

**Evaluating carbonate saturation effects on magnesium calcium core top calibration
in benthic foraminifera**

by

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ABSTRACT OF THE THESIS

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Magnesium calcium paleothermometry in benthic foraminifera is intended to provide a salinity-independent reconstruction of bottom water temperature. The temperature calibration is however, rather uncertain, due to evidence of additional carbonate saturation effects on Mg incorporation into benthic tests. The overarching goal of this thesis is to directly determine the magnitude of the carbonate saturation effect and the threshold at which this effect significantly alters temperature estimates based on the Mg/Ca content of benthic foraminiferal tests. My research has focused on using homothermal homohaline depth transects from the Norwegian Sea and Gulf of Mexico in the context of a global core top calibration. This thesis consists of 45 core tops from four cruises. In these transects, the relationship between carbonate saturation and Mg/Ca is not strongly pronounced, possibly due to the large variability in the data. As is, it does support the hypothesis that in saturated waters, temperature exerts the primary control on benthic foraminiferal Mg/Ca. A two-part global calibration equation has been constructed for under- $(\Delta[\text{CO}_3^{2-}] < 3 \mu\text{mol/kg})$ and over-saturated $(\Delta[\text{CO}_3^{2-}] > 3 \mu\text{mol/kg})$ waters. However, these equations produce unrealistic bottom water temperature reconstruction when applied to a downcore record in the eastern basin of the tropical

Atlantic Ocean (1°21'S 11°58'W; 3912 m). These results suggest that further work is needed to improve the reliability of the Mg/Ca-T- $\Delta[\text{CO}_3^{-2}]$ equation and to accurately determine the threshold at which $\Delta[\text{CO}_3^{-2}]$ effects become pronounced. Likewise, future studies should look into using multi proxy approaches for correcting Mg/Ca-T estimates for saturation effects, such as the use of B/Ca measurements as a proxy for $\Delta[\text{CO}_3^{-2}]$.

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I. Introduction

Past behavior of the climate system offers insight into key mechanisms of the system, which allows us to more accurately predict future climate changes. As the ocean plays an important role in storing and transporting heat and energy in the earth system, determining the past behavior of the ocean is key to understanding the past behavior of climate.

Proxy records are vital to understanding past climate change, due to the absence of long term instrumental records. Among the diverse proxies for marine and continental temperatures, chemical compositions of marine biogenic carbonates are commonly used. These include strontium to calcium ratios (Sr/Ca) in corals, planktonic and benthic foraminiferal magnesium to calcium ratios (Mg/Ca), oxygen isotopic composition ($\delta^{18}\text{O}$), and elemental ratios of calcareous marine microfossils such as pteropods and ostracods. Ideally multiple proxies are used together, to account for the fact that all proxies have associated uncertainties. An example, one of the most reliable and established quantitative proxies for past global temperature change is oxygen isotopic composition of benthic foraminifera (e.g., Shackleton and Kennett, 1975). The main uncertainty associated with $\delta^{18}\text{O}$ records results from the fact that the oxygen isotopic composition of foraminiferal calcite is dependent on both calcification temperature and the oxygen isotope composition of seawater ($\delta^{18}\text{O}_{\text{sw}}$). $\delta^{18}\text{O}_{\text{sw}}$ is largely determined by global ice volume, as the lighter isotope (^{16}O) is preferentially stored in ice sheets, as well as local variations in evaporation/precipitation balance known as the salinity effect. A salinity independent quantitative paleothermometer would allow both past ocean temperature

determination and reconstructions of global and local variation in $\delta^{18}\text{O}_{\text{sw}}$ when paired with $\delta^{18}\text{O}$ of foraminiferal calcite ($\delta^{18}\text{O}_{\text{calcite}}$). To best characterize the ocean and understand its behavior in relation to climate, ideally we would pair measurements of sea surface temperature (SST) and sea surface salinity with bottom water temperature (BWT) and bottom water salinity to more accurately determine past changes in temperature, ice volume, salinity, evaporation and precipitation balance, and circulation.

