irradiance decreases as the crater deepens due to changes in the effective area exposed to the laser beam (Liu et al., 2000), and therefore thermal effects dominating low irradiance could cause larger fractionation as ablation progresses and the pit deepens. Alternatively, the potential presence of a plasma confined within a deep crater could lead to fractionation too (Eggins et al., 1998). As a rule, the aspect ratio of ablation (depth to diameter ratio of the ablation crater) should not exceed six to minimize crater related fractionation phenomena during ablation. In this study, aspect ratio was less than one.

Previous measurements (LaVigne, 2010) have demonstrated that there is an optimal range in fluence (J/cm²) within which elemental ratios of static drill experiments are reproducible in NIST 612 standard and coral samples are reproducible for both low and high mass elements (Figure 2.3). The fluence threshold above which such stability is observed is ~4 J/cm², and it could potentially be related to a mass load effect (described below) but also to an energy limit for optimal coupling of the laser beam with the solid sample. All analyses were therefore performed at fluence of ≥4 J/cm² using either excimer or solid state 193nm lasers.
Figure 2.3. El/Ca ratios (normalized to mean ratio for fluence 4-12 J/cm²) for a 200 μm spot ablated in NIST 612 standard reference material (A) and coral (B) with varying fluence (from LaVigne 2010).

The fractionation factors generated by the selected laser systems were quantified, keeping conditions as similar as possible, but also quantifying matrix-specific fractionation
factors which are missing in the literature comparing the USGS carbonate standard MACS3 to the glass standard NIST 612 and in-lab pressed powder coral pellets (Figure 2.4, Table 2.4).

Figure 2.4. A 4min drilling experiment in carbonate MACS3 (top) and glass NIST 612 (bottom) standards (solid state laser, 120μm spot, 10Hz).
It was observed that for the elements of interest when aspect ratio (ratio of depth to diameter of ablation crater) exceeds 1 the signal becomes noisier for both MACS3 and NIST 612 standards with variation starting from 10% and reaching ~30% around the mean (2SD). Additionally, there is a ~25% upward drift in the P/Ca signal for both MACS3 and NIST 612 over the total crater depth. Therefore all laser ablation analyses were performed so that the ablation depth was less than the crater diameter. A comparison of the fractionation factors is compromised by sample heterogeneity as indicated by the standard deviation of replicate analyses (Table 2.4). Nevertheless, it is observed that both excimer and solid state 193nm lasers provide comparable fractionation factors for Ba and U in both carbonates and NIST 612 glass standards, while the excimer appears to have smaller fractionation effects for P compared to the solid state laser (Table 2.4).

2.5.1.5. Ablation cell design

The ablation cell design could be important for allowing analyses where high resolution data acquisition is required. For example, the HEAD cell (Lindner et al., 2010; Pisonero et al., 2006) creates a Venturi effect in the extracted sample aerosol during ablation, assisting in generation of smaller size particles necessary for complete vaporization within the ICP and increased signal stability. The two-volume laser ablation cell (Eggins et al., 2005; Müller et al., 2009) accommodates large samples while isolating ablation and its formed aerosol plume into a small funnel shaped sub-cell for rapid washout (<3s), reduction in cross-contamination, high and uniform sensitivity irrespective of position in cell, and smooth signals. In this study, the standard quick change sample cell holder by
NewWave (52mm ID X 52mm deep) was considered sufficient for the obtained data resolution and washout time. Another concern related to the cell design is preferential condensate build up enriched in certain isotopes (e.g. heavier masses) compared to lighter isotopes (e.g. boron) resulting in a variable wash out, and fractionation of one isotope relative to another (Eggins et al. 1998). Such an effect would be reduced if helium gas flow and distribution within the cell permits efficient and rapid washout.

To investigate preferential element loss or enrichment in the ablation cell two experiments were performed; in one four NIST 612 standard pellets were analyzed, two that were previously analyzed and another two that were new, after being placed within the central channel of the stage (Figure 2.5). Analyses occurred by ablating two 2mm lines at a 90° angle on each pellet moving from one pellet to the next in a continuous manner. The total ablation line acquired was therefore 16mm long and represents angled lines of four pellets. The El/Ca ratios obtained for each one of the pellets are within <2% after one preablation line suggesting minimal fractionation due to cell design when samples are placed in the central grove of the cell holder. In the other experiment, the same pellets were placed on a parafilm coated modeling clay extending 1cm below the top edge of the stage. The pellets were not positioned perfectly horizontally since they followed the curvature of the patty (Figure 2.6). The ablation pattern was similar to the previous experiment, but the length of the lines was ~1.5 mm instead of 2 mm. Therefore in this case the total ablation line was ~12.5 mm long. The resultant Ba/Ca, and U/Ca measurements are encouraging since they agree for all pellets within ≤ 2% after one preablation line, however P/Ca reproducibility is ≤ 4%, double that resulting from
ablating within the central groove of the laser cell. Therefore, although gas flow might be imperfectly homogeneous around the ablation cell, its effect on Ba/Ca, U/Ca, and P/Ca fractionation is minimal. Nevertheless, to obtain El/Ca ratios with the highest reproducibility possible, all analyses were performed by placing samples and standards within the central groove of the laser cell holder.
Figure 2.5. Effect of sample position within cell on determined El/Ca ratios. Four different NIST 612 standards placed within the central groove of the laser cell (inset drawing) and 4mm angle lines, 2mm each, are ablated on each pellet (solid state laser, 10Hz, 4mm lines, 100 μm spot size, 4 point moving average). The total ablation line was 16mm.
Figure 2.6. Ablation of four different NIST 612 standards placed within the cell holder on a custom-made patty (solid state, 10Hz, ~3mm lines, 100 μm spot size, 4 point moving average). Data acquired from each pellet are marked as 1-4 based on the inset picture. The sum of all ablation lines was ~12.5mm.
2.5.1.6. Preablations

Surface contamination, which in the case of the *D. dianthus* sections probably originated from sample sectioning and polishing, was removed with preablation laser passes (Sinclair et al., 1998). Such contamination was expected to be restricted to the upper few microns since deep sea coral aragonite is dense and generally free of voids ($^{43}$Ca shows ~10% signal intensity variation along an ablation line). Therefore preablation passes were performed until averaged elemental ratios were reproducible among successive ablations of the same line (typically better than +/-10%, see also Table 3-A1). Typically it was found that one ablation of ~6µm depth was sufficient to remove surface contamination in coral thick sections, identified as a laser pass in which resultant data did not satisfy the reproducibility requirements stated above. Ablation depth is estimated using a value of 1µm per 10 shots, similar to other laser systems (Günther et al., 2000; Hathorne et al., 2003).

2.5.1.7. Standardization

The analyses of the standard are handled in a similar manner to the coral analyses. No drift was observed showing a precision through the run similar to consecutive ablations of the standard without interspersed coral analyses. Each calcium normalized data point is therefore divided by an average standard elemental ratio for the run, and multiplied by the known TE/Ca ratio of the standard as explained below.

The NIST 612 standard is considered homogeneous for Ba, Ca, P and U (Eggins and Shelley, 2002), as observed in this study for 2 mm ablation lines (Figure 2.7, 2.8),
therefore published elemental concentrations were used (Ba: 39.7 ±0.4 ppm and certified U: 37.4 ±0.08 ppm; (Jochum et al., 2005; Reed, 1992), Ca: 84690ppm; (Eggins, 2003), P: 39.9ppm; (LaVigne et al., 2008)). The lack of appropriate carbonate standards for this study led to the use of the non-matrix matched glass standard. Any matrix dependent elemental fractionation is, however, minimized for Ba and U when using a 193nm laser (Guillong et al., 2003; Hathorne et al., 2008; Longerich et al., 1996a). For P/Ca measurements, it has been shown that analyses using solution SF-ICP-MS and certified solution standards agree with 193nm laser ablation SF-ICP-MS measurements in tropical corals using similar operating conditions to ours (LaVigne et al., 2008), demonstrating that standardization with NIST 612 is sufficient for accurate P/Ca measurements in carbonates.
Figure 2.7. Comparison of long post-preablation lines on coral pressed powder pellet (top) and NIST 612 glass standard (bottom) with a 193nm solid state laser (100 μm spot, 10Hz, 4 point moving average).
Figure 2.8. Repetition of a single line ablated on NIST 612 (top graph) and a section of the *D. dianthus* coral ID: 80358 (bottom graph). The lines are ~2mm long for both materials ablated using solid state laser at 10Hz and 120μm spot size. Y-axis shows ratio of mean for a single pass to mean of all passes after one preablation.

2.5.1.8. Data filtering and smoothing

Trace element signals in corals occasionally show a great deal of fine-scale variability that could represent different compositional features and inhomogeneity within the coral. This fine-scale variability is not however clearly linked to environmental interpretation (Sinclair et al., 1998). Therefore a moving average smoothing is applied to the data to remove such variability. The decision of the level of moving average is subjective and is based on specifics of each coral analysis. In analyses where the goal was to obtain one
El/Ca measurement representative of a coral, typically a 4 point moving average was enough to remove any fine scale variability. For time series analyses a 12 point moving average to the data is applied. Hence the effective resolution of the data series is reduced to around 250 µm (for 12 point moving average smoothing) providing approximately seasonal variations in El/Ca for an average of 1 µm/year growth rates for D. dianthus (Adkins et al., 2004).

Additional filtering was performed to the coral data to remove occasional extreme outlier points that probably represent dust or other discrete particulate contaminants or laser ablation particle re-deposition on the sample surface that enters the plasma. The filtering protocol for such cases was developed based on the relative increase in El/Ca signal. When a single ~2s acquisition El/Ca increases by >2-fold compared to the mean of the ablation line (removing that specific acquisition) and compared to El/Ca ratios from adjacent coral material, it is assumed it represents outlier points and was therefore removed from any reconstructions. Further data filtering protocols have been developed for excluding areas affected by apparent iron oxides (enriched in Fe, Mn and P), and areas containing centers of calcification affected by vital effects and potential diagenesis (variable P/Ca and depleted U/Ca, see Chapter 3).

2.5.1.9. Blank and detection limit
Blank signals for the analyte ions are measured with the laser shutter closed while the laser is either firing (typical for warm up conditions) or not firing. In the first case, blank represents a combination of instrumental noise plus contamination (from the ablation cell,
the tubing connecting the laser to the injector, and the ICP), while in the second case, laser noise is removed (Figure 2.9).

Based on the shaded lines (Figure 2.9), it is observed that instrumental noise contribution to the blank is minimal for most elements, with potentially larger contribution to higher masses, e.g. Ba and U. Nevertheless, the signal/blank ratio for typical standard and coral material is >10 (Table 2.5), therefore variations in the blank are not expected to affect reproducibility of analyses. Blanks may however change during the course of an analysis as sensitivity changes and contaminants build up in the system, so that and low abundance elements’ reproducibility may be affected more than calculated here. Therefore each ablation line is preceded by acquisition of a blank integrated for 45s, while the laser is warming up. This blank is considered the representative for each ablation line.
Figure 2.9. Blanks obtained through a day. Circled points represent blanks measured with the shutter open and the laser not firing. The rest of the blanks are measured at the beginning of each line, with the shutter closed and the laser firing while warming.

The detection limit is calculated as three times the standard deviation of the blank (shutter closed, laser firing). The major trace elements in corals (B, Mg, P, Ca, Ba, and U) are clearly well above detection limits (Table 2.5), with ratios of concentration to detection limit higher than 20. These elements are not therefore limited by detection limits and can be accurately and precisely quantified.
Table 2.5. Typical blank, coral, standard concentrations and detection limits

<table>
<thead>
<tr>
<th></th>
<th>B11</th>
<th>Mg25</th>
<th>P31</th>
<th>Mn55</th>
<th>Fe56</th>
<th>Ba138</th>
<th>U238</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank (ppm)</td>
<td>0.5</td>
<td>6.0</td>
<td>2.2</td>
<td>&lt;0.1</td>
<td>0.2</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Detection Limit (ppm)</td>
<td>0.2</td>
<td>2.6</td>
<td>1.1</td>
<td>0.1</td>
<td>0.5</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Typical D. dianthus (ppm)</td>
<td>91.9</td>
<td>710.3</td>
<td>45.9</td>
<td>0.1</td>
<td>2.4</td>
<td>11.4</td>
<td>5.2</td>
</tr>
<tr>
<td>NIST 612 (ppm)</td>
<td>35.0</td>
<td>77.0</td>
<td>51.0</td>
<td>38.0</td>
<td>51.0</td>
<td>39.7</td>
<td>37.4</td>
</tr>
<tr>
<td>MACS3 (ppm)</td>
<td>6.3</td>
<td>1954.9</td>
<td>104.4</td>
<td>521.1</td>
<td>9673.6</td>
<td>93.5</td>
<td>2.0</td>
</tr>
</tbody>
</table>

2.5.1.10. Counting statistics and total theoretical error

The counting statistics (CS) for elemental analyses could be limiting elemental ratio reproducibility. The CS are calculated using the integration window (I), segment duration time (SD), and the related cps for each element (S) (CS = 1/(S*I*SD)). For example, JFA24.8 and JFA20.10 D. dianthus CS (Chapter 5) are 7-10% for P/Ca, 3% for Ba/Ca, and 4% for U/Ca while the Smithsonian ID 84820 had 4% CS uncertainty for P/Ca and 5% for Ba/Ca and U/Ca. Performing moving average smoothing to the data reduces the counting statistics error below the reproducibility uncertainty (i.e. 2% P/Ca, and ≤1% Ba/Ca and U/Ca for JFA24.8 with 12 point moving average).

The total minimum theoretical error is dependent on the CS of each element, the blank subtraction error, and the CS error of the NIST 612 glass standard. The blank contribution to Ca, Ba, and U is negligible (Table 2.5). On the contrary the P blank could become significant source of uncertainty for low P samples, equal up to 15% of the coral signal. In such a case the blank contribution to the total CS error can be up to 1%, while the uncertainty in the blank which could be up to 25% could contribute up to 4% error to the P/Ca measurement. The CS error of NIST 612 analyses is typically ≤ 8% for P/Ca,
and ≤4% for U/Ca and Ba/Ca. Since, however, 2mm lines are averaged the CS error of NIST 612 drops to ≤ 1% for all P/Ca, Ba/Ca and U/Ca. Therefore the reproducibility of coral analyses results in an error significantly greater than that due to CS errors and standardization.

2.5.1.11. Reproducibility

2.5.1.11.1. Lines in coral and NIST 612 standard
Reproducibility in LA-ICPMS is strongly element dependent and it is also related to heterogeneity of samples and standards. For example, NIST 612 glass standard is more homogenous than an in-house coral pressed powder pellet (Figure 2.7) for B, Mg, P, Ba, and U. When 2mm lines are ablated on NIST 612 and a coral sample (Figure 2.8), precision of the line means is better than ±10% for P/Ca, U/Ca, and Ba/Ca ratios.

2.5.1.11.2. Static laser spots in coral and NIST 612 standard
In this work, static laser spots were avoided as a method for sampling corals, because although drilling down into the surface of the sample material allows long counting times, potentially producing high reproducibility, trace elements fractionate with depth as shown before for spot sizes 25-75 μm (Eggins et al., 1998) leading to unstable signals (Figure 2.4 and Figure 2.10).
Figure 2.10. Static 100 μm drilling of seven different spots in a pressed powder pellet (left) and a NIST 612 glass standard (right) (10Hz, 1min duration minus blank).
2.5.1.11.3. Day to day reproducibility

On occasion, coral elemental ratios display a high degree of variability, when different lines on each coral sample are ablated, while the repetition of ablation of a single line both within a day and subsequent days shows less variability. It is therefore important to analyze two or more parallel lines on each coral sample when possible to allow consistent geochemical horizons in the coral to be distinguished from local structurally induced variations. For this purpose ablation of different lines on the exterior of a coral septum were compared (ID 80358) (Figure 2.11). The ablations occurred on different analytical days and with different lasers (excimer and solid state 193nm). Although it is difficult to align the lines into a reference time and growth rate, since they are ~100 μm offset from each other approximately in parallel, it is noticeable that P/Ca, U/Ca, and Ba/Ca are in relative agreement not only in magnitude but also fine scale variation.
Figure 2.11. Ablation of parallel lines on the exterior surface of a septum of *D. dianthus* (Smithsonian ID: 80358) on different days and using excimer and solid state 193nm lasers. The inset shows the location of the parallel lines, color coded, on the analyzed septum.
Additionally analyses of a *D. dianthus* section (ID 62309) were repeated among different analytical days and instruments in the process of using this coral as an in-house consistency standard. The long term elemental ratio reproducibility was typically $\leq \pm 7\%$ (1SD) for Ba/Ca and U/Ca, and $\leq \pm 16\%$ (1SD) for P/Ca ($n=8$ lines, 4 mm long, ablated on the same septum, integrated to obtain mean El/Ca for each ablation pass).

### 2.5.1.12. Mass load effects

Using LA ICP-MS, variations in the amount of mass loaded into the ICP plasma (mass-load) were found to cause significant elemental ratio variations, with P and B being affected more than the high mass elements (Ba, U) (Figure 2.12). Increasing the mass-load into the plasma, elemental ratios vary following a logarithmic function of loading (traced by Ca signal), which is more pronounced at low Ca loads (Figure 2.13). When sensitivity is low due to tuning and cone selections, mass load curves for P/Ca could vary in slope from 0.0025 to 0.004 cps$^{-1}$, equivalent to a 60% change. This effect has been established in solution phase ICP-MS, likely related to plasma loading that enhances mass discrimination against low mass elements with high ionization potential, and is routinely corrected with matrix-specific standards (Rosenthal et al., 1999a). For example although P/Ca is characterized by strong mass load effects, Li/Ca appears to be insensitive, possibly because the 1$^{\text{st}}$ ionization potential of $^{31}\text{P}$ is 10.5V, much higher than the 5.4V for $^{7}\text{Li}$ (CHEMIX Ver:3.51).

These mass-load effects could originate either at the laser ablation or at the ICP plasma of the LA ICP-MS set up. Such mass load effects were however negligible or different
when Optical Emission Spectroscopy ICP (ICP-OES) was used instead of ICP-MS (LaVigne 2010) for the same laser conditions (Figure 2.12), indicating that the source of mass-load effects is within the ICP plasma. Additionally, NIST 612 glass standard and carbonate samples were ablated at variable Ca-loads and it was observed that mass-load effects were minimized at similar mass ablated of either NIST glass standard or carbonates instead of similar Ca-load conditions (Figure 2.12, 2.13), therefore it is not related to a unique Ca-matrix effect during ablation or within the ICP. Therefore, the flux of sample introduced to the plasma must be enough to maximize sensitivity and also minimize plasma load effects.

Since deep sea coral skeletons are dense, non-porous structures, Ca variations are typically restricted to <10%. Therefore within analyses mass load effects are expected to be negligible. Plasma load effects could become important however because of to day-to-day variations in matrix effects and when sensitivity is low (Figure 2.13). To avoid this, all analyses were performed when medium resolution $^{43}$Ca load was $0.4 \times 10^6$ cps or higher for carbonates (alternatively 50000 cps for NIST 612 that contains ~10% Ca) ablated at 10-15Hz, $>4$J/cm$^2$, and 100μm spot size with either excimer or solid state 193nm lasers.
Figure 2.12. Mass loading effects on elemental ratios of NIST 612 (top) and coral pressed powder pellet (middle) using UP-193SS. The bottom graph (modified from LaVigne 2010) describes excimer MS vs. OES comparison of MACS3 ablation. Red rectangular denotes analytical window in this study.
Figure 2.13. Mass load curves on MACS3 standard using excimer laser, adjusting Ca signal intensity by varying Hz, Fluence, and spot size.
2.5.1.13. Effective spatial resolution of ablation analyses

The duration of the laser method is 2 s; within this time the ICP-MS scans once through the mass range per 2s, integrating counts for a particular element for the duration of the segment time (Table 2.1), recording one data point for each element. Because SF-ICP-MS has only one detector, different elements are not measured simultaneously, and typically there is more than 1ms delay between measuring one element and another. The 2 s time-slice is a compromise between integrating for long enough to obtain a reasonably precise estimate of intensity, while keeping the time-slice short enough so that trace elements are measured approximately simultaneously while the sample moves under the laser. In this study, the typical beam size used was 100 μm in diameter, scanned at 25 μm/s, while the laser fired at 10-15Hz frequency. In 2 seconds the sample travels 50 μm. Therefore each 100 μm spot on the surface of the sample receives 40-60 individual laser pulses, each of which drills approximately 0.1 μm into the sample. As a result, in one second the laser has removed 3.2-4.7 x10⁴ μm³ of coral material. Assuming that D. dianthus aragonite density is ~2 mg/mm³, the laser removes 0.06-0.09 μg of coral per second of ablation.

2.5.1.14. Elemental ratio drift

Short term El/Ca drift is not common when using SF-ICP-MS instruments, and therefore it was not observed during ablation of both NIST 612 standards and coral samples (Figure 2.5, 2.6, 2.11, 2.14) (ablations ≤3min, 25μm/s, 3-4 mm long lines). For a long line ablated in coral (JFA24.8 D. dianthus, Figure 5.3, 100 μm spot, 10Hz, 13mm long, ~9min per ablation, 4 ablations reversing their direction between scans, 40min total time
of coral analyses), the fine scale features and trends of Ba/Ca, U/Ca, and P/Ca variations along the ablation line and among repetitions are reproducible within 10% deviation for Ba/Ca, ≤16% for U/Ca, and ≤13% for P/Ca. Nevertheless, when longer ablations are required, the drift could become more substantial, and repetition of ablation of the same line in reverse directions, similar to the approach here, would be necessary. Ultimately, the use of bracketing NIST 612 standards could be used to correct for El/Ca drift along long lines interpolating a linear mass-response gradient between standards (Eggins and Shelley, 2002; Hathorne et al., 2008).
Figure 2.14. Relative agreement of three repetitive ablations of the same line on *Dianthus* section (ID 62309) using solid state 193nm laser (100μm spot, 10Hz, 4 point moving average).
2.5.2. Solution-ICPMS

To test the accuracy of LA ICP-MS results for P/Ca, Ba/Ca and U/Ca in deep sea corals, that are standardized using non matrix matched NIST612 glass standard, crashed coral samples were dissolved in acid and analyzed using SF-ICP-MS following previously developed and described protocols (LaVigne 2010). All sample preparation and analyses followed standard laboratory protocols for trace element analysis under Class 100 conditions while all solutions were made with ultrapure reagents (OPTIMA grade, Seastar Chemicals Inc., BC, Canada) and 18.2 MΩ-cm Milli-Q water.

The sample tested was a *D. dianthus* coral (ID 62309) that has been used as a consistency standard for LA ICP-MS. Although this thesis laser sampling protocol was developed to avoid skeletal features of variable elemental composition in the coral, here a first attempt at large scale sampling was attempted, recognizing that the proportion of centers of calcification to the total coral mass sampled might create deviations in elemental ratio measurements compared to those of microsampling using LA ICP-MS. For that purpose the specific coral was selected because of its size, lack of exterior crust and organic material, and modern date. A portion of the coral skeleton was removed, cleaned similarly to the protocol for preparing thick sections described above, and crushed in a mortar and pestle. It was then separated into 2-5mg coral aliquots.
Solution cleaning was performed using a combination of steps following a technique adapted from established foraminifera and deep sea coral cleaning techniques (Eltgroth, 2006; Rosenthal et al., 1999b; Shen and Boyle, 1988). This technique was designed to remove detrital, mineral oxide, and organic contaminant phases of trace elements in powdered carbonate samples. Finally, each cleaned coral sample was transferred to a new weighed and acid-cleaned tube, which was dried overnight at 60°C so that final sample weights could be determined for dissolution.

<table>
<thead>
<tr>
<th>Table 2.6. Chemical cleaning protocol for coral samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Ultrasonicate (US) once in Milli-Q for 20min</td>
</tr>
<tr>
<td>2. US in methanol for ~20min, 3 times</td>
</tr>
<tr>
<td>3. Resuspension in Milli-Q with short US, 3times</td>
</tr>
<tr>
<td>4. Milli-Q rinse</td>
</tr>
<tr>
<td>5. 100μL 0.2% HNO₃ (v/v), US 1min, Milli-Q resuspension, 2 times</td>
</tr>
<tr>
<td>6. Milli-Q rinse</td>
</tr>
<tr>
<td>7. 250 μL of oxidizing solution (100μL H₂O₂ plus 30mL 0.1N NaOH)</td>
</tr>
<tr>
<td>8. 5min in hot bath (80°C) followed by brief US, 2 times</td>
</tr>
<tr>
<td>9. Resuspension in Milli-Q, let settle for 2min, siphon off, 2 times</td>
</tr>
<tr>
<td>10. Resuspension in Milli-Q, 5 min hot bath, US briefly, siphon off, 2 times</td>
</tr>
<tr>
<td>11. Milli-Q rinse, 3 times</td>
</tr>
<tr>
<td>12. Transfer to acid clean tubes</td>
</tr>
<tr>
<td>13. Dry overnight</td>
</tr>
</tbody>
</table>

Each sample was dissolved to a final solution of 100 mM Ca(+/- 10%) so as to minimize differential plasma matrix effects between samples during analysis (de Villiers et al., 1994; Rosenthal et al., 1999a). Samples were dissolved in ultrapure 1N HNO₃ (OPTIMA grade (Seastar Chemicals Inc., BC, Canada) acid and Milli-Q water). Before analysis, the 100 mM Ca sample stock solutions were diluted to 8mM Ca with a diluent solution consisting of ultrapure 3% HNO₃ and 1.0 ppb indium for ICP-MS measurements.
Measurements were carried out on an Element XR SF-ICP-MS with sample introduction system consisting of a microautosampler (SC-E2) connected to a self-aspirating PFA MicroFlow nebulizer (<100 mL min⁻¹ flow rate) and a PFA PureChamber spray chamber (all from Elemental Scientific Inc., Omaha, USA). The sample gas and additional gas flows were fine tuned before each analytical run to achieve a target sensitivity of ~1 x 10⁶ cps In/ppb in 3% nitric acid solution.

<table>
<thead>
<tr>
<th>TORCH POSITION (mm)</th>
<th>RANGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>X-POSITION</td>
<td>3.7</td>
</tr>
<tr>
<td>Y-POSITION</td>
<td>4.5</td>
</tr>
<tr>
<td>Z-POSITION</td>
<td>-4.9</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>GAS FLOWS (L min⁻¹)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>COOL</td>
<td>16</td>
</tr>
<tr>
<td>AUX</td>
<td>0.8</td>
</tr>
<tr>
<td>SAMPLE</td>
<td>0.757-0.766</td>
</tr>
<tr>
<td>AD1</td>
<td>0.162-0.172</td>
</tr>
<tr>
<td>AD2 (NH3)</td>
<td>0.071-0.072</td>
</tr>
<tr>
<td>RF POWER (W)</td>
<td>1450</td>
</tr>
<tr>
<td>LENSES (V)</td>
<td></td>
</tr>
<tr>
<td>EXTRACTION</td>
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</tr>
<tr>
<td>FOCUS</td>
<td>(-952)-(-1032)</td>
</tr>
<tr>
<td>X-DEFLECTION</td>
<td>4.66</td>
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<tr>
<td>Y-DEFLECTION</td>
<td>-1.41</td>
</tr>
<tr>
<td>SHAPE</td>
<td>131</td>
</tr>
</tbody>
</table>

| GUARD ELECTRODE         | YES   |
| OTHER (V)               |       |
| ROTATION QUAD1          | 3.63  |
| ROTATION QUAD2          | 2.18  |
| FOCUS QUAD1             | -1.64 |
| FOCUS QUAD2             | 0     |

<table>
<thead>
<tr>
<th>SENSITIVITY (10⁶ cps)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>In (1 ppb)</td>
<td>0.7</td>
</tr>
<tr>
<td>U (1 ppb)</td>
<td>1.2</td>
</tr>
<tr>
<td>UO/U (%)</td>
<td>4-5%</td>
</tr>
</tbody>
</table>

A multi-element standard stock was prepared gravimetrically in 3% HNO₃ (v/v) from primary single element standards (B, Y, Cd, Ba, U, P, Mn, Fe, and Zn; 10 ppm; High Purity Standards, Charleston, SC) to match typical elemental composition of coral
skeleton (Table 2.7). A single-element calcium standard stock was prepared separately to avoid cross-contamination for trace element analytes from high concentrations of calcium standard (LaVigne 2010). Concentrations of target elements in unknown samples were calculated using a four point standard addition calibration curve made by spiking an in-house consistency standard with dilutions of the multi-element standard to a final concentration of 8mM Ca spiked with 1ppb In (LaVigne 2010).

Indium was added as an internal standard at a concentration of 1ppb with the 3% nitric acid solution prepared each day for sample dilution. This In-spiked diluent solution was used to prepare all samples, standards, and tube blanks. Indium, which was analyzed in both medium and low resolutions, was used to monitor and correct for instrument drift in the calculation of data. Blanks were individual 0.5 mL aliquots of diluent added to acid-leached micro-centrifuge tubes and empty tubes which were carried through the entire sample preparation procedure including cleaning. The percent blank subtracted from sample signals was typically <5% for P, Ba, and U. The degree of blank subtraction for other elements i.e. Fe, Mn, Zn, etc. was variable (up to 100%), possibly because of low concentrations in the coral analyzed.

The resultant *D. dianthus* (ID 62309) P/Ca, Ba/Ca, and U/Ca ratios were in general agreement with laser ablation ICP-MS measurements with NIST 612 glass standardization. The laser ablation average (using solid state and excimer lasers) was 26.9 ± 4.3 μmol/mol P/Ca, 7.9±0.6 μmol/mol Ba/Ca, and 1.4 ± 0.1 μmol/mol U/Ca (total 8 replicates of 4 lines, 1SD). The solution ICP-MS results are 25.9 ± 3.4 μmol/mol P/Ca,
8.8 ± 0.2 μmol/mol Ba/Ca, and 1.5 ± 0.2 μmol/mol U/Ca (2SD of two samples processed and analyzed). This agreement is surprisingly good, but the sample was optimized on purpose, and evaluation of solution ICP-MS on bulk samples would require much more extensive comparison of solution and laser analyses.

<table>
<thead>
<tr>
<th>Table 2.7. Standard solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>μmol/mol Ca</td>
</tr>
<tr>
<td>----------------</td>
</tr>
<tr>
<td>B</td>
</tr>
<tr>
<td>Mg</td>
</tr>
<tr>
<td>Y</td>
</tr>
<tr>
<td>Cd</td>
</tr>
<tr>
<td>Ba</td>
</tr>
<tr>
<td>U</td>
</tr>
<tr>
<td>P</td>
</tr>
<tr>
<td>Mn</td>
</tr>
<tr>
<td>Fe</td>
</tr>
<tr>
<td>Zn</td>
</tr>
</tbody>
</table>

2.6. CONCLUSIONS

Laser ablation ICP-MS is a reliable approach for deep sea coral elemental ratio analyses. Although this method minimizes the time required for sample preparation, the need for manual data reduction of laser data at this point is at least equally time consuming to solution ICP-MS analyses. For deep sea corals, this work has proven the need to sample at the micron scale in order to obtain P/Ca, Ba/Ca, and U/Ca ratios reproducible at <10%. The use of micro-milling and low Ca solution ICP-MS analyses could prove equally powerful for seawater phosphate, barium and carbonate ion reconstructions.
Ultimately, in order to obtain high spatial resolution deep sea coral data (e.g. sub-annual) the need of laser ablation methods is required, considering that the average growth rate of these corals is roughly an order of magnitude lower than that found in surface corals. Therefore this study focuses solely on laser ablation analyses. Here the same ablation conditions were maintained between analyses so that reconstructions can be made based on this thesis global P, Ba, and U calibrations. The accuracy of LA ICP-MS remains a question. To obtain accuracy better than 10% it is advisable to develop matrix matched and homogeneous solid standards or alternative methods to further validate the LA ICP-MS results.

2.7. REFERENCES


CHAPTER 3

SEAWATER NUTRIENT AND CARBONATE ION CONCENTRATIONS RECORDED AS P/Ca, BA/Ca, AND U/Ca IN THE DEEP-SEA CORAL Desmophyllum dianthus

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Published: Geochimica et Cosmochimica Acta 75 (2011) 2529–2543
3.1. ABSTRACT

As paleoceanographic archives, deep sea coral skeletons offer the potential for high temporal resolution and precise absolute dating, but have not been fully investigated for geochemical reconstructions of past ocean conditions. Here the utility of skeletal P/Ca, Ba/Ca and U/Ca in the deep sea coral *D. dianthus* was assessed as proxies of dissolved phosphate (remineralized at shallow depths), dissolved barium (trace element with silicate-type distribution) and carbonate ion concentrations, respectively. Measurements of these proxies in globally distributed *D. dianthus* specimens show clear dependence on corresponding seawater properties. Linear regression fits of mean coral Element/Ca ratios against seawater properties yield the equations: 

\[ \frac{P}{Ca_{\text{coral}}} (\text{\(\mu\)mol/mol}) = (0.6 \pm 0.1) \frac{P}{Ca_{\text{sw}}} (\text{\(\mu\)mol/mol}) - (23 \pm 18), R^2=0.6, n=16 \]

\[ \frac{Ba}{Ca_{\text{coral}}} (\text{\(\mu\)mol/mol}) = (1.4 \pm 0.3) \frac{Ba}{Ca_{\text{sw}}} (\text{\(\mu\)mol/mol}) + (0 \pm 2), R^2=0.6, n=17; \] no significant relationship is observed between the residuals of each regression and seawater temperature, salinity, pressure, pH or carbonate ion concentrations, suggesting that these variables were not significant secondary dependencies of these proxies. Four *D. dianthus* specimens growing at locations with \(\Omega_{\text{arag}} \leq 0.6\) displayed markedly depleted P/Ca compared to the regression based on the remaining samples, a behavior attributed to an undersaturation effect. These corals were excluded from the calibration. Coral U/Ca correlates with seawater carbonate ion: 

\[ \frac{U}{Ca_{\text{coral}}} (\text{\(\mu\)mol/mol}) = (-0.016 \pm 0.003) [\text{CO}_3^{2-}] (\text{\(\mu\)mol/kg}) + (3.2 \pm 0.3), R^2=0.6, n=17. \]

The residuals of the U/Ca calibration are not significantly related to temperature, salinity, or pressure. Scatter about the linear calibration lines is attributed to imperfect spatial-temporal matches between the selected globally distributed specimens and available water column chemical data, and potentially to unresolved additional effects.
The uncertainties of these initial proxy calibration regressions predict that dissolved phosphate could be reconstructed to +/- 0.4μmol/kg (for 1.3-1.9μmol/kg phosphate), and dissolved Ba to +/- 19nmol/kg (for 41-82nmol/kg Ba\textsubscript{sw}). Carbonate ion concentration derived from U/Ca has an uncertainty of +/- 31μmol/kg (for 60-120μmol/kg CO\textsubscript{3}\textsuperscript{2-}). The effect of microskeletal variability on P/Ca, Ba/Ca, and U/Ca was also assessed, with emphasis on centers of calcification, Fe-Mn phases, and external contaminants. Overall, the results show strong potential for reconstructing aspects of water mass mixing and biogeochemical processes in intermediate and deep waters using fossil deep-sea corals.
3.2. Introduction

Tropical corals are widely used in paleoceanographic reconstructions to provide high resolution records of climate variability. The absence of zooxanthellate corals below the surface layer of the ocean is a limitation that could be compensated by the presence of deep-sea corals, if suitable geochemical proxies in the skeletons of these organisms were developed. Azooxanthellate deep corals are globally distributed, and can be dated precisely with U-Th radiometric techniques. Fossil deep sea corals of appropriate age can thus be used to study the ocean’s role in abrupt climate events including Heinrich events, the Younger Dryas, the Medieval Warm Period, and the Little Ice Age, if the range of useful proxies can be expanded.

The solitary coral *Desmophyllum dianthus* (*D. dianthus*) is an aragonitic scleractinian, azooxanthellate coral, with cosmopolitan geographic distribution, depth range of 35-2500m (Cairns 1994), and exceptional thermal tolerance of -1°C to 28°C (Stanley and Cairns 1988). Because of its century-long life span and relatively large skeleton (~10cm of vertical septal growth) (Cheng et al. 2000; Adkins et al. 2004), *D. dianthus* allows for both U/Th and radiocarbon dating (Cheng et al. 2000; Robinson et al. 2005) in addition to multi-proxy studies on a single specimen, providing the potential for subdecadal resolution of century scale windows into mesopelagic variability in the past (Adkins et al. 1998). There is great incentive, then, to develop new proxies that could provide high resolution information related to water mass mixing ratios and to the biogeochemical processes of nutrient supply and distribution, primary production, and biogenic particulate carbon flux to the intermediate and deep ocean.
Foraminiferal proxies currently used to reveal aspects of nutrient supply and utilization include $\delta^{13}C$, Cd/Ca (Keigwin and Boyle 1989; Rosenthal et al. 1997), Ba/Ca (Lea and Boyle 1990), and $\delta^{15}N$ (Altabet and Curry 1989). In tropical corals these biogeochemical processes are explored using $\delta^{13}C$, Ba/Ca (Lea et al. 1989; Tudhope et al. 1996; Alibert and Kinsley 2008), and Cd/Ca and P/Ca (Shen et al. 1987; LaVigne et al. 2010). A P/Ca proxy calibration was previously proposed for *D. dianthus* (Montagna et al. 2006), suggesting that P/Ca in the skeleton is ~7 times greater than P/Ca in ambient seawater. Questioning the validity of this outcome led to further research and resulted in the revised P/Ca calibration presented in this paper.

The deep sea coral *D. dianthus* also holds promise for reconstructing paleo-carbonate ion concentrations. Foraminiferal carbonate ion proxies, U/Ca in planktonics, and Zn/Ca and B/Ca in benthics (Russell et al. 2004; Marchitto et al. 2005; Yu and Elderfield 2007), offer great promise but lack the high resolution and precise dating potential of *D. dianthus*. In tropical corals, the effect of carbonate ion concentration on uranium incorporation has been investigated but is difficult to distinguish against the stronger influences of temperature and other variables (Min et al. 1995; Shen and Dunbar 1995). The limited temperature range of deep coral environments suggests that other influences on U/Ca variations, including potentially carbonate ion concentration, may emerge, but this potential has yet to be explored.

In this chapter, evidence is presented supporting three new proxy calibrations in the deep-sea coral *D. dianthus*: 1) a revised P/Ca proxy calibration for reconstructing seawater...
phosphate, 2) a Ba/Ca proxy for tracing variations in the silicate-type element Ba, and 3) a U/Ca proxy for carbonate ion concentration. The results constitute completion of the first steps required to greatly expand the potential utility of *D. dianthus* as a geochemical paleoceanographic archive. Further investigations will be required to fully quantify the effects of secondary environmental variables (temperature, salinity, pH, etc.) on the proposed proxies, through future field studies in which hydrographic parameters are well constrained, and through culturing experiments.

### 3.3. MATERIALS AND METHODS

#### 3.3.1. Sample preparation and analytical approach

Samples were obtained from the National Museum of Natural History (Smithsonian Institution, Washington, D.C.) and from Dr. E. Sikes (Rutgers University, New Jersey, USA). The corals were treated with the ultrasonic-cleaning protocol of Cheng et al. (2000), and then septa were removed, cut longitudinally, mounted in epoxy and prepared as polished thick sections (300µm) to ~1µm roughness ensuring a flat surface for maintaining laser focus and signal stability. The thick sections were subsequently rinsed with isopropyl alcohol (99.9% purity) in an ultrasonic bath for several seconds and dried with a soft cloth. These sections were oriented along the growth axis to enable sampling of the fibrous (acicular) aragonite portion of the septa, while visualizing the central band, septal exterior, and bioeroded features, all within the ~1mm width of a typical septum.
The samples were ablated using a 193 nm ArF excimer laser (UP-193, New Wave Research Fremont, CA). Pure He was used as the ablation atmosphere (Eggins et al. 1998), and the output from the laser ablation cell was then mixed with additional Ar before injection into the central channel of the MS. The sample was ablated at a fluence of ~6-7J/cm² and 15Hz shot frequency. Gas blanks were measured initially for 45s, while the laser beam was blocked by a shutter. The shutter was then opened, and the sample was ablated while the transient analyte signals were acquired for the ablation period.