Mg/Ca paleothermometry in benthic foraminifera is intended to provide a salinity independent reconstruction of BWT. Since its development, it has been considered a valuable and widely applied paleotemperature proxy, especially when paired with benthic foraminiferal $\delta^{18}\text{O}$ in order to estimate seawater $\delta^{18}\text{O}$ and provide insight into past variability in global ice volume, salinity, and ocean circulation (e.g., Keigwin et al., 2003; Lear et al. 2000; Martin et al., 2002). Mg/Ca is a robust proxy for paleothermometry work because of the relatively long residence times of Mg (13myr) and Ca (1myr) in the ocean. This should result in nearly constant Mg/Ca content of seawater on time scales shorter than 1Ma (Fantle et al., 2005; Fantle et al., 2006). This study focuses on investigating the effect of carbonate saturation at depth on calcite test formation, a process which affects benthic foraminifera rather than planktonic organisms.

1.1 Thermodynamic considerations

The theoretical basis for the Mg/Ca proxy is the thermodynamic effect when magnesium carbonate (MgCO_3) substitutes into calcium carbonate (CaCO_3) during formation. Furthermore, MgCO_3 is isostructural with calcite making it a logical choice for a proxy based on solid substitution of trace metals into calcium carbonate. The

substitution of Mg into CaCO_3 depends on the Mg/Ca activity of seawater and the distribution coefficient of Mg/Ca between calcite and seawater. The empirical homogeneous distribution coefficient based on the molar concentration ratio of Mg/Ca in calcite and seawater is $D_{\text{Mg/Ca}} = \text{Mg/Ca}_{\text{mineral}}/\text{Mg/Ca}_{\text{seawater}}$. At equilibrium, the partitioning between MgCO_3 and CaCO_3 depends on temperature; substitution of Mg is associated with a change in the heat of reaction, which is sensitive to temperature. As the substitution of Mg into calcite is an endothermic reaction, Mg/Ca of calcite is expected to increase with increasing temperature.

Thermodynamics of solid solution substitution of Mg for Ca in calcite predicts that Mg/Ca should increase by ~3% per °C increase in temperature (Lea et al., 1999). This is generally supported by inorganic precipitation experiments (e.g. Katz, 1973; Mucci, 1987). The thermodynamic relationship predicts an exponential response of Mg/Ca to temperature, which fits with early planktonic and benthic calibrations (Nurnberg et al., 1996; Rosenthal et al., 1997).

1.2 Biological control

In general, foraminifera, both planktonic and benthic, contain about an order of magnitude less Mg than inorganically precipitated calcite, and the response of Mg/Ca to temperature is larger. This suggests that foraminifera exert a strong biological control on the biomineralization process which influences the incorporation of trace metals into the test mineral. Recent calcification studies indicate it is likely foraminifera calcify from seawater that is encapsulated within an internal calcification pool, the composition of which may be altered by removal of Mg through cellular pumps and channels (Erez,

2003; Bentov & Erez, 2006). The strong biological control on Mg/Ca in foraminifera demonstrates the need for empirical calibrations.

1.3 History of the Mg/Ca paleothermometer

In addition to thermodynamic considerations and evidence from inorganic precipitation experiments, the argument that Mg/Ca in foraminifera is predominantly controlled by temperature is supported by the following observations: 1) the strong correlation of core top data with the overlying bottom water temperatures (e.g., Rosenthal et al., 1997); 2) evidence from cultured planktonic foraminifera in variable temperature experiments (Nurnberg, 1996; Lea, 1999); and 3) core top calibrations of planktonic foraminifera showing a strong correlation between Mg/Ca and SST (Anand et al., 2003; Elderfield and Ganssen, 2000).

Calibrations for using Mg/Ca in planktonic foraminifera to determine SST have been done via core top, sediment trap, and culture experiments (e.g. Elderfield and Ganssen, 2000; Anand et al., 2003; Lea et al., 1999). These calibrations established an exponential temperature dependence of about 9-10% mmol/mol per degree Celsius (°C) in most species (Nurnberg et al., 1996; Lea et al., 1999; Elderfield and Ganssen, 2000; Anand et al., 2003).