The sampling strategy of this chapter was to ablate lines along the growth axis of the corals, integrating several years of growth, to obtain mean elemental composition for the specimen. Surface contamination, which in the case of *D. dianthus* thick sections originated most probably from sample sectioning and polishing, was removed with preablation laser passes (Sinclair et al. 1998). Such contamination was expected to be restricted to the upper few microns since deep sea coral aragonite is dense and generally free of voids ($^{43}$Ca shows ~10% signal intensity variation along an ablation line). Therefore the approach here was to perform preablation passes until averaged elemental ratios were reproducible among successive ablations of the same line (typically better than +/-10%, see also Appendix, Table A1). Typically one ablation of ~6µm depth was sufficient to remove surface contamination in coral thick sections, identified as a laser pass in which resultant data did not satisfy the reproducibility requirements stated above. Ablation depth is estimated using a value of 1µm per 10 shots, similar to other laser systems (Günther et al. 2000; Hathorne et al. 2003).
Analyses were carried out on an Element 2 SF-ICP-MS (ThermoFinnigan, Bremen, Germany) using a combination of magnet jumps and electrostatic peak scanning (E-scan). All elements were analyzed in medium resolution (MR = 4000M/ΔM) to resolve molecular ion interferences on phosphorus (e.g. NO\(^+\) and NOH\(^+\)) and on iron (e.g. ArO\(^+\) and CaO\(^+\)), while acquiring time-resolved data in a near-simultaneous manner. The isotopes measured and the method parameters are listed in Table 1. For the selected laser and ICP conditions (Tables 1 and 2), elemental ratio precision of coral analyses in thick sections was typically <±3% (1SD) for Ba/Ca, <±5% (1SD) for U/Ca, and <±6% (1SD) for P/Ca for 3-4 replicate ablations of the same line, integrated to obtain mean El/Ca for each ablation pass. The length of ablated line varied depending on sample from 0.4 to 4.0mm. The gas blank, in counts per second (cps), as a fraction of mean coral signal intensity (cps), was <4% for P, <1% for Ba, and not detectable for U, while Ca blank was <1% and Fe and Mn blanks, depending on the sample, were typically <20%.
Table 3.1. SF-ICP-MS Acquisition parameters

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Sample time (s)</th>
<th>Detection mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{11}\text{B}$</td>
<td>0.010</td>
<td>Counting/Analog</td>
</tr>
<tr>
<td>$^{25}\text{Mg}$</td>
<td>0.003</td>
<td>Counting/Analog</td>
</tr>
<tr>
<td>$^{31}\text{P}$</td>
<td>0.010</td>
<td>Counting/Analog</td>
</tr>
<tr>
<td>$^{43}\text{Ca}$</td>
<td>0.003</td>
<td>Analog</td>
</tr>
<tr>
<td>$^{55}\text{Mn}$</td>
<td>0.003</td>
<td>Counting/Analog</td>
</tr>
<tr>
<td>$^{56}\text{Fe}$</td>
<td>0.003</td>
<td>Counting/Analog</td>
</tr>
<tr>
<td>$^{136}\text{Ba}$</td>
<td>0.003</td>
<td>Counting/Analog</td>
</tr>
<tr>
<td>$^{238}\text{U}$</td>
<td>0.003</td>
<td>Counting/Analog</td>
</tr>
</tbody>
</table>

Resolution m/$\Delta$m: 4000
Mass window: 40%
Search window: 10%
Integration window: 15%
Samples per peak: 40
Scan type: E-scan
Total duty cycle: 73%

Standardization was achieved by bracketing each coral ablation line with NIST 612 glass standard analyses (~2mm long scan), interpolating a linear mass-response gradient between standards (Egginns and Shelley 2002; Hathorne et al. 2008). To correct for variations in ablation yield and instrumental drift, element signals were normalized to Ca as the internal standard (Longerich et al. 1996b; Hathorne et al. 2003). Spreadsheet software was used for offline data reduction, which involved gas-blank subtraction, normalization to $^{43}\text{Ca}$, removal of signal spikes (rare: when present, El/Ca was at least a factor of 2 higher than the maximum El/Ca ratios within the rest of the ablation line) that probably represented contaminant particles entering the plasma (Sinclair et al. 1998), and finally, standardization. The NIST 612 standard is considered homogeneous for Ba, Ca, P and U (Egginns and Shelley 2002), therefore published elemental concentrations were used (Ba: 39.7ppm and certified U: 37.4ppm; Reed 1992; Jochum et al. 2005, Ca:
84690 ppm; Eggins 2003, P: 39.9 ppm; LaVigne et al. 2008). The lack of appropriate carbonate standards for this study led to the use of the non-matrix matched glass standard. Any matrix dependent elemental fractionation is, however, minimized for most elements when using 193 nm lasers, including Ba and U (Longerich et al. 1996a; Guillong et al. 2003; Hathorne et al. 2008). For P/Ca measurements, it has been shown that analyses using solution SF-ICP-MS agree with 193 nm laser ablation SF-ICP-MS measurements in tropical corals for specific operational conditions (LaVigne et al. 2008). To minimize mass load induced matrix effects and laser induced fractionations, selected laser and plasma conditions were similar to those of LaVigne et al. (2008) (Table 2).

### Table 3.2. SF-ICP-MS and Laser ablation parameters

<table>
<thead>
<tr>
<th>SF-ICP-MS</th>
<th>Element 2</th>
<th>ThermoFinnigan, Bremen, Germany</th>
</tr>
</thead>
<tbody>
<tr>
<td>RF power</td>
<td>1250 W</td>
<td></td>
</tr>
<tr>
<td>Sample gas (Ar)</td>
<td>0.8-0.9 L/min</td>
<td></td>
</tr>
<tr>
<td>Coolant gas flow</td>
<td>16 L/min</td>
<td></td>
</tr>
<tr>
<td>Auxiliary gas flow</td>
<td>1.06 L/min</td>
<td></td>
</tr>
<tr>
<td>Sampler, skimmer cones</td>
<td>Ni</td>
<td></td>
</tr>
<tr>
<td>Laser ablation</td>
<td>UP193HE</td>
<td>New Wave Research, CA, USA</td>
</tr>
<tr>
<td>Pulse width</td>
<td>20 ns</td>
<td></td>
</tr>
<tr>
<td>Energy</td>
<td>0.5-0.6 mJ</td>
<td></td>
</tr>
<tr>
<td>Fluence</td>
<td>6-7 J/cm²</td>
<td></td>
</tr>
<tr>
<td>Laser repetition rate</td>
<td>15 Hz</td>
<td></td>
</tr>
<tr>
<td>Laser spot size</td>
<td>80-100 µm</td>
<td></td>
</tr>
<tr>
<td>Scan speed</td>
<td>15-25 µm/s</td>
<td></td>
</tr>
<tr>
<td>Carrier gas (He)</td>
<td>0.75 L/min</td>
<td></td>
</tr>
</tbody>
</table>

A sub-set of three corals (47413, 83583, 82065) was analyzed using colorimetric techniques (Koroleff 1983) to quantify the contribution of inorganic phosphate to the total P content of the coral. Subsamples of the septa were removed and crushed, then dissolved in 0.8N hydrochloric acid (trace metal grade). For the purpose of color development, the final solution was diluted in distilled water to a working pH of ~1 (Anagnostou and Sherrell 2008). This method quantifies the soluble reactive phosphorus
fraction in solution, and includes monophosphates but excludes organic phosphorus compounds and non-reactive inorganic phosphates including pyro- and poly-phosphates.

3.3.2. Data Analysis

Deep-sea coral specimens were collected at locations characterized by a range of seawater properties. Hydrographic data were varyingly well constrained depending on station locations from the current global ocean database (WOCE, GEOSECS, and CLIVAR programs) as well as from other published data. When necessary due to geographic coverage of water column data, seawater properties were extrapolated along isopycnals from available hydrographic stations to coral collection sites (Appendix, Tables A1, A2). To quantify the uncertainty in seawater concentrations from potential spatial and temporal mismatch between the coral collection and the hydrographic station selected, all available data were compiled from locations within a range of latitude (5°) and longitude (35°) and within 27 years of the selected primary hydrographic station for each coral specimen (listed in Appendix, Table A2). None of the corals has been radiometrically dated, although they are thought to have been collected alive since all carried residual dried tissue but 94069 and 48739.

The calibration slopes, regression coefficients (R²), y-intercepts and associated errors were calculated using Type-2 Geometric Mean linear regression, otherwise known as Reduced Major Axis (Ricker 1973; Bevington and Robinson 1992), as modified for Matlab by E. T. Peltzer (for details, see http://www.mbari.org/staff/etp3/regress.htm).
The error envelopes were computed using the Matlab toolbox CurveFit (2009) for linear regression.

### 3.4. Microskeletal Variability

Before establishing a consistent procedure that generated reproducible elemental ratios, different structural features were analyzed in the deep sea coral *D. dianthus*. The phases examined included the fibrous aragonite, centers of calcification (COCs), Fe-Mn phases, and the exterior of the septa. Data acceptance criteria were developed for the elements of interest and best practices were established for measuring geochemical proxies in *D. dianthus* with laser ablation.

![Figure 3.1](image.png)

Figure 3.1. Transmitted light image of an S1 septum and two neighboring S2 septa of a *D. dianthus* coral showing the internal banding pattern (magnified picture on the right). Central band (with COCs) in dotted outline shows as dark color, in contrast to the region of fibrous aragonite crystals (solid outline). Lines with arrows are examples of laser ablation tracks.
analyzed. Ablation across the central band is used to explore elemental anomalies in that region. Scale bar represents 1mm.

3.4.1. Effects of Fe-Mn phases on intra-skeletal elemental ratio variations

It has been reported that Mn-rich phases can contain trace element contaminants, compromising elemental ratio reconstructions in foraminifera (Pena et al. 2008). In corals, such phases may be Fe-Mn oxide and hydroxide inclusions, contaminant particles (e.g. particulate phosphorus), Fe biominerals (Konhauser 1997), or carbonate material precipitated during conditions of high particulate organic matter flux and surface sediment suboxia, leading to enrichment in Fe, Mn, and P in the local benthic nepheloid layer (Sherwood et al. 1987).

To investigate potential contamination by Fe-Mn phases, lines were ablated on the surface of coral septa, cut and cleaned as described above for thick sections. Apparent contaminant phases were observed as evidenced by local peaks in Fe/Ca and Mn/Ca, associated with P/Ca signals elevated by at least a factor of 2 (Figure 3.2), which were typically removed with subsequent ablations of the same area, suggesting that their dimensions in the ablation z-axis were a few 10s of µm. Especially for corals recovered from suboxic waters, like *D. dianthus* specimen 84818 (11µmol/kg oxygen; Appendix, Table A2), proximity to sediment-source dissolved Mn\(^{2+}\) could lead to precipitation of Mn carbonates, with elemental composition distinct from that of the carbonate hosts (Pena et al. 2005).
Taking advantage of the multi-element analytical approach in this study, it is suggested that when Fe/Ca, Mn/Ca, and P/Ca co-vary, and there is a $\geq 2$-fold increase in Mn/Ca and Fe/Ca compared to the mean along the rest of a coral ablation line, discrete Fe-Mn phases enriched in P may be present. These phases did not show anomalous enrichment in Ba or U (Figure 3.2). However, ablation of interior septal aragonite accessible in thick sections, with preablation, allowed us to avoid these septal surface phases, such that no P/Ca data needed to be edited from the raw data set for association with high Mn or Fe. This evidence justified use of septal thick sections for the remainder of the study.
Figure 3.2. Elemental ratios for ablation of a 3.5mm line along the exterior of a *D. dianthus* septum. This coral has a distinct Fe-Mn phase that is associated with a factor of ~3 increase in P/Ca ratios at the center of ablation line. Symbols and thin lines represent raw data, while bold lines represent 4 point moving averages. The top panel shows Element/Ca normalized to the mean ratio for portions of the ablation line outside the central Fe-Mn-P peak. For reference, U/Ca and Ba/Ca raw ratios are also shown.
3.4.2. VARIATIONS IN THE CENTRAL BAND AND CENTERS OF CALCIFICATION

Two discrete structures (Figure 3.1) described in scleractinian coral skeletons are the centers of calcification (COCs) located in the central band, and clusters of fibrous crystals radiating out from the centers (Ogilvie 1896; Bryan and Hill 1941). The COCs are morphologically (Constantz 1986; Cohen et al. 2001) and compositionally (e.g. Adkins et al. 2003; Cuif et al. 2003; Meibom et al. 2006) distinct from the surrounding aragonite.

The variability of elemental ratios across the central band of coral 62309 was mapped by drilling 100µm spots on either side of and directly focused on central band material, for 4 regions along the central band of a single septum (Figure 3.3).

The behavior of Mg/Ca and U/Ca in the central band was in general agreement with the findings of other studies, displaying enrichment in Mg/Ca and depletion in U/Ca (Sinclair et al. 2006; Gagnon et al. 2007). Although no P/Ca anomalies in central band material were resolvable against P/Ca ratios in non-COC portions of the ablated areas, it was obvious that P/Ca was more variable in the central band than in fibrous aragonite regions (error bars in Figure 3.3). Additionally, Ba/Ca was largely invariant across the central band in contrast to recent observations in tropical corals and artificially precipitated granular aragonite aggregates (Holcomb et al. 2009). This chapter demonstrates clearly the importance of avoiding the central band if precise U/Ca and P/Ca measurements are to be made. The criterion for data removal due to inadvertent ablation of COCs in this study was that the data in the anomalous region displayed Mg/Ca ≥2-fold higher and U/Ca ≥2-fold lower than the mean of the remaining ablation line. Editing for the presence of COCs was required only for coral specimens 19168 and 84820.
Figure 3.3. Results of ablation of 100µm spots within centers of calcification (COCs; white central band under reflected light) and in the fibrous part of coral 62309, outside of the COCs, shown against a reflected light image of thick section of septum. In the areas where COCs are present, Mg/Ca is elevated and U/Ca is decreased. The Ba/Ca is nearly invariant while P/Ca is highly variable within COCs. Error bars represent SD of the mean of 4 spots drilled at different points along each side and within the central band. Data points are positioned relative to their respective scale bars, and do not reflect the positions of the ablation spots on the sample pictured.
3.5. Ablation of Thick Sections versus Exterior of Septa

In preliminary experiments, it was attempted to determine accurate and consistent values for the proxy element ratios by ablating the exterior surfaces of septa, seeing the advantage of the simplified sample preparation and expected avoidance of the central band by limiting ablation penetration depth, following the methods of Montagna et al. (2006). It was observed that this approach requires more extensive and thus deeper preablation (>20μm compared to <10μm for thick sections) to remove anomalous surface phases.

The nature of these phases on the surfaces of septa is likely complex and variable. They are separated, here, into two categories; phases precipitated or included during the coral polyp lifetime, and phases generated post mortem. Deep sea corals are frequently located in waters undersaturated with respect to aragonite, but the tissue layer protects the skeleton against dissolution. In times of environmental stress, however, corals may retract the polyp exposing the exterior of the corallite to corrosive waters and therefore to erosion and dissolution (Lazier et al. 1999), resulting in anomalous minor element ratios caused by differential leaching (Hendy et al. 2007). Endolithic borings could also be filled with aragonitic or calcitic cements (Nothdurft et al. 2007; Cusack et al. 2008). Post-mortem, dissolution, boring, and infilling may continue, and early marine aragonite cement may precipitate on the skeletal surface, altering the values of important geochemical proxies. Such cements can be avoided by assuring that sampling does not intersect the margins (e.g. external areas of septa and the coral wall) or surfaces of
internal structures (e.g. central band material and borings) (Nothdurft et al. 2007; Perrin and Smith 2007).

Preablation of the exterior of septa does not guarantee the removal of altered material at the surface of the coral. For example, following preablation, the analytical ablation lines on the exterior surfaces frequently intersected regions of elevated Mg/Ca and decreased U/Ca, indicating the presence of COCs near the septal surface (e.g. Figure 3.1), often not visible with light microscopy. It is concluded that altered phases on the septal surface can be too irregular in thickness and the presence of COCs too difficult to confirm, to make exterior ablation a viable method for obtaining precise and representative elemental data.

Given these potential problems with ablation of the exterior of septa, interior septal aragonite in thick sections was analyzed. Ablation lines were laid out within the fibrous aragonite regions of the polished sections, away from central bands and the exterior of the septa, and along the coral growth axis. The resultant mean elemental ratios were highly reproducible in different areas of the fibrous regions of a septum, and in neighboring septa of the same individual (Table 3).
### Table 3.3. Examples of P/Ca, Ba/Ca, and U/Ca means from different ablation lines on the same and different septa. Uncertainties are SD among replicates of the same ablation line.

<table>
<thead>
<tr>
<th></th>
<th>P/Ca +/-1SD</th>
<th>Ba/Ca +/-1SD</th>
<th>U/Ca +/-1SD</th>
<th>Replicates</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Coral 19249: 1.5-2mm lines at tips of different septa</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>line 1 (μmol/mol)</td>
<td>118 +/- 7</td>
<td>8.1 +/- 0.8</td>
<td>2.1 +/- 0.2</td>
<td>n=3</td>
</tr>
<tr>
<td>line 2 (μmol/mol)</td>
<td>118 +/- 9</td>
<td>7.7 +/- 0.3</td>
<td>2.0 +/- 0.3</td>
<td>n=3</td>
</tr>
<tr>
<td><strong>Coral 62309: 4mm parallel lines on S1 septum</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>line 1 (μmol/mol)</td>
<td>27</td>
<td>8.4</td>
<td>1.5</td>
<td>n=1</td>
</tr>
<tr>
<td>line 2 (μmol/mol)</td>
<td>22 +/- 3</td>
<td>8.3 +/- 0.4</td>
<td>1.4 +/- 0.1</td>
<td>n=3</td>
</tr>
<tr>
<td><strong>Coral 94069: lines on different corals from the same location</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>coral 1 (μmol/mol)</td>
<td>65 +/- 7</td>
<td>7.7 +/- 0.4</td>
<td>1.65 +/- 0.04</td>
<td>n=6 (2 lines)</td>
</tr>
<tr>
<td>coral 2 (μmol/mol)</td>
<td>61 +/- 3</td>
<td>7.7 +/- 0.2</td>
<td>1.76 +/- 0.07</td>
<td>n=6 (2 lines)</td>
</tr>
</tbody>
</table>

### 3.6. RESULTS AND DISCUSSION

#### 3.6.1. THE P/Ca NUTRIENT PROXY

To generate a global calibration of P/Ca against dissolved phosphate, twenty corals were analyzed from a number of geographic locations (Figure 3.4) and depths, spanning nearly the full oceanic range of seawater phosphate (~0.5-3.0μmol/kg). Among all hydrographic variables considered, coral P/Ca is most strongly correlated with dissolved phosphate, evidenced by regression against hydrographic data from nearby stations (Figure 3.5a). The resultant slope was 0.6 +/- 0.1 (R^2=0.6), and the y-intercept of -23μmol/mol is indistinguishable from zero within the regression error envelope (Figure 3.5a). Four samples were excluded from the calibration regression, for reasons stated below.
Figure 3.4. Locations of *D. dianthus* corals (closed circles) used to generate proxy calibrations (GeoMap).

The measured P/Ca linear regression slope of 0.6 differs markedly from the slope of ~7 measured in a previous calibration of P/Ca in the same species (Montagna et al. 2006). It is suspected that the discrepancy between the regression slope and that of Montagna et al. (2006) is a product of sampling approach. The authors acquired data by ablating the exterior of the septa, rather than thick sections, preceded only by a peroxide cleaning step and ~11μm depth of preablation (assuming average laser ablation of 0.1μm per shot, see Methods above). As described above, however, ablation of the exterior of septa requires more vigorous preablations to remove diagenetically altered material, Fe-Mn phases and other contaminants.
Although a useful test would be to analyze the same corals for Fe, the strong co-variation that Montagna et al. (2006) observed between Mn/Ca and P/Ca in *D. dianthus* ($R^2 \approx 0.5$, up to 0.8 along some ablation paths) is an indication of presence of Fe-Mn phases and co-occurring P. Such correlation was only seen in corals with anomalous Fe-Mn areas associated with high P, during ablations of the exterior of septa (Figure 3.2). It is proposed, here, that the 0.6 slope of the P/Ca proxy calibration represents more closely the composition of the uncontaminated fibrous aragonite, and that this material is only analytically accessible in *D. dianthus*, within practical limitations, by microsampling techniques on septal thick sections.

To investigate the sources of scatter in the P/Ca calibration, the correlation between linear regression residuals and candidate secondary variables was tested. For the corals used in the calibration no significant correlation was found between P/Ca residuals and temperature, salinity, pressure, pH or carbonate ion (all $R^2 < 0.3$). Since many hydrographic parameters in seawater co-vary, however, (e.g. seawater phosphate correlated with pH) this analysis of regression residuals needs verification through culture studies in which environmental variables can be isolated. Therefore dependence of P/Ca on both seawater phosphate and other variables, while not specifically observed in this study, could contribute to the scatter in the P/Ca-regression.

The mechanism(s) of P incorporation in corals remain poorly understood; hence the calibration presented in this chapter is fundamentally empirical. In tropical coral skeletons, P has been shown to be dominantly intra-crystalline in nature, meaning it is
distributed in or between individual aragonite crystals (LaVigne et al. 2008). Because *D. dianthus* corals are less porous than tropical corals, it is assumed that after preablation of thick sections, and accepting data that are reproducible with depth of ablation, the analyzed P/Ca in *D. dianthus* is also dominantly intra-crystalline.

Both inorganic and organic phosphorus are thought to be present in coral aragonite (Dodge et al. 1984; Shotyk et al. 1995, LaVigne et al. 2008). In support to this hypothesis, preliminary soluble reactive phosphorus (SRP; Koroleff 1983) analyses performed on three corals yielded inorganic phosphorus concentrations at <10% of the total coral phosphorus content. Intra-crystalline inorganic phosphorus could be the result of ionic substitution within the coral aragonite or inclusion of discrete particulate phases like hydroxylapatite (Macintyre et al. 2000) and iron-phosphates. Although the possibility of hydroxylapatite present in *D. dianthus* skeleton cannot be excluded (though it should dissolve and be analyzed as SRP), the presence of iron-phosphate can be refuted, because P/Ca is at least an order of magnitude higher than Fe/Ca in the studied corals, whereas Fe phosphates have a typical P/Fe ratio <0.12-0.23 (Feely et al. 1994).

Similarly to tropical corals, deep sea scleractinian corals contain up to 2.5% organic material (Cuif et al. 2004). Among the P rich organic material potentially present within the coral skeleton are lipids, DNA remnants and enzymes like alkaline phosphatase (Goreau et al. 1971). Recently, Farré et al. (2010) suggested that lipids are an important component of organic matter in the skeleton of deep sea scleractinia, dominated by phospholipids. So far, there is no available quantification of total lipids in the skeleton of
deep sea scleractinian corals. Performing a calculation similar to that in LaVigne et al. (2008), assuming up to 0.03% lipids per total *D. dianthus* skeletal material (Isa and Okazaki 1987), and an average phospholipid molecular weight of 800, phospholipids in *D. dianthus* could contribute up to 39µmolP per mol Ca. This concentration is within the lower range of the corals studied here, suggesting that phospholipids may contribute a significant portion of total skeletal P. Specialized studies are needed to further examine the nature of phosphorus in coral skeleton including synchrotron-XRF and NMR approaches. Despite the apparent organic nature of coral P/Ca, the results of this chapter indicate strongly that skeletal P concentrations are driven by variations in seawater inorganic phosphorus.

The possible effect of sample location on the scatter in the P/Ca calibration line was also examined. The coral specimens used in this study were collected from the Southern Ocean (poleward of 45°S), the N. Atlantic, the N. Pacific, and Pacific upwelling regions (Gulf of Alaska, California Coast, and Galapagos). No location-related bias was observed in the P/Ca values, with the exception of the four corals that were collected from upwelling regions, at depths where ambient waters are undersaturated with respect to aragonite ($\Omega_{\text{arag}} \leq 0.6$). The P/Ca values for these corals deviated markedly below the calibration regression defined by the remaining points and were not included in the regression (square symbols in Figure 3.5a). Although the regression residuals excluding the four outlier points do not correlate with any ambient seawater parameters, when the upwelling corals are included in the sample set, the regression residuals do show an overall correlation with pH ($R^2=0.4$).
It is suspected that corals living in seawater that is undersaturated with respect to aragonite are affected indirectly by bulk seawater pH. Undersaturation can drive slower net calcification rates, as observed for $\Omega < 0.8$ in tropical corals (Ries et al. 2010), due to the metabolic cost of achieving required levels of calcifying fluid supersaturation (Cohen et al. 2009). The mechanisms by which growth rate might affect P/Ca are not understood. Predictions and hypotheses are hindered at this point as the mechanism of P incorporation is unknown; models for elemental incorporation in non-biogenic carbonate are not directly comparable. Future studies in cultured corals could separately test the effect of aragonite undersaturation on coral P/Ca, especially for *D. dianthus*, in an effort to explain the observed offset in this study.

**3.6.2. The Ba/Ca Nutrient-Type Proxy**

The Ba/Ca ratios for 18 specimens of *D. dianthus*, plotted against available ambient Ba/Ca$_{SW}$ data, yield a proxy calibration over a wide range of Ba concentrations, with small error bars and a y-intercept near zero (Figure 3.5b). This is the first systematic calibration of the Ba/Ca proxy in a deep-sea coral. The *D. dianthus* Ba/Ca ratios are similar to those previously reported for the same species (Montagna et al. 2006), and the linear regression slope is $1.4 \pm 0.3$ ($R^2=0.6$), comparable to that determined previously for tropical corals and inorganic experiments for relevant temperatures (Lea et al. 1989; Dietzel et al. 2004). Of the corals analyzed, specimen 48470, located off the northern region of the Bay of Biscay, was located furthest away from a station with available
Ba\textsubscript{sw}, and thus the isopycnal approach employed here for deriving local Ba\textsubscript{sw} carries more uncertainty. Indeed this sample plotted as a notable outlier in the regression, and was thus excluded from the calibration (square symbol, Figure 3.5b).

The mechanism by which barium is incorporated into biogenic carbonate has been suggested to involve ionic substitution for Ca\textsuperscript{2+}, forming orthorhombic BaCO\textsubscript{3} (witherite) (Speer 1983; Dietzel et al. 2004). It was expected that Ba/Ca in \textit{D. dianthus} would have some degree of temperature dependence based on the work of Lea et al. (1989). Plotting the Ba/Ca calibration residuals against corresponding \textit{in situ} temperature, however, did not reveal a significant correlation (R\textsuperscript{2}=0.1). In support of this observation, Dietzel et al. (2004) reported <10% variation in average distribution coefficient of Ba/Ca for inorganic aragonite precipitated over the temperature range of 10-19°C. Therefore while some degree of Ba/Ca temperature dependence cannot be ruled out, it is expected to be small relative to dependence on dissolved Ba. Similarly, the dependence of Ba/Ca regressions residuals on salinity, potential pressure (McCorkle et al. 1995), pH, and carbonate ion, was investigated but none was observed (R\textsuperscript{2}<0.03 in all cases). Finally, there was no consistently unique behavior for corals from upwelling regimes as was found for the P/Ca calibration.

The Ba/Ca ratio therefore appears to be a relatively uncomplicated proxy for dissolved barium. The scatter around the calibration line is suspected to result primarily from the uncertainty in hydrographic data for Ba\textsubscript{sw}, but may also be affected by biological, growth rate, or regional effects that were not identified or quantified in this calibration work.
3.6.3. The U/Ca Carbonate Ion Concentration Proxy

Coral U/Ca (µmol/mol) is most strongly correlated with ambient seawater carbonate ion concentration (µmol/kg), among the hydrographic variables tested (temperature, salinity, pressure, pH). This correlation is strongly negative with a slope of -0.016 +/- 0.003 and y-intercept of 3.2 +/- 0.3µmol/mol (Figure 3.5c, R²=0.6, n=17). Carbonate ion concentrations were calculated from other reported carbonate system parameters using CO₂sys.exe (Ver. 1.05; Lewis and Wallace 1998; K₁ and K₂ were selected according to Mehrbach et al. (1973) refit by Dickson and Millero (1987)). The temperature, salinity, and pressure dependence of U/Ca was found to be negligible in D. dianthus, evaluated as above by plotting the residuals of individual samples in the carbonate ion linear regression against ambient hydrographic properties (R²<0.2 in each case).

Since the aqueous chemistry of uranium is influenced by the carbonate ion, which forms complexes with the uranyl ion (UO₂²⁺) (Langmuir 1978), variations of U/Ca in tropical corals are suspected to be related to changes in seawater carbonate ion, but U/Ca is demonstrably correlated with temperature, the dominant influence (Min et al. 1995; Shen and Dunbar 1995). In ooid formations, U content has also been shown to be inversely related to carbonate ion (Chung and Swart 1990). The results of this chapter showed that D. dianthus U/Ca declined by ~58% for a 100µmol/kg increase in carbonate ion, comparable to the 32% mean decline for the same carbonate ion increase observed in planktonic foraminifera cultures (Russell et al. 2004) but offset to higher U/Ca ratios in D. dianthus. This offset is expected since the ionic radius of UO₂²⁺ is larger than Ca²⁺ (Kitano and Oomori 1971), and therefore the aragonite lattice with its orthorhombic
structure and non-planar $\text{CO}_3^{2-}$ group would allow more freedom for large ion substitutions than would calcite (De Villiers 1971).

The scatter in the U/Ca carbonate ion calibration could be attributed to a number of factors, similar to those discussed for the P and Ba proxies; diagenesis and sample heterogeneity are not expected to have a major influence on the U/Ca calibration based on the sampling strategy followed. Further studies are needed however to fully quantify potential dependence of coral U/Ca on other hydrographic variables, e.g. temperature, which could cause an uncertainty in this calibration, although the hydrographic data did not indicate such an effect. The age of the analyzed corals is somewhat uncertain, adding potential error in the hydrographic properties assumed to be characteristic of ambient seawater conditions when the corals grew.
Figure 3.5. Calibrations of P/Ca, Ba/Ca, and U/Ca proxies in *D. dianthus* with seawater compositional variables. Uncertainties in equations represent 1SD, and the error envelope (dotted lines) is calculated from the 95% confidence interval of the slope. Error bars in y-axis represent SD of replicate ablation lines on single and/or neighboring septa. For symbols without error bars, error is smaller than symbol or single ablation lines were analyzed (Appendix, Table A1). Error bars in x-axis represent uncertainty (1SD) in relevant hydrographic data. Closed squares are outliers not used in the calibration regressions (see text).
According to physicochemical models of coral calcification, aragonite is precipitated from modified seawater within an extracellular calcifying compartment, where carbonate ion concentration is actively elevated above ambient concentrations, facilitating crystal nucleation and growth (Al-Horani et al. 2003; Holcomb et al. 2009). Nevertheless, calcification processes (e.g. calcification rate) could be sensitive to variations in the saturation state of the external environment (Langdon et al. 2000; Cohen and McConnaughey 2003; Ries et al. 2010), with implications for elemental incorporation, U speciation, U adsorptive efficiency, and ultimately coral U/Ca ratios. Potential routes by which carbonate ion could affect U/Ca incorporation in the coral aragonite are related to: 1) aqueous uranium speciation and diffusion, 2) subsequent adsorption and desorption, 3) ligand exchange reactions and rearrangement of ligand coordination, and 4) processes within the solid (e.g. solid diffusion and coordination changes; Russell et al. 2004 and references therein). The inverse relationship between coral U/Ca and carbonate ion could be a net result of several factors.

One of the processes affecting U/Ca in corals could be inhibition of adsorption of uranyl complexes on mineral and organic phases by high carbonate ion concentration because of competition for anion adsorption sites (Langmuir 1978; Barnett et al. 2000). Additionally, assuming that *D. dianthus* calcification rates increase with higher carbonate ion concentrations similarly to tropical corals (Kleypas et al. 1999; Schneider and Erez 2006), the U/Ca calibration implies that higher calcification rates suppress U incorporation. Coral studies and inorganic aragonite precipitation experiments suggest that tris-carbonated uranyl species are the dominant U-form in aragonite (Swart and
Hubbard 1982; Reeder et al. 2000). The precipitation studies of Reeder et al. (2000), however, were conducted at $\Omega_{\text{arag}}=15-28$ and pH>8, not realistic conditions for a coral environment. The calcite precipitation experiments at lower pH (Reeder et al. 2001), where mono- and bi-carbonate uranyl complexes were also observed, could be more suitable for revealing the uranyl complex structure within the coral skeleton. If coral aragonite incorporates these uranyl complexes, the increasing coral U/Ca at lower carbonate ion concentrations in this study could imply the additional incorporation of mono and bi-carbonate uranyl complexes whose abundance increases at lower pH.

Therefore, while the mechanisms may be complex and multiple, the result for *D. dianthus* is a simple and empirical anticorrelation between U/Ca and bulk seawater carbonate ion concentration. As a next step, inorganic aragonite precipitation experiments should be carried out to evaluate the carbonate ion effect on U/Ca ratios independent of vital effects and therefore to test the applicability of this proxy to paleoreconstructions.

### 3.7. Conclusions

In this work, P/Ca in the deep-sea coral *D. dianthus* is shown to be a linear function of seawater phosphate concentration. Further, it is demonstrated that a previously published calibration of *D. dianthus* P/Ca is valid in concept but incorrect quantitatively (~10 times lower slope in this work), while corals growing at $\Omega_{\text{arag}}<1$ have unusually low P/Ca relative to the main calibration regression. This work also establishes linear relationships for *D. dianthus* between Ba/Ca and dissolved barium concentration, and U/Ca and carbonate ion concentrations. These proxy calibrations do not display primary
or secondary residual dependence on temperature, salinity, or pressure. Additionally, P/Ca and Ba/Ca proxies appear to be insensitive to carbonate ion and pH variations.

The use of P/Ca and Ba/Ca in *D. dianthus* as complementary nutrient proxies is proposed. Whereas phosphate is regenerated mainly at thermocline depths, dissolved barium profiles resemble those of silicate and alkalinity (Chan et al. 1977; Ostlund et al. 1987) as particulate Ba is regenerated deeper in the water column (Bishop 1988). As tracers of water mass reorganizations in the past, reconstructed Ba concentrations would be more sensitive to shifts in the biogeochemical structure of deepwater, where the phosphate profile is relatively invariant, and phosphate would have more sensitivity to changes in the structure of thermocline and intermediate waters.

A carbonate ion proxy, measured in a regional set of depth-age distributed *D. dianthus* skeletons, would allow direct reconstruction of lysocline depth in the water column, which when combined with other proxies could provide clues to the importance of atmospheric CO₂, weathering, organic matter rain rate and burial, and carbonate dissolution on the relative position of carbonate saturation horizon and carbonate compensation depth (Archer and Maier-Reimer 1994; Sigman et al. 1998).

The P/Ca, Ba/Ca, and U/Ca calibrations could be used simultaneously with ¹⁴C and U- Th dating to derive ventilation rates in the past from the mixing ratio of distinct endmember water masses in regions with active mixing of intermediate and deepwater sources, like the Atlantic and Southern Oceans. Reconstruction of nutrient abundances and carbonate
ion distributions in regions where deep advection is sluggish and nutrient regeneration is relatively more important, like the deep North Pacific, could provide clues about basin-scale variations in export production, changes in whole-ocean nutrient inventory, and shifts in carbonate system equilibria on geological timescales.

The calibrations reported here are based on a globally distributed set of corals, and the scatter around the linear relationships suggests caution in using these calibrations for regional paleo-applications. Given the uncertainties in the calibration regressions of these proposed proxies, seawater phosphate can be reconstructed to +/-0.4μmol/kg (from 1.3-1.9μmol/kg P_{sw}), and seawater Ba to +/-19nmol/kg (from 41-82nmol/kg Ba_{sw}). Carbonate ion concentration derived from U/Ca has an uncertainty of +/-31μmol/kg (from 60-120μmol/kg CO_{3}^{2-}). The calibrations presented here provide a proof of concept and support the fundamental dependencies of the P/Ca, Ba/Ca and U/Ca proxies in *D. dianthus* on important biogeochemical variables for which paleo-records are currently sparse or controversial.
3.8. References


20\textsuperscript{th} CENTURY ACIDIFICATION IN SOUTH CHATHAM RISE RECORDED IN \textit{D. dianthus} CORAL USING $\delta^{11}$B AND A NOVEL GLOBAL CALIBRATION OF $\delta^{11}$B AS A PH PROXY

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4.1. ABSTRACT

The boron isotope ratio ($\delta^{11}B$) of some types of marine carbonates has been suggested to record seawater pH. To test the veracity and practicality of this potential paleo-pH proxy in deep sea corals, ten archived modern *Desmophyllum dianthus* (*D. dianthus*) corals were analyzed from a depth range of 274-1470m in the Atlantic, Pacific, and Southern Oceans, and compared measured $\delta^{11}B$ to ambient pH derived from the global hydrographic data base. The array of $\delta^{11}B$ values for these corals plotted above the seawater borate $\delta^{11}B$ vs. pH curve (Klochko et al., 2006b) by a constant value of 11.7 ± 2.3‰. This offset is attributed to either partial incorporation of boric acid from seawater, or to physiological manipulation of the calcifying fluid to 8.7-9.0pH, or some combination of the two processes. The uncertainty in calculation of seawater pH from $\delta^{11}B$, dominated by uncertainty in the offset value, currently limits the precision of absolute pH reconstructions to ±0.18pH units. However, with reasonable assumptions, the empirical calibration can be used to examine relative pH changes during the life of a single individual coral. The precision is then improved because it does not include the uncertainty in the offset of the $\delta^{11}B$-pH curve and replicates from a single coral agree within 0.35‰ (2SD). The calibration was applied to a specimen collected alive on the South Chatham Rise (New Zealand) at 275m depth. This coral grew for about one hundred years, so that independent $\delta^{11}B$ measurements on samples taken from the older and younger extremes of the skeleton were interpreted as a potential record of ambient pH over the 20th century “anthropocene”. The observed decrease of $\delta^{11}B$ over the lifetime of the coral, $1.25 \pm 0.16‰$ (2SD), is equivalent to a decline in pH of $0.19 \pm 0.08$, comparable within error to that predicted from atmospheric and local seawater records for
the effect of anthropogenic pCO$_2$ on upper ocean pH over this period. This study provides the first evidence that $\delta^{11}$B in deep sea corals can record ambient seawater pH.

4.2. INTRODUCTION

It is now well documented that atmospheric carbon dioxide (pCO$_2$) varied with the growth and decay of polar ice sheets over the last 800ka (Luthi et al., 2008; Petit et al., 1999). When atmospheric pCO$_2$ increases, it equilibrates with the surface ocean, decreasing seawater pH, an effect ultimately buffered by calcium carbonate compensation on long time scales (Archer and Maier-Reimer, 1994; Broecker and Peng, 1987). However, the driving mechanisms that cause these pCO$_2$ variations, and how they relate to the Earth’s climate are not well constrained. Additionally, since the Industrial Revolution, atmospheric CO$_2$ has varied beyond the range of natural Pleistocene variations, displaying a sharp increase (Keeling, 1961; Luthi et al., 2008; Petit et al., 1999) resulting mainly from burning of fossil fuels (Boden et al., 2010). There is concern for the long term response of marine calcifying organisms to this abrupt ocean acidification (Hoegh-Guldberg et al., 2007). Insights into these issues as they pertain to the recent and distant past can be gained by developing paleo-proxies for aspects of the ocean carbonate system, including the boron isotope proxy ($\delta^{11}$B) for seawater pH. An important test of such proxies can in principle be carried out using corals that grew over the last ~ one hundred years, during which time variations in both atmospheric CO$_2$ and upper ocean pH are relatively well known.
The biogenic carbonate $\delta^{11}$B proxy has been explored and described in extensive detail
(Hemming and Hanson, 1992; Hönisch and Hemming, 2005; Klochko et al., 2006a; Sanyal et al., 1996; Spivack et al., 1993; Zeebe et al., 2001; Zeebe et al., 2003). At
a typical modern seawater pH boron (B) exists mostly in the forms of boric acid (B(OH)$_3$) and borate ion (B(OH)$_4^-$) with a distinct isotopic fractionation between the two species (boric acid is 27.2‰ heavier than borate ion (Klochko et al., 2006a)). The relative
abundance of these two B species is pH dependent and the total B isotope composition of seawater is constant over periods substantially shorter than the residence time of B in the ocean (14 million years for boron compared to ~3 million years for boron isotopes, Lemarchand et al. 2000, Paris et al. 2010). Therefore the isotopic composition of each
species for recent times in earth history depends entirely on pH.

On the basis of the similarity of the boron isotopic composition of all marine carbonates to that of seawater borate, boron has been believed to be incorporated into biogenic and inorganic carbonates largely as the borate species (Hemming and Hanson, 1992), and such preferential incorporation results in the $\delta^{11}$B of marine carbonates tracking the $\delta^{11}$B of borate ion and thus being sensitive to pH variations, with a typical ~1‰ increase in $\delta^{11}$B for every 0.1 unit increase in seawater pH. Boron isotope measurements in foraminiferal calcite and tropical coral aragonite have been used extensively as a proxy of surface oceanic pH (Hönisch and Hemming, 2005; Hönisch et al., 2009; Palmer and Pearson, 2003; Pelejero et al., 2005; Sanyal and Bijma, 1999). However, there have been only a few efforts to reconstruct the evolution of intermediate to deep ocean pH using this proxy (Hönisch et al., 2008; Sanyal et al., 1995; Yu et al., 2010). Verifying the boron
isotope–pH proxy in a new carbonate archive - Deep Sea Corals (DSC) – will allow the
generation of deep ocean pH records, with very precise absolute dating and the potential
for annual to decadal scale resolution within one coral specimen.

The boron isotope proxy applied to DSC offers several advantages compared to
foraminifera: DSC are not only cosmopolitan in geographic distribution but also provide
snapshots of climate records with a subdecadal resolution that only ice cores can rival;
most species are aragonitic, so they are relatively rich in B (~70 ppm) allowing analyses
of small samples with high precision. DSC do not harbor symbiotic algae, hence
physiological processes related to zooxanthellae activity, which are sources of pH
sensitive vital effects in corals (Al-Horani et al., 2003), are not present, potentially
simplifying the development of a pH proxy in this material. Yet DSC are often found
growing in conditions unfavorable for aragonite precipitation (\( \Omega_{\text{arag}} < 1 \), where \( \Omega_{\text{arag}} = [\text{Ca}^{2+}][\text{CO}_3^{2-}]/K'_{\text{arag}} \), and \( K'_{\text{arag}} \) is the apparent solubility product of aragonite) (Guinotte et al., 2006) raising the suspicion that they have mechanisms to modify significantly the
pH of their internal fluids to elevate the aragonite saturation of the calcifying fluids and
thus induce carbonate precipitation. Additionally, vital effects could be caused by
respiration or other aspects of polyp metabolism or by variations in calcification rate (e.g.
(Adkins et al., 2003; Goreau, 1977; Krief et al., 2010; McConnaughey, 1989)). In
foraminifera modeling studies it was shown however that the presence of such biological
factors does not necessarily compromise the \( \delta^{11}\text{B} \)-pH proxy if their effect is considered
constant over a range of relevant pH (Zeebe et al., 2003).
One of the most studied DSC with respect to paleo-proxy development is the solitary species *Desmophyllum dianthus (D. dianthus)*. This coral grows a ~10cm long aragonitic skeleton over a period of ~100y with linear extension rate of 0.5-2mm/y (Adkins et al., 2004). One of the major advantages of this species for paleoceanographic reconstructions is the ability to date individual specimens very precisely with U-series radiometric measurements (Cheng et al., 2000; Edwards et al., 2003; Goldstein et al., 2001; Schroder-Ritzrau et al., 2003). Coupled radiocarbon and U/Th measurements on *D. dianthus* have been used to test theories of climate change across a number of abrupt transitions (Adkins et al., 1998; Frank et al., 2004; Mangini et al., 2010; Robinson et al., 2005). The relatively large size of these corals provides enough aragonite to allow the measurement of multiple geochemical proxies, thereby revealing complementary aspects of paleoclimate in a single carbonate archive, a rare luxury.