Use of Mg/Ca in planktonic foraminifera for determining local SST histories and evaluating climate change has been successful. For example, Lea et al. (2000) used Mg/Ca in planktonic foraminifera to resolve late Quaternary SST variations in the equatorial Pacific; Rosenthal et al. (2003) looked at amplitude and phasing of climate change during deglaciation.

Planktonic calibrations have typically been expressed as: $Mg/Ca = Be^{AT}$, where A is the exponential constant, and B is the pre-exponential constant. The exponential constant controls the sensitivity to temperature while the pre-exponential constant determines the absolute temperature. Most show good agreement between multi-species calibrations (Elderfield and Ganssen, 2000; Rosenthal and Lohmann, 2002) which suggests that the temperature signal in the foraminifera tests is reliably recorded in the sediment.

As offsets are seen between species in both culture and sediment trap calibrations (Elderfield and Ganssen, 2000; Anand et al., 2003) single-species calibrations may be more robust. Many planktonic calibrations show consistent exponential constants (Nurnberg et al., 1996; Lea et al., 1999; Elderfield and Ganssen, 2000; Anand et al., 2003) which suggests the temperature sensitivity in planktonic foraminifera is a robust feature of the proxy. However other sources of uncertainty in absolute temperature, diagenetic overprints, and both intra- and inter-species variability suggest that Mg/Ca-paleothermometry is more accurate in estimating relative changes than in determining absolute temperatures.

Mg/Ca analyses on benthic foraminifera from core tops by Rosenthal et al. (1997), Lear et al. (2002) and Martin et al. (2002) indicates benthic foraminifera perform similarly to the temperature sensitivity of 10% mmol/mol per degree Celsius well established in planktonic foraminifera. As the calibration progressed, researchers moved towards single-species calibrations (e.g. Rosenthal et al., 1997; Lear et al., 2002; Marchitto et al., 2007).

1.4 History of benthic foraminiferal Mg/Ca

The positive correlation between Mg and temperature in biogenic calcites was noted decades ago (Chave, 1954), but it was not investigated as a temperature proxy for several decades. Izuka (1988) proposed that temperature was the primary control on Mg content in the benthic foraminifer *Cassidulina*. Core top data provided the first estimate of the temperature dependence of Mg in foraminifera (Russell et al., 1994).

Early calibration work was done on a single species (*Cibicidoides pachyderma*) at a single location (Little Bahama Bank – BWT range from 5° to 18°C) (Rosenthal et al., 1997). Later core top calibrations (Lear et al., 2002; Martin et al., 2002) suggested the same temperature sensitivity for *Cibicidoides*, ~10% Mg/Ca change per degree Celsius temperature change seen in many planktonic species. Similar temperature sensitivity has also been observed in benthic species such as *Planulina spp.*, *Oridorsalis umbonatus*, *Melonis spp.*, and *Uvigerina spp.* (Lear et al., 2002). Additional work on benthic calibrations provided adjustments for analytical and cleaning offsets (e.g., Billups and Schrag, 2002; Lear et al., 2000; Martin et al., 2002).

With better calibrations between Mg/Ca in benthic foraminifera and BWT, deep water temperature histories can be more reliably reconstructed to investigate some important paleoclimate problems such as glacial-interglacial deep sea temperature change, past ocean circulation changes, and the long term evolution of global ice volume (Billups and Schrag, 2002; Lear et al., 2000; Lear et al., 2003; Lear et al., 2004; Keigwin et al., 2003; Martin et al., 2002).

1.5 Non-temperature effects on Mg/Ca

Non-temperature effects have been observed in planktonic foraminifera Mg/Ca. A weak positive relationship between foraminifera Mg/Ca and seawater salinity (Lea et al., 1999; Nurnberg et al., 1996) and an inverse relationship with pH (Lea et al., 1999; Russell et al., 2004) offer evidence that temperature is not the sole control on Mg/Ca in foraminiferal calcite. Another factor that needs to be accounted for is the effect of post depositional dissolution on test chemistry. This is clearly demonstrated in planktonic studies and has been corrected for by methods such as size normalized shell weight (Dekens et al., 2002; Rosenthal et al., 2000; Rosenthal and Lohmann, 2002). These relationships are not clearly defined in terms of a calibration, but should be explored in benthic foraminifera to better isolate the temperature relationship.