Here the first calibration of the $\delta^{11}B$ proxy in globally distributed modern *D. dianthus* coral specimens is presented, against ambient pH for their growth locations. The resulting calibration is then used to interpret a $\delta^{11}B$ shift over the lifespan of a single coral collected live in South Chatham Rise (NZ) in the context of observed 20th century acidification of the upper ocean at this location.

### 4.3. Materials and Methods

#### 4.3.1. Sample preparation and analytical approach

Corals were sampled from the National Museum of Natural History (Smithsonian Institution, Washington, D.C.) and from the National Institute for Water and Atmosphere
Coral septa were separated mechanically and cleaned with a power dental saw to remove any surface crust material. For the Z9725 coral, which was sampled for determination of isotopic composition changes over its lifetime (below), two septa were isolated and sub-sampled, with one sample coming from the most recently calcified top 7mm of the two septa, and the other from the oldest, bottom 10mm section of both septa combined (Table 4.1, Figure 4.2). Subsequently, the coral pieces were rinsed and ultrasonicated with distilled water several times, and any remaining tissue was removed with a brush. Next, the corals were dried in a laminar flow clean bench and crushed to < 2mm pieces. The sampling strategy was aimed at collecting enough coral material to average any sample inhomogeneity with respect to boron (B) isotopes (Blamart et al. 2007) (Table 4.1).

Boron purification followed the micro-sublimation method established by Wang et al. (2010), and isotopic analyses were performed using multi-collector inductively coupled plasma mass spectrometry (MC-ICPMS) (Neptune, Thermo Scientific) at the National
Cheng Kung University, Taiwan, modified from previously published methods (Foster 2008). Typical operating conditions and introduction system details are summarized in Table 4.2. Similarly to the methods of Foster et al. (2008), sample gas flow rate was tuned daily to optimize signal stability rather than intensity. Instrumental mass bias was adequately corrected using a standard-sample bracketing technique (Foster, 2008; Wang et al., 2010). The standard used was NIST SRM 951 boric acid. Solution concentrations were typically 20ppb B, which gave 0.4-0.5 V of $^{11}$B signal intensity. Each analytical session allowed the measurement of 24 samples with < 5% drop in sensitivity. Every sample was analyzed in duplicate and an average value with the $2\sigma$ uncertainty is reported. A number of corals were sub-sampled, and the sub-samples crushed and processed as different samples, while for two corals the crushed skeleton was homogenized and split into duplicate subsamples (Table 4.1).
Table 4.1. The *D. dlugoszorum* corals used in this study.

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<th>weight (mg)</th>
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<th>δ¹⁵N (%)</th>
<th>δ¹³C - 2SD(%)</th>
<th>δ¹³C range (%)</th>
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* subsampled from the same solid aliquot, while rest of replicate analyses were separate subsamples of the same coral, crushed and processed.
Given the poor wash out and increased memory effect characteristics of B compared to other elements (see e.g. Al-Ammar et al. 2000) B concentrations in standards were kept to 20ppb B, and samples were diluted to 20-40ppb B prior to analyses. Samples, standards and washes were introduced in 0.1M HNO$_3$. The wash out using this protocol reduces signal to less than 2.5% of initial in 110s, following introduction of 50ppb B samples. The blanks of a typical run that included a variety of samples (20-40ppb B) and NIST SRM 951 boric acid standard (typically 20ppb B) were monitored. It was observed that the magnitude of the wash out is sufficient to result in a reproducible and quantifiable contribution of blank to measured NIST SRM 951 intensities through the whole run (<1ppb B or 0.01V for $^{11}$B).

There are two known interferences associated with $\delta^{11}$B measurements. The isobaric interference of $^{40}$Ar$^{4+}$ on $^{10}$B is fully resolved at low mass resolution mode ($M/\Delta M = 500$) on the MC-ICPMS. In contrast, the $^{10}$B$^{+}$H$^{-}$ molecule interference on $^{11}$B is not resolvable at the selected resolution on the Neptune instrument, but no satellite peak was observed on scans at high resolution, indicating negligible hydride formation.
Figure 4.2. Sampling of *D. dianthus* sample Z9725: Left is the whole coral after removal of septa. Middle is the septa-cluster that was removed prior to cleaning (see text). Right is the cleaned, partially joined septa used to sample the top and bottom portions for $\delta^{11}\text{B}$ (orange lines describe vertical extent of sampling of each area). White scale bar represents 7mm.

4.3.2. **Accuracy and precision**

To overcome the lack of accepted reference standards for B isotope composition, the JCp-1 carbonate standard was used that has been extensively tested for $\delta^{11}\text{B}$ by MC-ICPMS, N-TIMS and P-TIMS (Aggarwal et al., 2009; Wang et al., 2010). In this work analyses give a long-term precision of $24.41 \pm 0.30\%\_\text{SD (n=10)}$, in agreement with $24.22 \pm 0.28\%\_\text{SD$ as reported in Wang et al. (2010). Additionally, repeat analyses of an in-house high purity solution standard (Alfa-Aeser) exhibited a high level of reproducibility ($-5.41 \pm 0.19\%\_\text{SD; n = 16}$). Based on typical external reproducibility at the 95%
confidence level, only coral analyses with less than ±0.35‰ uncertainty in duplicate $\delta^{11}$B measurement of the same solution were accepted for use in this study. In total 24 samples were analyzed, of which five did not meet the uncertainty criteria and were therefore rejected.

### 4.3.3. Data analysis

The ten deep-sea coral specimens used for the calibration analyses were selected based on the availability of close proximity seawater pH data. Although the corals were not dated, they are assumed to have been collected alive since residual animal tissue was observed on all corals but specimens 94069 and 48739. These corals were growing in areas with varying well-constrained seawater properties, depending on availability of reliable alkalinity and dissolved inorganic carbon (DIC) concentrations from the CDIAC ocean carbon system database (http://cdiac.ornl.gov). Using the carbonate system calculation software CO2sys.xls (Pelletier et al., 2007) with constants from Mehrbach et al. (1973) refit by Dickson and Millero (1987), available alkalinity and DIC concentrations was used to calculate ambient pH. Typically, independent direct pH measurements listed in the CDIAC database are within ± 0.01pH of the calculated pH values derived from CDIAC alkalinity and DIC data. Larger pH differences are observed between temporal reoccupations and between pH values determined at similar depths at relatively nearby stations, particularly for coral locations in the Gulf of Alaska and along the California coast, possibly related to secular trends or temporal variations in hydrographic properties driven by climate change or natural oceanic variability (Table 4.1). Since independent pH measurements were carried out only at some of the coral
locations, the pH uncertainty of ± 0.01 was used for stations where calculated pH could not be thus verified. This conservative estimate of uncertainty was based on station reoccupations and measurements at nearby stations, when available, taking into consideration oceanographic distance from the coral site and seasonal variations. Corrections for anthropogenic CO₂ by subtracting its total regional cumulative contribution to DIC and recalculating pH (Sabine et al., 2004) was also attempted. Such a correction resulted in ~0.01 pH error when seawater data were available, and thus was ignored.

4.4. RESULTS AND DISCUSSION

4.4.1. Calibration

The B isotopic composition of the *D. dianthus* corals displays a strong dependence on pH across a wide range of oceanographic locations (Figure 4.3, Table 4.1). The Figure 4.3 includes the seawater borate $\delta^{11}$B-pH curve (Klochko et al., 2006a) and the $\delta^{11}$B-pH relationship from various published tropical coral culture studies. Since a significant error in the vibrational spectrum term of borate used by Kakihana et al. (1977) was identified recently (Klochko et al., 2006a; Rustad and Bylaska, 2007), the value of $\alpha_B=1.0194$ (Kakihana et al., 1977) was considered as a lower extreme of empirical fractionation factors used to describe some marine carbonates (Hönisch et al., 2004; Reynaud et al., 2004; Sanyal et al., 2001; Sanyal et al., 1996). It was observed that all published coral results plot above the seawater borate curve, while the Kakihana et al. curve (1977) approximates the $\delta^{11}$B-pH curve for tropical corals (Figure 4.3). The *D.
dianthus $^{11}$B values are substantially lower than those measured on another deep sea coral, Lophelia pertusa (L. pertusa) (Blamart et al., 2007). Blamart and co-authors used an ion-microprobe technique to determine $^{11}$B of centers of calcification and fibrous aragonite within the skeleton of L. pertusa, resulting in values that were mostly $>$30‰ $^{11}$B, with $\sim$10‰ $^{11}$B spatial variations. Although these results have not been replicated so far, and the variations in $^{11}$B cannot be explained by previously considered mechanisms of calcification (Rollion-Bard et al., 2011), large enough skeletal samples were excised to average any structural inhomogeneities in $^{11}$B, and test the potential of a $^{11}$B-pH proxy method characterized by good reproducibility and ease of $^{11}$B measurements.

The corals analyzed grew over a wide depth range, in waters of differing temperature and salinity, making a direct comparison of coral $^{11}$B to the seawater borate $^{11}$B-pH curves (typically at 25°C, 1 atm, and S=35) problematic since each coral $^{11}$B corresponds to a different seawater borate curve determined by these same factors. Instead the predicted $^{11}$B was calculated using ambient seawater pH (total scale) and the following equation:

$$\text{pH} = \text{pK}_B^* - \log\left(-\left(\delta^{11}\text{B}_{sw} - (\delta^{11}\text{B}_{coral})/(\delta^{11}\text{B}_{sw} - \alpha_B)(\delta^{11}\text{B}_{coral}) - (1-\alpha_B)*1000)\right)\right) \ (a)$$

where $\text{pK}_B^*$ is the equilibrium constant between boric acid and borate at ambient temperature and salinity conditions (Dickson, 1990; Wang et al., 2010), $\alpha_B$ is 1.0272
(Klochko et al., 2006a), $\delta^{11}B_{sw}$ is the isotopic composition of seawater (39.5‰), and $\delta^{11}B_{coral}$ the measured isotopic composition of *D. dianthus*.

Figure 4.3. Coral $\delta^{11}B$ plotted against ambient seawater pH. Error bars represent 2SD uncertainties based on replicate analysis (see also Table 4.1). Pairs of closed circles at the same pH represent two crushed skeleton subsamples from the same *D. dianthus* coral, carried through the entire preparation and analysis as independent samples. The lines represent seawater borate $\delta^{11}B$ vs. pH as calculated by Kakihana (dashed blue) and Klochko (solid orange). Published data from tropical coral $\delta^{11}B$-pH culture studies are also included.
The $D.\ dianthus$ $\delta^{11}\text{B}$ are $\sim 5\%$ heavier than that of tropical surface corals $Porites\ sp.$ and $S.\ pistillata$ for similar ambient pH conditions (Klochko et al., 2006a; Krief et al., 2010) and $\sim 8\%$ heavier than those for the foraminifera $O.\ universa$ at pH $= 8.19$ (Kasemann et al., 2008). The difference in absolute $\delta^{11}\text{B}$ content point potentially to different mechanisms of calcification and B isotope incorporation between these groups of calcifying organisms. Although the bulk analysis approach that was followed in this study cannot offer a clear understanding of the mechanism of boron inclusion in the biomineralization of $D.\ dianthus$, the heavy $\delta^{11}\text{B}_{\text{coral}}$ compared to seawater borate $\delta^{11}\text{B}$ indicates several potential causes. The tropical coral and planktonic foraminifera $\delta^{11}\text{B}$ offset is suggested to be the result of some combination of of (1) unidentified vital effects, (2) manipulation of calcifying fluid pH through a net light-calcification influenced by photosynthesis (resulting in recording higher pH than expected from ambient seawater pH) (Hönisch et al., 2004; Krief et al., 2010; Reynaud et al., 2004), and (3) possible uptake and incorporation of the isotopically heavier boric acid species during mineralization with potential subsequent isotopic redistribution through intermediate boron-complexes (Klochko et al. 2009).

The offset for deep sea corals could not be caused by photosynthesis, because deep corals have no symbiotic algae and they grow in the absence of light. Instead, polyp metabolism, physiological modification of the calcifying fluid pH, and possible incorporation of boric acid are possible mechanisms contributing to the observed offset. First, it is not clear how polyp metabolism affects $D.\ dianthus$ $\delta^{11}\text{B}$. The deep sea coral
D. dianthus has been shown to calcify using seawater DIC instead of metabolic CO₂ (Adkins et al., 2002), therefore respiration is not expected to affect significantly calcifying fluid pH and δ¹¹B.

Second, it is reasonable that corals need to increase the calcifying fluid pH to enhance calcification (Erez et al., 2011), a mechanism especially relevant to D. dianthus surviving in waters with Ω₉₅<1 (Table 4.1). How physiological pH adjustment will affect boron isotopes and incorporation in coral aragonite remains an unanswered question (Rollion-Bard et al. 2010; 2011). To achieve desirable pH and control their DIC composition, tropical corals use two enzymes: carbonic anhydrase (Furla et al., 2000) and Ca-ATPase (Cohen and McConnaughey, 2003; McConnaughey and Whelan, 1997). The combined action of Ca-ATPase, which assists proton transfer and thus carbonate ion increase, and of carbonic anhydrase, which speeds the dissociation of bicarbonate ion to carbonate ion, can result in Ω₉₅>1 in the calcifying fluid without the assisting influence of zooxanthellae photosynthesis.

Third, if boric acid is incorporated in the coral aragonite, as suggested for L. pertusa (Rollion-Bard et al., 2011) and other marine carbonates (Klochko et al., 2009), an increase in coral δ¹¹B relative to that resulting from borate uptake and incorporation would be expected. Most of the corals reside at pH ~8, with an average δ¹¹B ~27‰. At this pH, seawater boric acid is ~82% of total boron, while the isotopic composition of boric acid and borate ion are ~44‰ and ~16‰ respectively (using α₉ of Klochko et al.
Thus if corals incorporate boron for example as 40% boric acid and 60% borate, their δ¹¹B would be expected to equal 27.2‰, explaining the mean skeletal δ¹¹B, without further isotopic modification or alteration of calcifying fluid away from ambient pH. If it is assumed that both *D. dianthus* and *L. pertusa* are characterized by similar boron biomineralization mechanisms, and that the pH of calcification fluid equals that of ambient seawater, δ¹¹B measurements imply that bulk coral samples have boric acid fractions more closely related to that recently published for centers of calcification (47.7 ± 5.3%, Rollion-Bard 2011) which are suggested to record seawater pH more directly than fibrous aragonite, based on NMR measurements in *L. pertusa* (18.2 ± 2.6%, Rollion-Bard 2011). The significant incorporation of boric acid in *D. dianthus*, however, remains a hypothesis that is yet to be thoroughly tested.

The apparent pH at the calcifying site was calculated using the seawater borate fractionation factor and the coral δ¹¹B (Figure 4.4), assuming in this case incorporation of borate ion only, to investigate potential variations in the pH of the calcifying fluid as a function of ambient pH. The data suggest that the corals modify their calcifying fluid pH by a variable amount that is inversely related to ambient pH. The calcifying fluid pH calculates to within 8.7-9.0, consistent with the few published results from micro-sensor studies (Al-Horani et al., 2003) and with δ¹¹B measurements in tropical corals (Krief et al., 2010). For a calcifying fluid pH of 8.8, calculated as the average Klochko-based predicted pH for the corals, and dissolved inorganic carbon concentration (DIC) unaltered
from that of ambient seawater, the $\Omega_{\text{arag}}$ is within the range of 7-9 for all of the $D. dianthus$ specimens, which is in general agreement with nighttime calcification $\Omega_{\text{arag}}$ (<10) as predicted for tropical corals (Cohen and McConnaughey, 2003). These results suggest that physiological pH adjustment of the calcifying space, greater at lower ambient pH, without an isotopic effect of boric acid incorporation in the skeleton, could reasonably explain these results.

A physiologically driven variable pH adjustment to a calcifying fluid pH of 8.7-9.0 could result in an observed constant offset in the $\delta^{11}$ B from the seawater borate curve. Alternatively, incorporation of a constant amount of boric acid, independent of ambient pH would also result in the same observation. How these two mechanisms might combine to result in the observed $\delta^{11}$ B for $D. dianthus$ corals is unclear. Graphically and mathematically, offsetting the seawater borate curve by a constant value requires a pH offset that is more pronounced at lower pH values (Figure 4.5). Additional studies, however, on the boron species and their isotopic composition in both the centers of calcification and in fibrous aragonite skeletal regions, specifically for $D. dianthus$, are required to distinguish bulk skeletal measurements from signals contained in component microstructures, and to distinguish the isotopic effects of physiological pH adjustment from those of potential boric acid incorporation. Determining directly the pH at the calcifying site of DSC is surely needed and should be further developed, but is methodologically very difficult.
Figure 4.4. Offset between ambient pH (total scale) and the pH recorded in corals assuming only borate ion is incorporated. Predicted pH is calculated using the seawater borate curve (equation (a) with Klochko fractionation factor) for ambient conditions. Diamonds are coral data, and red line represents a 1:1 relationship between coral-recorded pH and ambient pH.
Figure 4.5. Scenario of seawater borate $\delta^{11}\text{B}$ curves offset by a constant number resulting in variable changes in pH at certain $\delta^{11}\text{B}$ concentrations, as a result of this offset, with largest difference observed at lower pH.

Nevertheless, using a constant offset in $\delta^{11}\text{B}$ from the seawater borate curve is practical for paleoreconstructions. When the coral $\delta^{11}\text{B}$ is plotted against the predicted $\delta^{11}\text{B}$ of seawater borate calculated for ambient conditions, the resultant relationship is linear and offset from the 1:1 line by a constant value, within error (Figure 4.6) ($R^2 = 0.6$, $p < 0.05$). For this calculation, the temperature and pressure dependence of the Klochko $\alpha_{\text{B}}$ value is ignored, because it currently remains unresolved. If instead Zeebe’s (2005) scenarios are followed on the temperature sensitivity on $\alpha_{\text{B}}$, similar to the approach of Hönisch et al. (2008) and Rae et al. (2011), the resultant offsets between coral $\delta^{11}\text{B}$ and predicted borate
\( \delta^{11}B \) are highly variable \((R^2 \leq 0.5 \text{ compared to } R^2 = 0.6 \text{ for no temperature dependence})\).

Additionally, there is no significant relationship \((R^2 = 0.1)\) between the offsets of coral \( \delta^{11}B \) from predicted borate \( \delta^{11}B \) and ambient temperature, consistent with observations for benthic foraminifera \( \delta^{11}B \) (Rae et al., 2011).

Based on this empirical result, the equation that best describes the relationship between pH and the \( D. dianthus \) \( \delta^{11}B \), is:

\[
pH_{\text{tot}} = pK_B^* \cdot \log\left(-\left(\delta^{11}B_{\text{sw}} - \delta^{11}B_{\text{coral}} + 11.7\right)/(\delta^{11}B_{\text{sw}} - 1.0272*(\delta^{11}B_{\text{coral}} - 11.7) - 27.2)\right) \quad (b)
\]
The uncertainty in the $\delta^{11}$B offset is $\pm 2.3\%$ (1SD), which includes the uncertainty in the assumption that the relevant value of $\alpha_B$, as it applies to boron incorporation in $D$. 

$dianthus$ is that of Klochko et al. (2006). For coral Z9725, the application sample discussed below, such uncertainty propagates to a 0.15 pH error, but the constant $\delta^{11}$B model implies that the error could be amplified for corals growing at lower ambient pH conditions. The uncertainties for $\delta^{11}$B$_{coral}$, $\delta^{11}$B$_{sw}$, and pK$_B$* are equal to $\sim 0.35\%$, $\sim 0.15\%$ (derived from comparison to Foster et al. (2010)), and $\sim 0.004$ (Dickson, 1990) contributing pH errors of 0.02, 0.01, and 0.004, respectively. The uncertainty of pH reconstruction, propagating all errors, is as much as $\pm 0.18$ pH units, dominated by the error in the calculation of the $\delta^{11}$B offset, as driven by the scatter in the coral data. Thus the current proxy calibration uncertainty does not allow usefully accurate pH reconstructions on a single coral given expected seawater pH variations during the Pleistocene and since the Industrial Revolution.

However, it is observed that sub-samples of the same corals are characterized by closer agreement than is implied by the scatter evident in the calibration data as a whole (see replicate analyses of Table 4.1). This is a potential indication of consistent vital effects within a single coral, or similar skeletal heterogeneity within a single specimen, compared that occurring across specimens. At present, therefore, the use of gradients in $\delta^{11}$B$_{coral}$ within one specimen is suggested with the goal to reconstruct decadal to centennial changes in pH, overcoming not only the error in the mean offset of $\delta^{11}$B$_{coral}$, but also intra-specimen variations due to heterogeneous sampling and variable vital
effects. The uncertainty in the assumed value of $\alpha_B$ remains however a difficult number to estimate and it is expected to become more important at lower pH where the slope of the $\delta^{11}$B-pH curve is more sensitive to the value of $\alpha_B$ (e.g. Kakihana vs. Klochko on Figure 4.3). Alternatively, using average $\delta^{11}$B from multiple co-located corals of the same age could potentially provide a better constraint on absolute pH reconstructions offering therefore the potential for time series reconstructions using fossil corals dated to various paleo-ages (this assumes freedom for diagenetic artifacts in fossil corals, an issue not yet investigated).

To test the potential influence of other hydrographic parameters on $\delta^{11}$B, the offsets of coral $\delta^{11}$B from the $\delta^{11}$B predicted using the Klochko fractionation factor were plotted against ambient salinity, pressure, carbonate ion concentration, or temperature. For the ten corals used for the calibration here, there was no obvious relationship between coral $\delta^{11}$B and any of these ambient seawater properties (all correlations resulted in $R^2 \leq 0.2$).

### 4.4.2. Application of $\delta^{11}$B to pH variations during a single coral lifespan

As a further test of the validity of the B isotope proxy in *D. dianthus*, the changes in skeletal $\delta^{11}$B over the lifespan of a single specimen was examined and compared to seawater pH changes at the growth site resulting from anthropogenic CO$_2$ invasion over the past century. Coral specimen Z9725 was collected alive in 1999 at 275m depth on the South Chatham Rise east of New Zealand. Its length along the maximum growth axis is
Assuming a 0.5-1mm/y growth of this species (Adkins et al., 2004; Cheng et al., 2000), this represents 55-110 years of growth.

In this region, radiocarbon measurements during January to March of 1979 to 2000 showed penetration of bomb radiocarbon to depths below that of this coral, indicating significant atmospheric CO₂ mixing below this depth (Sikes et al., 2008; Sparks, 1989). In support of this observation, mixing depths in this region of the southern ocean are regularly on the order of 500m (Sallee et al., 2010). Additionally, it is observed that during the same months dissolved CO₂ concentrations in the surface mixed layer are representative of annual mean sea surface conditions (Munida Time Series, Currie et al. 2009). It is assumed, therefore, that the coral location at 275m, and the resulting pH record in the coral, will be related to surface water pH.

The δ¹¹B of the bottom, older section of this coral was 27.57 ± 0.10‰ (2SD) and the top section gave a value of 26.32 ± 0.13‰ (2SD) (Table 4.1). This shift in coral δ¹¹B is consistent with a drop in ambient pH during the lifespan of the coral, as expected from the rise in atmospheric pCO₂ over the 20th century. The difference in δ¹¹B between the top and bottom part of the coral was used to calculate the magnitude of the pH change. Although individual pH reconstructions using the paleo-pH equation (b) have a large uncertainty, the δ¹¹B in the top and bottom parts of the coral correspond to reasonable pH of 7.85 and 8.04 respectively. The pH change is thus equivalent to 0.19 units. If, as an exploration of uncertainty, the Kakihana curve is used as an empirical analogue of
tropical corals’ fractionation factors, but offset by 5‰ (offset between \textit{D. dianthus} and tropical corals) then the pH change is equivalent to 0.21 units.

The pH reconstructions for top and bottom parts of the coral are reasonable for surface seawater, within the 0.18 pH uncertainty, while the reconstruction of change in pH carries a much smaller error, assuming the magnitude of the offset remains constant over the life of a single specimen. If so, then the uncertainty in the pH change does not include the uncertainty in the δ\textsuperscript{11}B offset (which results from analysis of multiple specimens) and the uncertainty is reduced to ±0.03 pH units (which includes the propagated uncertainty of measurement and seawater δ\textsuperscript{11}B and that of pK\textsubscript{B*}), ignoring uncertainty in the assumed value for α\textsubscript{B}. The latter uncertainty can be estimating by examining the difference between the pH change reconstructions using the Kakihana vs. Klochko fractionation factors. Inclusion of this uncertainty brings the total error to ±0.04 pH units. Any error due to sample heterogeneity can be estimated conservatively using the coral with the largest sub-sampling uncertainty, \textit{D. dianthus} 47413 (±0.40‰ 2SD or ~ 0.04 pH, Table 4.1). Therefore the total error of this pH change reconstruction is calculated to be up to ±0.08 pH.

To estimate coral pH, the LDEO (WAVES) database (V.2009) (Takahashi et al., 2010) was used for pCO\textsubscript{2} measurements within the South Chatham Rise region from 44°S to 46°S and from 173°E to 179°E. Seawater CO\textsubscript{2} measurements (pCO\textsubscript{2_local}) are offset by ~40μatm from atmospheric pCO\textsubscript{2} measured in the Law Dome ice core (Etheridge et al.,
1996) and in flask air samples (Keeling et al., 2001) (Figure 4.7) suggesting a constant disequilibrium of surface seawater of the South Chatham region, making it a net sink for atmospheric pCO₂. To estimate the surface water pH trend from these data, the pCO₂ data from the WAVES database (http://cdiac3.ornl.gov/waves/underway/) were used in combination with salinity and temperature data from the same database. Salinity and alkalinity are linearly correlated for the upper 400m of WOCE line P15S stations proximate to South Chatham Rise (Table 4.3), and missing salinity data can be interpolated with salinity values from nearby stations and times. Using the alkalinity-salinity relationship alkalinity was derived for the LDEO time series and calculated pH (pHtot_local) as described in the Methods above. Additionally, a pH trend was calculated for the entire 1900-1999 period using Law Dome and air sample CO₂ concentrations, offset by -40μatm and assuming that temperature, salinity, and thus alkalinity was approximately unchanged. This pH trend was then compared with the 1961-1999 period where hydrographic data including seawater pCO₂ in the region are available (Figure 4.7).

<table>
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<th>Latitude (N)</th>
<th>Longitude (E)</th>
<th>Year</th>
<th>Temp (°C)</th>
<th>Salinity (psu)</th>
<th>pCO₂ (μatm)</th>
<th>Alkalinity (μmol/kg)</th>
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Table 4.3. Available hydrographic data for South Chatham Rise (LDEO underway database V.2009). Alkalinity is calculated from a regional salinity-alkalinity relationship while pHtot is calculated using CO₂sys. Blue (bold) denotes assumed values (see text).
The resultant derived trend in surface water pH for the ~40 year period from 1961 to 1999 implies a temporal gradient of 0.0017pH units per year (Fig. 4.7). If the coral is 100y old, and assuming as a rough approximation that the pH gradient is ~constant over the 20th century, then the hydrographic data predict a total change of 0.17pH over the life of the coral. Performing the same calculation but using instead the pH prediction for the year 1900 from the Law Dome ice core pCO2 data, the total change in mixed layer pH from 1900-1999 is ~0.10 units. The top to bottom pH difference of 0.19±0.08 determined from the Z9725 coral specimen is in reasonable agreement with the expected pH change derived from hydrographic observations, given the multiple uncertainties in this analysis, not least of which is the true age of the coral. These findings, the first attempt to reconstruct pH in subsurface waters over the lifetime of a deep coral, support the overall findings of the δ11B proxy calibration and upon further development could be used to reconstruct both mean ambient pH over the growth period of individual *D. dianthus*, and temporal pH gradients over its lifetime.
Figure 4.7. Shipboard underway historical data (LDEO WAVES V.9) for the South Chatham Rise, compared to estimates of regional surface water pH variations based on atmospheric pCO₂ measurements and estimated degree of local surface mixed layer disequilibrium. All local measurements are described in Table 4.3. Green line represents linear regression of time series of local surface ocean pHₜot (green squares) calculated from pCO₂ measurements (blue diamonds), while dashed line represents reconstructed mixed layer pH using Law Dome pCO₂ (orange line with asterisks (Etheridge et al. 1996)) offset by -40µatm (blue line) to represent local sea surface pCO₂ values, as derived from local data (blue diamonds). Solid, orange triangles represent atmospheric pCO₂ measurements from Bearing Head, NZ (Keeling et al. 2001).
4.5. Conclusions

This study demonstrates the feasibility of using $\delta^{11}B$ in the scleractinian deep sea coral *D. dianthus* to reconstruct seawater pH. Calibration of *D. dianthus* $\delta^{11}B$ against seawater pH results in a curve that is parallel to, but plots above, the seawater borate $\delta^{11}B$ vs. pH curve (Klochko et al., 2006a) by $\sim$11.7‰. Such behavior could be explained through modification of the calcifying fluid pH to a value of 8.5-9.0, partial incorporation of the heavier boric acid species, or some combination of boric acid incorporation and pH modification with larger apparent modification at low pH (and therefore low aragonite saturation) in the ambient seawater environment. Nonetheless the constant offset suggests a consistent relationship that is usable for reconstructing pH.

This proxy was applied within a single modern coral from 275m depth on the South Chatham Rise east of New Zealand. The $\delta^{11}B$ measurements showed significant seawater pH decrease, following the 20th century acidification trend observed from atmospheric and regional surface ocean pCO$_2$ records. The reconstructed pH change of 0.19 ± 0.08 is within reasonable agreement with hydrographic data from the region, but larger than the expected 0.10 pH change calculated using ice core pCO$_2$ data offset to match seawater pCO$_2$ data where present, and assuming constant alkalinity and temperature between 1900 and 1961 (where actual seawater data exist for region).

Considering the lack of available hydrographic data prior to 1961, the expected pH change of the mixed layer at the South Chatham Rise cannot be fully constraint.
Nevertheless, the coral records an acidification history of the region and therefore encourages the application of this proxy for reconstruct paleo-pH change within a single individual. Currently, the error for reconstruction of absolute pH is relatively large (±0.18 units for ambient pH 8), attributed mostly to the uncertainty in the offset between coral and seawater borate $\delta^{11}$B, which becomes more pronounced at low pH conditions that were not fully explored here.

Reproducibility, based on replicate analyses of coral samples and on long term precision of standards, and accuracy, based on agreement in standard quantification using various analytical approaches, was good for these coral analyses. The deviation of coral $\delta^{11}$B from a 1:1 line with the $\delta^{11}$B of seawater borate, after removing a constant offset, suggests the presence of unresolved sampling issues using this paper’s approach.

Potential differences in the isotopic composition between centers of calcification and fibrous aragonite (Blamart et al., 2007) might not be averaged here in a consistent way among samples. Further SEM and micro-sampling studies in *D. dianthus* could potentially provide more information on intra-skeletal variability, the presence of contaminant phases for example magnesium hydroxide and iron-manganese crust, and potential effects of diagenesis on coral $\delta^{11}$B. How such phases might affect $\delta^{11}$B is largely unknown and thus could have an effect on the measurements presented here. Additionally, uncertainty in hydrographic pH could be resolved through culture studies under tightly controlled conditions. By minimizing the error in the $\delta^{11}$B homogeneity and the ambient pH, a tighter regression would be expected resulting in an improved empirical $\alpha_B$ and $\delta^{11}$B offset for the *D. dianthus* $\delta^{11}$B-pH proxy.
4.6. References


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CHAPTER 5

MAJOR REORGANIZATION OF INTERMEDIATE NORTHWEST ATLANTIC AT 15.4KA AND
HEINRICH 1 EVENTS RECORDED IN D. DIANTHUS CORALS

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5.1. ABSTRACT

Recovery from ice age conditions during the last deglaciation is known to have occurred discontinuously, with step-wise increases in sea-level, and uncertain, possibly short-term reorganizations of circulation in the Atlantic Ocean. The recently calibrated P/Ca, Ba/Ca and U/Ca proxies (Anagnostou et al., 2011) were applied to fossil D. dianthus corals from the northwest Atlantic (1800m), U-Th dated to 15.4ka calendar age. Several specimens captured a radiocarbon age reversal, with the biologically younger end of the skeleton being older in radiocarbon age than the base of the coral (Adkins et al., 1998), attributed to an abrupt event leading to change in the ventilation age of the ambient seawater. These results allow for the first time an estimate of seawater phosphate concentrations; phosphate increased within one century from concentrations near modern values for this location (1.1 µmol/kg) to substantially higher concentrations following the event (1.7 µmol/kg), a relative change consistent with previously determined gradients of Cd/Ca in the same coral. In addition, the modern calibration of U/Ca against seawater carbonate ion concentration indicates that [CO$_3^{2-}$]-decreased by 30% during this event. It is concluded that P-enriched and [CO$_3^{2-}$]-depleted Southern Source Water (SSW) flooded the coral location at 15.4ka, displacing a mixture of Glacial North Atlantic Intermediate water (GNAIW) and SSW. Such an increase was not observed in a slightly older and deeper coral, supporting the rapid nature of the event. Four corals from the same location with preliminary dates matching Heinrich Event 1 (H1) (~16.5ka) show similar P/Ca to the post-15.4ka coral, suggesting that the 15.4ka and H1 events share similar water mass composition at intermediate depths. Using P/Ca in the 15.4ka coral as a conservative tracer, and estimating phosphate concentrations for the endmembers, the contribution of
SSW to the coral prior to the event is calculated to be 50%, and following the event to be 100%. This interpretation compares well with studies based on Nd isotopes (Pahnke et al., 2008), and the nutrient data, combined with previously determined radiocarbon measurements, imply a transit time to this site of about ~300 years for SSW, much slower than modern Antarctic Intermediate Water transit times. In contrast with the rapid changes in phosphate and carbonate ion through this period of deglaciation, dissolved Ba reconstructions are consistently higher than Holocene concentrations for all H1 and 15.4ka corals, suggesting that coral Ba/Ca captures the effect of Ba-rich meltwater input to the North Atlantic, increasing the Ba inventory in the basin such that Ba concentrations are apparently insensitive to the water mass shifts affecting nutrients and carbonate ion.
5.2. Introduction

The Labrador and Greenland Seas are locations of deep open ocean convection in the North Atlantic (Marshall and Schott, 1999) forming well ventilated, nutrient poor, and carbonate ion rich North Atlantic Deep Water (NADW). This water mass spreads southwards, occupying the deep Atlantic to a large extent (Lozier, 2010). There is strong evidence that this convection was altered during glacial/deglacial periods (Figure 5.1) with the formation of a shallower Glacial North Atlantic Intermediate Water (GNAIW) in place of NADW. Its presence and volume varied, most likely as result of abrupt climate shifts across the North Atlantic resulting from changes in the northward flux of heat through the return of warm surface waters (Denton et al., 2010). Additionally, variations in freshwater input may have triggered changes in deep water convection (Figure 5.2), for example during the Younger Dryas (YD) and Heinrich 1 (H1) (Broecker et al., 1989; Marchitto et al., 1998).

The last deglaciation in the North Atlantic seems to have been characterized by a plethora of changing convection modes (Figure 5.2). Limitations in the ability to reconstruct the timing and rate of deep convection changes relative to the timing of abrupt climate events and freshwater perturbations have obstructed understanding of the mechanisms that associate convection modes with a general deglaciation mechanism (Thornalley et al., 2011). Several pieces of evidence support increased influence of Antarctic Intermediate Water (AAIW) in the North Atlantic when Atlantic overturning circulation weakens (e.g. Boyle and Keigwin, 1987; Curry and Oppo, 2005; Pahnke et al., 2008; Rickaby and Elderfield, 2005). These periods are accompanied by changes in ventilation ages of
North Atlantic intermediate waters, switching rapidly within a period of 100-300y, from extremely old to very young ages (Figure 5.1) (Robinson et al., 2005; Thornalley et al., 2011). Young ventilation ages are observed during warm intervals like the Bølling-Allerød (B-A) and reflect the convection of North Atlantic surface waters that have equilibrated with atmosphere, an analogue to modern ocean conditions. Intermediate depth waters that are extremely depleted in radiocarbon are observed in the western and eastern North Atlantic during the cold intervals of H1, 15.4ka, and YD. The occurrence of such events requires shoaling or diminution of convection and intrusion of a radiocarbon depleted southern source water mass, possibly linked to enhanced vertical mixing in the Southern Ocean Polar Front zone (Anderson et al., 2009; Sigman et al., 2007; Skinner et al., 2010). Such mixing could assist in the formation of AAIW, and the northward migration of this nutrient rich, carbonate ion and radiocarbon depleted water mass from the surface waters of the Southern Ocean to intermediate depths of the global ocean.

The 15.4ka event is an extremely abrupt event that is often considered part of the H1 period (Thornalley et al., 2011). Deep sea coral studies in the northwest Atlantic provided evidence to distinguish the post-event period as one of significantly reduced intermediate water mass ventilation (Adkins et al., 1998; Robinson et al., 2005). Since the northwest Atlantic deep waters are formed by convection in both the Northeast and Northwest Atlantic, the 15.4 ka event suggests that open ocean convection in the Irminger and/or Labrador Sea was weakened substantially over the course of the event.
Figure 5.1. Radiocarbon concentrations during the last deglaciation. Top panel represents atmospheric radiocarbon (Reimer et al. 2009), while middle and bottom panels depict radiocarbon ventilation ages for this period in the Northeast and Northwest Atlantic water column, reconstructed from deep coral (closed squares) and foraminifera records (open symbols) (Thornalley et al. 2011 and Robinson et al. 2005). Red rectangle surrounds the 15.4ka event.
Sedimentary records (Figure 5.2) suggest that at the end of H1 southward flow rates at ~2km depth in the northwest Atlantic were also reduced, based on an increase in $\varepsilon_{Nd}$ ratio towards heavier SSW signatures (Pahnke et al., 2008; Stanford et al., 2006). In addition, the northeast intermediate Atlantic is also characterized by radiocarbon depletion (Thornalley et al., 2011) suggesting that the whole North Atlantic basin flooded with SSW to 60°N (Figure 5.1). During the same period, Greenland ice core $\delta^{18}O$ records plateau at cold temperatures (Blunier and Brook, 2001) while EPOCA Dome C $\delta^{18}O$ records show an increase in Antarctic atmospheric temperature (Stenni et al. 2003) as a manifestation of the “bipolar seesaw” (Broecker, 1998) (Figure 5.2). Sea level does not display a noticeable alteration in rate of change during the H1 and YD melt water pulses (Figure 5.2), nevertheless the Atlantic Meridional Overturning Circulation (AMOC) is significantly altered possibly as a result of the nature and location of melt water discharge rather than the actual mass and rate of freshwater input (Stanford et al., 2006). For example iceberg (Figure 5.2) and freshwater discharges from the Hudson Strait during H1 (Fairbanks, 1989; McManus et al., 1999) may have had little influence on sea level rise but significant effects on surface salinity of the Nordic seas and therefore on NADW formation.
Figure 5.2. Multi-proxy climate records. a, b. Ice core atmospheric temperature reconstructions for (a.) Greenland (Blunier and Brook 2001), and (b.) Antarctica (Stenni et al., 2003). c. Sea level; from Barbados corals (Stanford et al. 2006). d. $^{231}$Pa/$^{230}$Th sedimentary proxy for circulation strength, 33° 42’ N, 57° 35’ W 4550 m (McManus et al 2004). e. Nd isotope ratio, a circulation proxy, 12° 9’ N, 61° 23’ W 1330m (Pahnke et al. 2008). f. IRD abundance, a proxy for iceberg discharge, 55° 29’ N, 14° 42’ W 2179 m (McManus et al. 1999). Note that during Northern Hemisphere cold periods (low ice $\delta^{18}$O), AMOC is reduced (high $^{231}$Pa/$^{230}$Th), contribution of AAIW is increased (more radiogenic $\varepsilon_{Nd}$ at 2000m depth in Tobago basin), and IRD abundance increases.
The P/Ca, Ba/Ca, and U/Ca nutrient and carbonate ion proxies in deep sea corals could provide an independent method to reconstruct changes in circulation at precisely dated times in the past, and to infer endmember properties, assuming no significant production or consumption of nutrients and carbonate ion along the flow path of each water mass. Thus these proxies can be used in combination with radiocarbon measurements to estimate transit times of water masses. To achieve this goal, fossil solitary deep sea corals *Desmophyllum dianthus* (*D. dianthus*) were analyzed from the Manning seamount, that were previously precisely dated to be 15.4ka old with U/Th radiometric techniques. Records from these corals were compared with those obtained from corals from the Kelvin and Rehobath seamounts, and dated within the preceding H1 period (Adkins, pers. comm. 2010). Here, therefore, the first paleoreconstructions are presented based on previously established coral P/Ca, U/Ca, and Ba/Ca proxies, interpreted as changes in water mass chemistry of the northwest Atlantic which are in agreement with records from sedimentary and foraminifera records. This work also suggests potential inventory changes in Ba concentrations of the North Atlantic as a result of freshwater discharges associated with deglaciation. Finally, using the new proxy data to estimate water mass mixing ratios, estimates of changes in rate of transport of southern origin intermediate water masses during the 15.4 ka event are presented, which are in agreement with interpretations of previously reported radiocarbon measurements, encouraging the utility of *D. dianthus* as a multi-proxy geochemical paleoceanographic archive.
5.3. MATERIALS AND METHODS

Two corals (JFA 24.8 and JFA 20.10) were collected from Manning Seamount in the northwest Atlantic, at 38°N and 60-62°W (1800-2000m depth). Both corals have radiocarbon ages that increase during their life span (Adkins et al., 1998), capturing an age reversal, with the biologically younger part of the coral skeleton (tip of septum) being older in radiocarbon age than the older portion (bottom of septum). Additionally, four corals preliminarily dated as coincident with H1 (J. Adkins, pers. comm., 2010) were analyzed. All fossil corals were collected in the northwest Atlantic by Dr. Jess Adkins (Caltech). The corals were cleaned with the ultrasonic-cleaning protocol of Cheng et al. (2000), and then septa were removed, cut longitudinally, mounted in epoxy, cut into thick sections, and polished to 1μm roughness. The sections were subsequently rinsed with isopropyl alcohol (99.9% purity) in an ultrasonic bath and dried.