The temperature calibration for benthic foraminifera is rather uncertain at present. Benthic foraminiferal tests from deep transects in both the Atlantic and Pacific show decreases in Mg/Ca beyond the change predicted by the global calibration and the local temperature profile (see Figure 1; Russell et al., 1994; Martin et al., 2002). This suggests the presence of additional non-temperature influence on the Mg content of benthic foraminiferal calcite.

Core top data for multiple species of *Cibicidoides* from sites with BWT less than 3°C are anomalously low with respect to Mg. These data fall on a steeper Mg/Ca-temperature slope than data above 3°C (Lear et al., 2002; Martin et al., 2002; Elderfield et al., 2006). This combined with observations of other trace elements exhibiting strong gradients with water depth (McCorkle et al., 1995; Elderfield et al., 1996; Marchitto et

al., 2000) gave rise to the hypothesis that carbonate ion (or more accurately carbonate saturation) effects the partitioning of trace metals into benthic foraminiferal calcite. Anomalies among benthic species for different published calibrations have also been attributed to the carbonate ion effect (Elderfield et al., 2006). Elderfield et al. (2006) quantified the carbonate ion effect in common calcitic benthic species covering -2 to 20°C. However, this calibration has not yet been used in the construction of a long term downcore temperature record.

There has been some debate as to whether the saturation related decrease in trace elements is due to preferential dissolution of metal from calcite tests (McCorkle et al., 1995) or metal uptake during test formation (Elderfield et al., 1996). Study of foraminiferal Zn/Ca (Marchitto et al., 2000) suggests the depth related decrease is primarily due to an effect on the chemistry during calcification, rather than post-depositional dissolution.

Multiple benthic calibration studies support that the dominant control on foraminiferal Mg/Ca is temperature (Lear et al., 2002; Martin et al., 2002; Elderfield et al., 2006). However questions remain about the accuracy of the calibrations. Early *Cibicidoides* calibrations used a data set from the Little Bahama Bank (LBB) (Rosenthal et al., 1997) which is now thought to contain samples contaminated by inorganic precipitation of high Mg calcite (Lear et al., 2002; Marchitto et al., 2007). Subsequent calibrations have removed the highest Mg data points (Lear et al., 2002; Rosenthal et al., 2006) or removed the LBB data set altogether (Elderfield et al., 2006). A new study of *C. pachyderma* results in a low slope (4% rather than 10% per degree C) linear

dependence of Mg/Ca over a temperature range of 6 to 19°C (Marchitto et al., 2007).

This is part of a growing body of evidence which suggests the temperature sensitivity of benthic foraminifera Mg/Ca_{calcite} is significantly lower than previous studies indicated.

1.6 Carbonate ion effect

It is difficult to separate the effects of bottom water temperature and saturation on foraminiferal test chemistry because these two parameters are positively correlated in the ocean; both properties vary with depth. This is easily demonstrated via ocean survey data (GEOSECS, WOCE) and in our study sites. Uptake of inorganic carbon at the surface by photosynthetic organisms leads to relatively high pH. pH decreases with depth as organic particulates are recycled and carbon dioxide is released. These processes result in relatively high carbonate ion concentrations in surface waters, and low carbonate ion concentrations at depth. As equilibration with the atmosphere (with respect to carbon dioxide) is temperature dependent, surface water concentrations of carbonate ion also decrease with latitude. Carbon dioxide has greater solubility at low temperature, which causes lower pH, and thus carbonate ion concentration is lower in cold surface waters relative to warm. This character is largely conserved when a water mass is advected to the deep ocean, however, as carbonate system constants are dependent on temperature and pressure, some modification to carbonate ion content does occur.