All samples were analyzed by laser ablation Inductively Coupled Plasma Mass Spectrometry (LA ICP-MS) using a 193 nm solid state laser (UP-193, New Wave Research Fremont, CA) following the method and analytical approach of Anagnostou et al (2011; see also Chapter 3), at a fluence of 4-5 J/cm² and 10 Hz shot frequency. Analyses were carried out on an Element XR sector field ICP-MS (ThermoFinnigan, Bremen, Germany) using a combination of magnet jumps and electrostatic peak scanning (E-scan). All elements were analyzed in medium resolution (MR = 4000M/ΔM) to resolve molecular ion interferences on phosphorus (e.g. NO and NOH) and on iron (e.g. ArO and CaO), while acquiring time-resolved data in a near-simultaneous manner. The isotopes measured and the method parameters are listed in Table 5.1.
Since calibrations of the P/Ca, U/Ca and Ba/Ca proxies were obtained using an excimer 193nm laser coupled to an Element 2 SF-ICP-MS (Anagnostou et al. 2011), rather than the solid state laser and Element XR used for the present analyses, one coral section (ID 62309) was reanalyzed as a consistency standard among analytical sessions using both instrumental configurations to allow direct comparison and application of the calibrations. For the laser and ICP conditions employed, the long term elemental ratio reproducibility of average lines ablated on this coral was ≤±7% (1SD) for Ba/Ca and U/Ca, and ≤±16% (1SD) for P/Ca, while typical within-day reproducibility is <5% for Ba/Ca and U/Ca, and <10% for P/Ca (see Chapter 2). The gas blank, as a fraction of mean coral signal (in counts per second), was <15% for P, and <1% for Ba and U, and <1% for Ca.
Table 5.2. Background information on 15.4 ka *D. dianthus* specimens
(Adkins et al. 1998; Adkins and Boyle 1999)

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<th>Bulk ∆¹⁴C (%o)</th>
<th>∆¹⁴C (‰)</th>
<th>¹⁴C age (y)</th>
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<th>Lifespan (y)</th>
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</tbody>
</table>

Spreadsheet software was used for offline data reduction, which involved gas-blank subtraction, normalization to $^{43}$Ca to correct for variations in ablation yield and instrumental drift, and standardization by bracketing each coral ablation line with NIST 612 glass standard analyses (Hathorne et al., 2003; Longerich et al., 1996b). Correction of $^{86}$Sr$^{2+}$ on $^{43}$Ca is accomplished by measuring $^{87}$Sr$^{2+}$. The NIST 612 standard is considered homogeneous for Ba, Ca, P and U (Eggins and Shelley, 2002), therefore published elemental concentrations were used (Ba: 39.7ppm and certified U: 37.4ppm (Jochum et al., 2005; Reed, 1992), Ca: 84690ppm (Eggins, 2003), P: 39.9ppm (LaVigne et al., 2008)). Any matrix dependent elemental fractionation due to non-matrix match standardization is minimized for most elements when using 193nm lasers, including P, Ba, and U (Guillon et al., 2003; Hathorne et al., 2008; Longerich et al., 1996a), as verified here by the precision of the consistency standard standardized with NIST612 glass standard.
The counting statistics (CS) of the coral analyses are dependent on the concentration of analyte within the specific coral, the sensitivity of the ICP-MS and the analytical method defined for the ICP-MS analyses. As an example, the CS for coral sample JFA 24.8 contribute an error of ±7% for P/Ca, ±3% for Ba/Ca, and ±4% for U/Ca (1SD). Here, 12 point moving averages are reported of data acquired along a line ablated on the coral skeleton, for which CS error for P/Ca drops to 2%, for U/Ca to 1%, and for Ba/Ca to <1%. Therefore the CS error is considered a minimal contribution to the overall reproducibility of coral analyses.

5.4. RESULTS AND DISCUSSION

5.4.1. 15.4ka corals

5.4.1.1. Coral specimen JFA 24.8

Coral sample JFA 24.8 displayed a top-to-bottom change in radiocarbon content equivalent to 670y (Table 5.2). The same coral was analyzed for Cd/Ca (Adkins et al., 1998), clearly showing an increase of Cd/Ca at the top of its septum (neighboring septum to that analyzed here) potentially associated with the presence of more nutrient-rich SSW at the site of the coral, displacing North Component Waters (NCW) (Figure 5.1). A direct quantification of seawater phosphate concentrations based on coral Cd/Ca measurements is hindered by a poorly established Cd-calibration in deep sea corals (Adkins et al., 1998; Eltgroth, 2006) and uncertainties in the quantitative relationship between seawater Cd and P through geologic time (Elderfield and Rickaby, 2000). If the distribution coefficient of Cd in D. dianthus (ratio of coral Cd/Ca with seawater Cd/Ca =
$D_{\text{Cd}}$ is 1.3 (Eltgroth, 2006) to 1.6 (Adkins et al., 1998), then the reconstructed SSW phosphate, as recorded in the top, younger part of coral JFA 24.8, is 3.2-3.9$\mu$mol/kg (using 0.4mmol Cd / mol P in seawater for phosphate concentrations higher than 1.2$\mu$mol/kg in the modern ocean), higher than deep Pacific phosphate concentrations in the modern ocean and thus an unlikely conclusion unless oceanic phosphate inventory was substantially elevated during this period of deglaciation. Alternatively, the Cd/P ratio could be altered during the last glacial and deglacial period, but the magnitude of the variation in oceanic Cd inventory is expected to be relatively small on the basis of estimated oceanic residence time for Cd (Rosenthal et al., 1995; van Geen et al., 1995), which suggests that either the effective D for Cd in $D. dianthus$ is not fully resolved, or large and unconstrained changes in Cd inventory occurred during deglaciation. Results of this study, explained below, suggest that the shift in phosphate concentrations over the life of this coral were in a range that is consistent with P distributions and inventory in the modern ocean.
Thick sections were obtained from a different septum of the JFA 24.8 coral from that analyzed previously (Adkins 1998). The section was cut along the growth axis (Figure 5.4), and was subsequently analyzed by ablating 7mm to 14mm long lines for determination of P/Ca, U/Ca and Ba/Ca. The ablation speed (25\(\mu\)m/s) and spot size (100\(\mu\)m) allowed spatial resolution of 153\(\mu\)m along the growth axis with a 2.13s analytical method. The raw data were smoothed (12 point moving average), so that each point in the smoothed record represents the mean of a 685\(\mu\)m segment. Assuming a mean growth rate for *D. dianthus* of ~1mm/y (Adkins et al., 2004), the resolution displayed in Figures 5.3 and 5.5 is therefore sub-annual. The data were examined for presence of undesired Fe-Mn phases and centers of calcification (Anagnostou et al., 2011). The gaps in the profiles shown in Figure 5.5 represent areas where the elemental
Data indicate that at least one of these phases was observed, and data from these intervals were omitted from the record.

![Image](image.jpg)

**Figure 5.4. JFA24.8 section.** Red line shows the 1.5cm ablation path on the coral, chosen to avoid exterior diagenesis and centers of calcification.

Data acquired from the first 1mm and the last 8 mm of the ablated line 1 (Table 5.3) were averaged to provide a measure of El/Ca change along the growth of this coral, while removing higher resolution variability (Figure 5.5). Line 2 was used to provide additional proof of the measurements. On average (using two different lines ablated on one septum), coral P/Ca decreased by 42% ± 2% from top to bottom (Table 5.3), similar in magnitude to the change reported in Cd/Ca for a different septum of the same coral (42%, Adkins et al. 1998). Additionally, U/Ca decreased by 33% ± 2% from the top to the bottom of the same septum, whereas Ba/Ca remained unchanged within the uncertainty of the measurement (Table 5.3). The same coral has been analyzed for Ba/Ca, using isotope dilution ICP-MS, through microsampling along the growth axis of another of its septa (Adkins 1998). The resultant Ba/Ca ratios of 20 ± 2μmol/mol agree with the LA ICP-MS measurements supporting both the magnitude and stability of seawater Ba within the growth of this coral. Re-ablations of the same line provide not
only similar overall El/Ca change along the growth axis of the coral, but also good agreement for the fine scale El/Ca variations (Figure 5.5).

The seawater phosphate reconstruction from the top part of the coral is equal to 1.7µmol/kg based on previously established P/Ca calibration for D. dianthus (Anagnostou et al., 2011), similar to estimates of ~1.7µmol/kg based on Cd/Ca measurements in foraminifera (Rickaby and Elderfield, 2005) for deglacial intermediate SSW, using a modern deep seawater Cd/P relationship of 0.4µmol/mol (Elderfield and Rickaby, 2000). Therefore the nutrient signature of 1800m water in the northwest Atlantic during the 15.4ka event is dominantly that of SSW, as has also been suggested on the basis of radiocarbon measurements (Adkins et al., 1998; Robinson et al., 2005). The bottom part of the coral records phosphate concentrations of 1.1µmol/kg, and is assumed to have been bathed by a mixture of this SSW and GNAIW. Seawater phosphate is then used as a quasi-conservative tracer to calculate the mixing ratio between the two endmembers. The SSW endmember properties are calculated from the top part of the coral, and the phosphate concentration of GNAIW is equal to 0.6µmol/kg based on Cd/Ca measurements in benthic foraminifera (Boyle and Keigwin, 1987) (Table 5.4). Thus, the bottom part of the coral was bathed by 50% GNAIW and 50% intermediate SSW just prior to the 15.4ka event (Figure 5.6). The carbonate ion reconstructions are however lower by 20-30µmol/kg for periods both before and after the 15.4ka event, compared to what is expected from the above mixing scenario (Table 5.3, Figure 5.6). Although the SSW endmember carbonate ion concentration estimate for 15.4ka is uncertain (Rickaby et al., 2010), it is still notable that reconstructed SSW
phosphate concentration is similar to present AAIW, WOCE A23, Sta. 56, 996m (~2 μmol/kg) while carbonate ion is lower (40 μmol/kg compared to AAIW of 80 μmol/kg). While the uncertainties are large, the data suggest that the SSW was characterized by a combination of phosphate and carbonate ion concentrations that is not found in the modern ocean, with carbonate ion very low (very corrosive) for the moderate phosphate concentration. Such a shift would signal a fundamental change in the production, composition, and/or remineralization and dissolution of sinking particulate matter in the ocean. The sense of the change suggests either a larger C/P remineralization ratio that sets the composition of the SSW intermediate water endmember (no further remineralization or change in phosphate allowed under the assumptions of the phosphate-based mixing model), or a remineralization with a higher organic/inorganic carbon rain ratio, either of which change might occur with a change in the composition of the phytoplankton assemblage.
Table 5.3. Summary of JFA 24.8 and JFA 20.10 El/Ca measurements and reconstructions.
Line 1 and 2 are different lines on the same septum.
*errors represent 1SD of triplicate analyses of the same line
**errors are 95% CI of reconstruction based on relevant calibration error envelope

<table>
<thead>
<tr>
<th>JFA 24.8</th>
<th>Line 1 (used for reconstruction)</th>
<th>Line 2 (used for confirmation)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(μmol/mol)</td>
<td>TOP:0-1mm, BOTTOM:6-14mm</td>
<td>TOP:0-1mm, BOTTOM: 6-7mm</td>
</tr>
<tr>
<td>El/Ca top</td>
<td>76±2</td>
<td>22±1</td>
</tr>
<tr>
<td>El/Ca bottom</td>
<td>43±1</td>
<td>20±1</td>
</tr>
<tr>
<td>El/Ca % change</td>
<td>40</td>
<td>6</td>
</tr>
<tr>
<td>El/Ca difference</td>
<td>33</td>
<td>2</td>
</tr>
<tr>
<td>Reconstructed seawater μmol/kg</td>
<td>PO₄**</td>
<td>Ba**</td>
</tr>
<tr>
<td>top</td>
<td>1.7±0.1</td>
<td>0.16±0.02</td>
</tr>
<tr>
<td>bottom</td>
<td>1.1±0.2</td>
<td>0.15±0.02</td>
</tr>
<tr>
<td>change</td>
<td>0.56</td>
<td>0.01</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>JFA 20.10</th>
<th>Line 1</th>
<th>Line 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>(μmol/mol)</td>
<td>TOP:0-3mm, BOTTOM:3-7mm</td>
<td>TOP:0-3mm, BOTTOM:4-6mm</td>
</tr>
<tr>
<td>El/Ca top</td>
<td>43</td>
<td>18</td>
</tr>
<tr>
<td>El/Ca bottom</td>
<td>37</td>
<td>18</td>
</tr>
<tr>
<td>El/Ca % change</td>
<td>14</td>
<td>2</td>
</tr>
<tr>
<td>El/Ca difference</td>
<td>6</td>
<td>0</td>
</tr>
<tr>
<td>Reconstructed seawater μmol/kg</td>
<td>PO₄**</td>
<td>Ba**</td>
</tr>
<tr>
<td>top</td>
<td>1.1±0.2</td>
<td>0.14±0.02</td>
</tr>
<tr>
<td>bottom</td>
<td>1.0±0.2</td>
<td>0.13±0.02</td>
</tr>
<tr>
<td>change</td>
<td>0.10</td>
<td>0.01</td>
</tr>
</tbody>
</table>
Figure 5.5. Ablation line 1 of septum of *D. dianthus* JFA 24.8 depicted in Figure 5.4, analyzed in triplicate. Grey lines represent raw un-smoothed data corresponding to the smoothed data in black lines. Black, green and purple lines are all 12 point moving averages, and represent re-ablations of the same path on the coral showing up to 10% deviation for Ba/Ca, ≤16% for U/Ca, and ≤13% for P/Ca. The black and green lines are directed from the top to the bottom of the septum (younger to older part of coral), while purple line is ablated on the reverse direction.
Figure 5.6. Mixing scenario of SSW and GNAIW at 1800m northwest Atlantic using the reconstructions from the top and bottom part of the JFA 24.8 coral.

Table 5.4. Summary of available endmember properties in glacial-deglacial Atlantic

<table>
<thead>
<tr>
<th></th>
<th>SSW</th>
<th>Time</th>
<th>Source</th>
<th>GNAIW</th>
<th>Time</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>PO₄ (µmol/kg)</td>
<td>1.7</td>
<td>15.4</td>
<td>Rickaby &amp; Elderfield 2005</td>
<td>0.6</td>
<td>Glacial</td>
<td>Boyle &amp; Keigwin 1987</td>
</tr>
<tr>
<td>Ba (nmol/kg)</td>
<td>125</td>
<td>deglacial</td>
<td>GEOSECS modified: Lea &amp; Boyle 1990</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO₃²⁻ (µmol/kg)</td>
<td>50</td>
<td>deglacial</td>
<td>Rickaby &amp; Elderfield 2010</td>
<td>135</td>
<td>Glacial</td>
<td>Yu et al. 2008</td>
</tr>
<tr>
<td>△¹⁴C (%o) relative to atm</td>
<td>-299</td>
<td>deglacial</td>
<td>Goldstein et al. 2001</td>
<td>-39</td>
<td>Glacial</td>
<td>Robinson et al. 2005</td>
</tr>
</tbody>
</table>
5.4.1.2. Calculation of SSW transit times to northwest Atlantic

The combination of radiocarbon and inferred seawater nutrient data allows calculation of ventilation rates of the SSW to the coral location. This is because the nutrient data can be used to estimate water mass mixing ratios, which can then be used to calculate the radiocarbon concentration at the coral site and, by comparison with the radiocarbon concentration of the endmember, the transit time of the water mass to that site. The coral is located close to the formation region of GNAIW therefore the only significant decay due to water mass transit time is expected to occur during transit of SSW to this location. Phosphate reconstructions were used as quasi-conservative tracers in the Atlantic Ocean since changes in circulation and advection dominate the distribution of nutrients at intermediate depths in the Atlantic, with a minor role for non-conservative behavior driven by nutrient remineralization along the flow path. Such an assumption might however become more uncertain when flow rates are reduced, allowing more time for remineralization and dissolution of sinking particles to have an effect on the chemical signature of intermediate water masses. All calculations were performed using radiocarbon concentrations (per mil) from recent literature and the difference in top to bottom radiocarbon content of the JFA 24.8 coral. The reason for this approach was to avoid uncertainties in reservoir age estimations and the radiocarbon content of the atmosphere at 15.4ka, equal to 295 ± 19‰ (Reimer et al., 2009), in addition to the large uncertainties in radiocarbon measurement of the top and bottom part of the coral, >30 ‰ (Adkins and Boyle, 1999). The GNAIW radiocarbon is -39‰ relative to the glacial atmosphere at 25ka close to the location of the coral, based on a deep sea coral $\Delta^{14}C$ analysis (Robinson et al., 2005). Therefore at 15.4ka the GNAIW is expected to be 295-
39 = 256‰, assuming constant offset from the atmosphere. The intermediate water SSW endmember radiocarbon is taken as equal to the mean of two deep sea corals collected in the Drake Passage with a range of 99-121‰ at 16.5-16.7ka (Goldstein et al., 2001) (Table 5.4).

Using the above radiocarbon values and assuming a) the bottom part of the coral is bathed in a mixture of 50% SSW and 50% GNAIW as determined from paleo-phosphate reconstructions above, and b) the top part of coral is bathed by 100% SSW, the ventilation rate of the SSW is calculated using an approach similar to that of Adkins et al. (1998):

\[ \text{Top minus bottom coral radiocarbon content} = -92‰ \quad (1) \]

\[ \text{Top part coral seawater radiocarbon} = SSW \text{ radiocarbon} + \text{transit decay} \quad (2) \]

\[ \text{Bottom part coral seawater radiocarbon} = (SSW \text{ radiocarbon} + \text{decay}) \times (1-0.5) + (GNAIW \text{ radiocarbon}) \times 0.5 \quad (3) \]

Therefore, for equations (1), (2), and (3):

\[ \text{Top part coral seawater radiocarbon} - \text{Bottom part coral seawater radiocarbon} = \text{Top - bottom coral radiocarbon content} \]

Or written symbolically:

\[ (S_o+d) - ((1-0.5) \times (S_o+d) + 0.5 \times N_o) = -92 \pm 53‰ \ (\text{propagated error of coral radiocarbon measurement}) \quad (4) \]
Where:

\[ S_0 = \text{SSW endmember radiocarbon} = 110 \pm 10\% \text{ (1SD of 2 corals; Goldstein et al., 2001)}, \]

\[ N_0 = \text{GNAIW endmember radiocarbon} = 256 \pm 83\% \text{ (propagated error of atmospheric estimate and coral radiocarbon measurement)} \]

\[ d = \text{decay (or transit time, in per mil radiocarbon units)} \]

Then: \[ 0.5 \left( (110 + d) - (256) \right) = -92, \text{ therefore } d = -294 - (-256) = -38\% \]

The SSW at the JFA 24.8 coral location is characterized by 38‰ decay in radiocarbon compared to its source in the South Atlantic, which is equivalent to 310y of transit time. Considering that typical AAIW radiocarbon age in the modern equatorial Atlantic is calculated to be \(~160\text{y (20\%)}\) older than source water radiocarbon ages today (Broecker and Peng, 1982), the transit time of \(~300\text{y at 15.4ka}\) implies slow intermediate ocean circulation during this cold event. Due to the large uncertainties in the values used in the calculation, especially for the coral radiocarbon content, this back-of-the-envelope calculation is uncertain with a propagated error of 135‰. In the best case scenario where corals from within the end member geographic region are available growing during the same time period and all have radiocarbon measurement uncertainty of up to 10‰, a reasonable error for radiocarbon measurements, then the error of transit time could be reduced to 24‰. Therefore, better constrained end-member radiocarbon properties and lower uncertainties in radiocarbon measurements are required to make a more tightly constrained estimate of SSW transit time to the northwest Atlantic at 15.4ka.
5.4.1.3. Coral specimen JFA 20.10

Coral specimen JFA 20.10 was collected 170m deeper and 175km distant from JFA 24.8 (Manning Seamount), has the same absolute age within error of the U-Th dating, and provides a useful comparison sample (Table 5.2). However, the top to bottom difference in the determined P/Ca reflected a change of only 12% between the younger and older part of the coral, while Ba/Ca and U/Ca remained practically unchanged over the lifetime of this coral (Table 5.3). These observations are in agreement with radiocarbon measurements that show a difference between top and bottom radiocarbon age of only 140 years, compared with 670 years for coral JFA 24.8 (Table 5.2). Additionally, P/Ca, Ba/Ca, and U/Ca ratios in JFA 20.10 are much more similar to values for the bottom part than the top part of the septum analyzed from coral JFA 24.8 (Table 5.3). Therefore the JFA 20.10 coral either captures hydrographic conditions prevailing just prior to the 15.4 ka event or is located below the depth range at which the 15.4 ka circulation change is manifested (e.g. Robinson et al. 2005).