It is also important to note that the deep ocean can be considered an unfavorable environment for calcification. Though it is well documented that benthic foraminifera live in undersaturated waters, this should require them to manipulate the calcifying solution to initiate and maintain test precipitation. Theoretically, the lower the carbonate

saturation, the greater degree of manipulation necessary for foraminifera to calcify, possibly leading to increased vital effects on test chemistry and an overprinting of the temperature signal in Mg/Ca. Due to organic matter decay and release of carbon dioxide, lowering pH, conditions at the sediment-water interface and within sediment pore water may be of lower saturation than the overlying bottom water. It is not determined to what degree even epibenthic foraminifera are influenced by pore water rather than bottom water (Zeebe, 2007).

1.7 Objectives

The purpose of this study is to evaluate the temperature dependence of benthic foraminiferal Mg/Ca, and to identify and quantify non-temperature effects, specifically the carbonate ion effect. Elderfield et al. (2006) determined the magnitude of the carbonate ion effect by removing an assumed temperature component from the larger data set, which in turn was determined using a best fit to the data. In contrast, this study attempts to directly determine the magnitude of the carbonate ion effect and the threshold at which it becomes significant to the Mg/Ca content of benthic foraminifera tests. The Norwegian Sea and Gulf of Mexico sites were chosen specifically for their hydrographic properties. Below 1000m in both basins, bottom waters are at a nearly constant temperature; -1°C and 4°C, respectively. Salinity is relatively constant below 1000m in both basins as well, measuring 34.90 to 34.91 in the Norwegian Sea and 34.97 to 35.00 in the Gulf of Mexico. A constant temperature and salinity depth transect allows us to determine what contribution, if any, carbonate saturation makes to the Mg/Ca composition of foraminiferal calcite.

I hypothesize that in sites overlain with bottom water that is saturated with respect to carbonate, temperature will be the primary control on benthic foraminiferal Mg/Ca. I further hypothesize that where the carbonate ion effect is present, the dependence of Mg/Ca on carbonate will be approximately an order of magnitude lower than the dependence on temperature. I propose to quantify the sensitivity of foraminiferal Mg/Ca to bottom water carbonate saturation in homothermal depth transects, and by contrasting core tops from saturated bottom waters to those from undersaturated bottom waters along the same transect. I further propose to construct a two part calibration equation based on the dual influence of temperature and carbonate saturation on Mg/Ca, and to test the resulting benthic calibration equations on downcore Mg/Ca data from the literature, in order to determine the applicability and usefulness of a two part calibration equation.

II. Methods

2.1 Sample locations and hydrographic data

Samples for this study were obtained from four depth transects: 1) Norwegian Sea (Nor), 2) Gulf of Mexico (GoM), 3) Cape Hatteras Continental Shelf (CH), and 4) New Zealand (NZ). The sites were chosen to cover a variety of bottom water temperature (BWT) and calcite saturation conditions, thus complementing sites studied in previous calibrations (Figure 2).

2.1.1 Norwegian Sea

Norway Basin is in the southern Norwegian Sea, east of the Voring Plateau. It is bounded by the Jan Mayen Fracture zone to the north, the Iceland-Faeroe and Wyville-Thomson Ridges to the south, and the Norwegian continental shelf to the east. The maximum depth is 3900m, and the primary water mass is homothermal, homohaline Norwegian Sea Bottom Water (NSBW). The boundary between NSBW and the homohaline Norwegian Sea Deep Water (NSDW) is at about 1400m and shoals to 900m towards the continental margin, enabling a depth transect of sites bathed in NSBW to be constructed. An extension of the North Atlantic Drift forms the Norwegian Current, and is separated from the NSDW by a narrow transition layer. Modern regional sedimentation rates are low (2-6cm/kyr) but increase downcore due to increased flux of glacial material. The sediment is primarily foraminiferal ooze (>30% CaCO₃) below about 1300m. Shallower than 1300m the terrigenous component is greater and the CaCO₃ content may be as low as 15%. Significant down slope reworking is not observed below 500m (Mackensen et al., 1985)

The Norwegian Sea site was chosen to address the carbonate ion effect, as it covers a range of calcite saturation levels at a constant temperature and salinity. Species of benthic foraminifera typically used in paleoceanographic work are common in these sediments (Mackensen et al., 1985), including *Planulina wuellerstorfi* and *Oridorsalis umbonatus*, which are used in this study. Twelve core top samples were collected using a multicore during the KN177-2 (*R/V Knorr*) cruise in 2004 (Figure 3). The samples span depths from 965 to 3341m, which covers small ranges of BWT and salinity of -0.6 to -0.9°C, and 34.90 to 34.91, respectively (Table 1; Figure 7).