5.4.2. Heinrich 1 corals

To investigate if the water mass properties of the northwest Atlantic before or after the 15.4ka event are similar to those during the H1 event, especially considering their similarities as events in terms of freshwater input and SSW intrusion to the north Atlantic (Robinson et al., 2005; Thornalley et al., 2011), four H1 corals were analyzed collected at depths of 1800-2600m (Table 5.5, Figure 5.7). The 1400m coral is visibly diagenetically altered (Figure 5.8), therefore elemental ratios for this specimen were considered with caution. These samples currently have preliminary “reconnaissance” radiocarbon
determinations (Adkins pers. comm. 2010) that correspond to approximately 16.5ka calendar age.

Focusing on the ~1800-2000m depth reconstructions, the nearest depth to the 15.4ka corals available, it was observed that post-15.4 ka reconstructions for both phosphate and carbonate ion concentrations are similar to the H1 results, suggesting higher than modern values as represented by GEOSECS Station 29, while the pre-15.4 ka measurements reveal a temporary recovery towards modern seawater conditions for this location. Therefore H1 intermediate water conditions are proposed to be similar to the post-15.4ka event showing enrichment in phosphate and depletion in carbonate ion concentrations at ~1800m northwest Atlantic, suggesting the presence of nutrient rich and corrosive SSW flooding the coral location. The reconstructed phosphate concentration for the 1800m H1 coral agrees within uncertainty with the post-15.4ka reconstruction. However, its reconstructed carbonate ion concentration sits between the pre- and post- 15.4ka carbonate ion values, suggesting that it grew within the recovery period from H1 or during the transition to the 15.4 ka event. All H1 and 15.4 ka corals are bathed in waters with significantly lower carbonate ion concentration than presently exists at this location (WOCE-A22), most likely because of varying degrees of influence of carbonate ion-depleted SSW (Fig. 5.7).
The 2593m H1 coral, shows a similar depletion in carbonate ion compared to corals within the water column above, but an increase to the highest paleo-phosphate concentrations, an indication of presence of a deep SSW, potentially different in composition from the intermediate source water. The 1427m coral shows a phosphate concentration similar to modern NADW, possibly reflecting the upper depth limit of SSW intrusion to the north Atlantic. Reconstructed Ba in this coral also seems slightly lower than that of the deeper corals, but carbonate ion appears very similar. Although this coral specimen has visibly obvious diagenesis (Fig. 5.8, left), the discrepancy in phosphate to barium to carbonate ion ratios between this coral and those located deeper, and between all of these coral reconstructions and modern hydrographic relationships, may reflect fundamental shifts in biogeochemical processes as they affect vertically segregated water masses during deglaciation. Possible mechanisms driving these shifts include barium removal and remineralization processes, degree of endmember surface water exchange with atmospheric CO₂, shifts in P/C remineralization ratios and depths and changes in Corg/Cinorg particulate rain ratio. These processes may be altered from the modern condition during deglaciation, especially during extreme climate events when
sea ice cover, freshwater induced stratification, and variations in surface water nutrient utilization efficiency variability are all possible scenarios.

Figure 5.7. Vertical profile of reconstructed seawater chemistry in the northwest Atlantic during H1 (~16.5ka; closed squares), the 15.4ka event (open large: pre-15.4, closed small: post-15.4), and present day hydrographic data (closed triangles). Open circles represent the top and bottom measurements on coral JFA 20.10 (15.4ka). Error bars represent uncertainty at 95% CI derived from the the proxy calibration error envelopes.
All H1 corals show similar Ba/Ca ratios to the 15.4ka *D. dianthus* specimens, and imply dissolved Ba concentrations throughout this period that are more than twice the values in the modern northwest Atlantic (GEOSECS, Station 29; Fig. 5.7). Although temporally and spatially limited, the Ba reconstructions based on 15.4 ka and H1 corals imply a larger dissolved Ba inventory for the deglacial North Atlantic compared to the Holocene. The similarity between H1 and post 15.4 ka for all three reconstructed water mass properties implies that the 15.4ka event, like H1, could also be associated with iceberg discharge, melt water pulses, and stratification (Bond et al., 1992; Hemming, 2004). It is unlikely that the magnitude of this Ba addition can be correlated quantitatively to volume of freshwater discharge or iceberg calving. Assuming that different meltwater pulse sources have different Ba concentration and timing with a relatively fast time constant scavenging, reconstructed Ba could assist in distinguishing among iceberg discharge, Mississippi outflow, and melt water input, and in such a way it might reconcile the sea
level curve with major deglacial cooling events and changes in deep water convection in the North Atlantic.

5.4.3. Mechanism of deglaciation

It is useful in summary to place my results for the 15.4ka and H1 periods in the context of the current understanding of the overall process of deglaciation and its discontinuous sub-periods. The sequence of events that initiated the last deglaciation seems to have started from the North Hemisphere, with recession of the Laurentide and Scandinavian Ice sheets as early as 20ka (Denton et al., 2010). This recession, that potentially was the result of increased summer insolation (Milankovitch, 1941), resulted in meltwater and gradual sea level rise (Toucanne et al., 2010). At around 18ka, melting and surging of ice sheets resulted in the initiation of H1 (Bard et al., 2000), characterized by collapse of large portions of the Laurentide, Greenland, and European continental glaciers into the North Atlantic, and cold North Atlantic sea surface temperatures (Naughton et al., 2009). The oceanic bipolar see-saw (Broecker, 1998) and the southward shift of the southern westerlies (Anderson et al., 2009) during H1 could explain the warming in Antarctica (Ahn and Brook, 2008), the increase of Subtropical Front sea surface temperature (Barrows et al., 2007), and upwelling in the Southern Ocean (Anderson et al., 2009). The warm conditions in the Southern Ocean persisted for sufficient time to result in rise of atmospheric CO$_2$ to maintain globally warm conditions and result in deglaciation (Denton et al., 2010). This work suggests that between the main core of H1 (~17ka) and 15.4ka, as characterized by the pre-15.4 intermediate water chemical properties, there was a
recovery period of AMOC as a result of the SSW input of heat and salinity to the North Atlantic. This period might have been interrupted by an additional meltwater input (Bard et al. 2000) resulting in a short term slow down of AMOC (the post-15.4 period) resembling again the H1 conditions, and occurring just before the Allerød, when the North Atlantic surface waters returned to warm conditions, thermohaline circulation and the production of NADW increased, and colder Antarctic temperatures prevailed (Bard et al 2000, (McManus et al., 2004; Wang et al., 2001).

5.5. Conclusions

Here, the first reconstructions of paleo-seawater chemistry are presented based on previously established and calibrated phosphate, barium, and carbonate ion proxies in the deep sea coral *D. dianthus*. A coral dated at 15.4ka suggests the presence of ~100% intermediate SSW at 40°N at the 1800-2000m interval in the northwest Atlantic. This water mass was enriched in phosphate and depleted in carbonate ion concentrations as expected from modern AAIW. These results are in general agreement with radiocarbon and Cd/Ca measurements in the same 15.4ka coral (Adkins et al. 1998), but extend those results to include absolute reconstructions of a key nutrient and an important carbonate system variable.

Additional analyses in corals that grew during the H1 event, along with published records of radiocarbon estimates for the intermediate North Atlantic (Robinson et al. 2005, Thornalley et al. 2011) suggest that the H1 and post-15.4ka event periods share
similarities. During these periods, ~1800-2000m waters in the entire North Atlantic are characterized by a rapid reduction in radiocarbon, and the northwest Atlantic corals studied here show comparably enriched phosphate and depleted carbonate ion concentrations for intermediate waters during these two periods. Deeper corals though have a different behavior, with a further enrichment in phosphate at 2500m, implying the presence of a deeper SSW intrusion to the North Atlantic.

These results are in general agreement with Nd isotope estimates of the presence of intermediate SSW in the North Atlantic (Pahnke et al., 2008), although Nd isotopes do not capture the 100% SSW transition during the 15.4ka event but do indicate a smaller ~40% AAIW contribution to Tobago basin at 1330m depth. It may be that the Nd measurements reflect the upper depth limit of the AAIW contribution to the Northwest Atlantic, also evident in the H1 phosphate reconstructions from the 1400m coral, and in radiocarbon records (Robinson et al. 2005, Thornalley et al. 2011).

Preliminary estimates of the SSW transit time to the 15.4ka coral were made using the mixing ratio of SSW and GNAIW at the coral location, calculated using reconstructed phosphate concentrations and estimates of endmember radiocarbon and GNAIW phosphate reconstructions (Table 5.4). The resultant transit time suggests that intermediate SSW required ~300y to travel from the Drake Passage to the northwest Atlantic, substantially longer than the ~160y transit time of AAIW to the equatorial modern North Atlantic. Since small variations in the endmember radiocarbon and
nutrient properties could affect this result significantly, endmember properties need to be constrained with a smaller uncertainty to provide confidence to such a calculation.

The barium reconstructions implied by the Ba/Ca measurements on 15.4 ka and H1 corals are uniformly higher than Holocene North Atlantic concentrations regardless of water mass mixing ratios, resembling instead the Ba concentration of modern AAIW. This is an interesting outcome when compared to increased IRD abundance (McManus et al., 2004; Thornalley et al., 2010). Whether freshwater re-routing (e.g. through Mississippi or through an alternative path in the North Atlantic (Broecker et al., 1989)) or iceberg discharge, or another mechanism yet to be identified, was most effective in driving increases in Ba in the North Atlantic, remains unanswered. Time series Ba reconstructions on fossil D. dianthus corals that are more widely distributed in space and time, with comparisons to planktonic foraminiferal Ba/Ca measurements, have the potential to provide insight to the timing, duration, and magnitude of this Ba input.
5.6. References


The work presented in this dissertation is separated into two parts: a. establishment of calibrations and b. paleo-reconstructions.

6.1. Calibrations

This thesis constitutes the first rigorous development of a proxy for deep sea phosphate, barium, carbonate ion, and pH recorded as phosphorus to calcium (P/Ca), barium to calcium (Ba/Ca), uranium to calcium (U/Ca) ratios and boron isotopes respectively in the skeleton of the deep sea coral Desmophyllum dianthus (D. dianthus). A significant method development for obtaining precise elemental ratios on the micron scale of D. dianthus is described in Chapter 2. These lead to further protocols on coral sampling and calibrations of corals located from the Atlantic, Pacific, and Southern Oceans with local hydrographic data establishing global correlations describing these proxies (Anagnostou et al. 2011, and Chapter 3). The B isotope calibration was based on previously
established analytical methods and resulted in a global $\delta^{11}$B-pH calibration using *D. dianthus* (Chapter 4).

These proxies provide the initial evidence of the geochemical abilities of *D. dianthus* in recording ambient nutrient and carbonate system parameters, although additional validation is necessary to provide sub-annual records with decreased uncertainty. First, secondary dependencies of these proxies with more than one hydrographic parameters is possible but difficult to study in regions were physical and chemical properties are dependent on each other. For example, seawater phosphate and pH are strongly correlated in seawater because they both describe primary production at the surface and respiration at depth. Culturing studies, however, at controlled seawater conditions could overcome this problem allowing calculations of e.g. phosphate dependence on carbonate ion (and therefore also aragonite saturation as implied in Chapter 3), pH, temperature, and salinity. Deep sea coral culturing is challenging but feasible (Orejas et al., 2008) if corals are allowed to grow for 1-2 years so that enough aragonite is precipitated for geochemical analyses. Culturing studies could be coupled to time series analyses using corals located proximal to surface seawater in fjord areas. With these, high resolution seawater analyses could be coupled with coral geochemistry for further validating the proxies established in this dissertation.

Second, the mechanism of incorporation for P, U, and B isotopes is uncertain. Organic forms of P are potentially incorporated in coral aragonite, but the amount, form, and location of this P source is not well understood. Preliminary evidence of the presence of
skeletal organic phosphorus (Chapter 3) has been observed only in a limited number of corals with soluble reactive phosphorus measurements. These could be biased by the presence of colloidal-associated inorganic phosphorus perhaps also present in *D. dianthus* skeleton. Alternatively, solid state NMR studies and synchrotron mapping have the potential to provide direct evidence of the location and form of skeletal P.

Inorganic precipitation experiments might prove useful, especially in testing mechanisms of uranyl complexes incorporated in *D. dianthus*. Measurements of U/Ca ratios in calcite and aragonite precipitated in a well controlled mixture of variable carbonate ion concentrations, by addition of either carbonate salts or CO$_2$ gas modifying the carbonate system, could provide an inorganic basis for understanding the mechanism behind coral U/Ca dependence on carbonate ion. For example, is there competition between uranyl complexes and carbonate ion at adsorption sites prior to crystal nucleation and growth? How would the form of uranyl complex affect coral U/Ca ratios? Is there a kinetic effect on El/Ca incorporation dependent on coral growth rate, even when complex forms are potentially incorporated in coral skeleton?

The presence of borate and boric acid in deep sea coral aragonite was recently demonstrated (Rollion-Bard et al., 2011). Do corals, though, modify their internal pH to oversaturation levels in respect to aragonite to assist crystal nucleation and growth? Do they fractionate boron during uptake? Micro-sampling using high precision, low mass B isotopes analyses with multi-collector ICP-MS (Rae et al., 2011), could provide estimates
of B isotope behavior within centers of calcification and fibrous aragonite potentially suggesting mechanisms of boron incorporation and associated vital effects.

Third, for this thesis a relatively large number of *D. dianthus* corals was used for the suggested calibrations. Additional corals will be required to expand the calibrations to oceanographic extremes of low pH, low phosphate and high Ba concentration, as well as to oceanic regions that are excluded, like the Mediterranean, the Great Barrier Reef, and fjords. If not possible, culturing studies could be an alternative approach to provide more confidence and reduce the error envelope of this dissertation’s calibrations.

### 6.2. Paleo-reconstructions

The proxies suggested in this dissertation were applied for paleo-reconstructions. A coral from the mixed layer depth of the South Chatham Rise recorded surface ocean acidification within the 20th century as reconstructed by B isotopes in *D. dianthus* skeleton (Chapter 4), while corals from the 1800-2000m depth, 15.4ky northwest Atlantic, characterized by a reversal in their radiocarbon age, provided the first direct evidence of endmember phosphate concentrations, in addition to carbonate ion and seawater barium reconstructions (Chapter 5). Nutrient and carbonate ion reconstructions based on these corals show similarities with additional corals from the Heinrich 1 (H1) event (Chapter 5). Lastly, phosphorus reconstructions were used as conservative tracers to calculate mixing ratio of north and south source water to the northwest Atlantic during the 15.4ky event, and they were coupled to radiocarbon measurements to provide transit time for the southern source waters to the North Atlantic (Chapter 5).
With further development and testing, the nutrient, circulation, and carbonate system proxies presented here could be applied to reconstruct glacial-deglacial climate variability. The location of *D. dianthus* in intermediate ocean depths is well suited for not only reconstructions of intermediate water formation and flow, when for example deep sea convection was altered during the last deglaciation (Chapter 5), but also as a location sensitive to deep water upwelling, like in the Southern Ocean, when wind induced changes in deep mixing allowed surfacing of isolated glacial deep Antarctic waters (Sigman et al. 2010, Anderson et al. 2009). Therefore variable depth distributed *D. dianthus* could serve as paleo–monitors of lateral and vertical migration of water masses.

Deep sea corals could provide snap shots of climate variability through reconstructions based on radiocarbon and the nutrient and carbonate system proxies developed in this thesis. Therefore they are especially suited to test theories behind the bipolar seesaw (Barker et al., 2009) between north and south hemisphere deglaciation. Key periods of interest are the H1, the 15.4ky event, the Bølling-Allerød (B/A) and its southern hemisphere counterpart the Antarctic Cold Reversal (ACR), the Younger Dryas (YD), and Holocene variability as described by the 8.3ky event, the Medieval Warm Period (MWP) and the Little Ice Age (LIA).

Ultimately a great use of deep sea corals is to study transitions in circulation and oceanic chemistry within the life span of a single coral (Adkins et al. 1998, Chapter 5) in addition
to time series at a single location (Robinson et al., 2005). When *D. dianthus* records are coupled with contemporaneous continuous foraminifera records, long time series reconstructions are also possible, with *D. dianthus* corals providing the anchor necessary for comparing different climate records. For example precisely dated *D. dianthus* corals with reconstructions implying abrupt changes in Northwest Atlantic phosphate concentrations could be used to align a foraminifera derived Cd/Ca record.

Finally, Chapter 5 suggests a Ba inventory change in the deglacial North Atlantic compared to Holocene. Further analyses of deep sea corals from the last glacial maximum to the Holocene period could provide insight of the duration of this change, and therefore whether it is a single time anomalous input in Ba, or if it is a repeated or continuous event during several freshwater pulses characterizing cold events in the North Hemisphere (H1, 15.4ky event, YD, and 8.3ky event). Comparison of North Atlantic with Southern Ocean corals will also assist in identifying if this Ba source is associated with a freshwater input in the North Atlantic or a whole ocean inventory change of Ba. If the North Atlantic proves to be the only place with elevated Ba concentrations during the deglaciation, additional corals from the Mediterranean outflow and the northeast Atlantic could provide insight of the source of this meltwater pulse. For example was this Ba source originating from early European ice melting and river discharge (Toucanne et al., 2010) or was it also originating from Laurentide ice sheet calving occurring potentially later within the H1 event? These questions are critical for understanding freshwater discharge routes in the north Atlantic and how they are related to sea level changes (Bard et al., 2010; Fairbanks, 1989; Stanford et al., 2006).
6.3. REFERENCES


Table A1

Summary of information on coral location, coral chemical properties, and hydrographic parameters at each coral specimen location.

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Table A2

Continued summary from Table A1. Uncertainties in PO$_{4}$, and CO$_{2}$ are SD of 2-8 nearby hydrographic stations (see text for details).

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<td>191</td>
<td>P96W</td>
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<td>2003 700 −31 −177 34 7 211 1.6 (0.2)</td>
<td>2284 21.46 104</td>
<td>Fukuwana, Masa, Rintoul, Stephen R. Rintoul, Stephen R. Swift, James</td>
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<td>47408</td>
<td>713</td>
<td>−49</td>
<td>−165</td>
<td>27</td>
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<td></td>
<td>1993 797 −49 −155 34 6 198 1.9 (0.2)</td>
<td>2159</td>
<td>Bullister, John L. Swift, James</td>
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<td>80207</td>
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<td>−148</td>
<td>23</td>
<td>P11A</td>
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<td>1993 1058 −47 −155 34 4 196 2.2 (0.2)</td>
<td>2159</td>
<td>Bullister, John L. Swift, James</td>
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<td>19468</td>
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<td>1888</td>
<td>−52</td>
<td>74</td>
<td>260</td>
<td>P15C</td>
<td></td>
<td>1993 680 −52 88 34 5 249 1.9 (0.1)</td>
<td>2156 437 97 (1)</td>
<td>Bullister, John L. Swift, James</td>
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<td>45669</td>
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<td>1963</td>
<td>−56</td>
<td>66</td>
<td>76</td>
<td>A34</td>
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<td>1972-1973 −58 66 34 2 214 2.3 (0.3)</td>
<td>2288 21.30 117</td>
<td>Ostlund et al., Bullister, John L. Swift, James</td>
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<td>−172</td>
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<td>1996 265 (350 for typical parameters)</td>
<td>115 249</td>
<td>Swift, James</td>
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References:
Curriculum Vitae
Eleni Anagnostou

**Education**
1997 -2003  B. Sc., Chemical Eng National Technical University of Athens, Greece
2003  Environmental Science,  NJIT, Newark, NJ
       Master’s program
2004-2005  M.S. Environmental Science  Rutgers, New Brunswick, NJ
2005-present  Oceanography,  Rutgers, New Brunswick, NJ
       Ph.D. program

**Principal post-graduate research**
2004-2005  Phosphorus cycling in the oligotrophic Lake Superior and Sargasso Sea;
       Focus on quantification of dissolved phosphorus pools
2005-2006  Trace metal concentrations in seawater and particulate matter
2006-2011  Element ratio and B isotope calibrations in the deep sea coral
       *D. dianthus*
2010-2011  Application of nutrient and carbonate ion proxies to fossil *D. dianthus*
corals from the North Atlantic and the Southern Ocean.

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Anagnostou, E. (2005) A Novel method for detecting nanomolar orthophosphate in  
freshwater systems: implications for phosphorus cycling in Lake Superior, USA.  
Masters Thesis in Environmental Science, Rutgers University, New Brunswick,  
New Jersey.