2.1.2 Gulf of Mexico

The Gulf of Mexico is a simple basin, roughly circular in shape with a diameter of about 1500km. The basin is nearly enclosed by continental land masses. With most of the circumference ringed by continental shelf and slope only about 20% of the basin by area is abyssal zone (>3000m water depth; Darnell and Defenbaugh, 1990). The North Equatorial Current and part of the Caribbean Current merge to form the Yucatan Current. The latter current enters the Gulf via the Yucatan Strait and becomes the Loop Current. The Loop Current exits through the Florida Strait to join the Gulf Stream after circulating the basin (Nowlin, 1971).

Twenty box cores from the Deepwater Program: Northern Gulf of Mexico Continental Slope Habitats and Benthic Ecology (DGoMB) project (Gilbert T. Rowe, TAMU, 2000) were subsampled. The box cores were taken from six transects across the northern Gulf of Mexico (Figure 4) at depths from 1060m to 3150m water depth and BWT, salinity, and [CO₃] ranging from 4.9 to 4.3°C, 34.94 to 35.00, and 102.5 to

116.7 $\mu\text{mol/kg}$, respectively (Table 2; Figure 7). Sedimentation rates in the Gulf of Mexico are high, between 34 and 43 cm/kyr (Richey et al., 2006). Below about 1000m the Gulf of Mexico is also homothermal, allowing us to observe the effect of varying carbonate chemistry with depth on Mg/Ca in foraminiferal calcite in a warm end member.

2.1.3 Cape Hatteras

The Cape Hatteras site was chosen because it was expected to contain an abundance of common paleoceanographic benthic foraminiferal species used to refine the cold end of the Mg/Ca calibration, specifically *Planulina wuellerstorfi* and *Cibicidoides pachyderma*. The main interval of interest is oversaturated waters below 2km water depth. The 12 core top samples were collected along a transect from Woods Hole, MA to Cape Hatteras, NC. Samples were collected using a multicorer on the KN178 (*R/V Knorr*) cruise in 2004 (Figure 5). The Cape Hatteras samples span depths from 830 to 3979m, associated with BWT, salinity, and $[\text{CO}_3]$ changes of 5.8 to 2.1°C, 34.88 to 35.08, and 116.7 to 90.8 $\mu\text{mol/kg}$, respectively (Table 3; Figure 7).

2.1.4 New Zealand

The New Zealand site (cruise RR05-03, 2005, *R/V Roger Revelle*) was chosen to collect surface sediments along a transect covering variable depths and low to undersaturated carbonate saturation over a relatively small range of bottom water temperature (Figure 6). This transect provides an undersaturated analog to the saturated conditions tested in the Atlantic core top study sites. This transect extends the calibration into mostly undersaturated waters in the cold end of the Mg/Ca-temperature calibration. The 12 New Zealand samples cover depths from 663 to 4375m and BWT, salinity, and

[CO₃] ranges of 4.88 to 1.20°C, 34.29 to 34.71, and 110.0 to 80.4 μmol/kg, respectively (Table 4; Figure 7).

2.1.5 Sites from previous studies

This study uses a combination of new and published core top data from sites throughout the globe (Figure 2; Appendix 2). Samples were previously obtained from the Hawaiian Islands (cruise MW98-13, 20.72°-20.92°N, 157.05°-159.15°W) and the Sulawesi margin in Indonesia (cruise BJ8-03, 2.87°N-5.85°S, 117.41°-120.28°E). Details of core location, bottom water temperature (BWT) and Mg/Ca data for the Hawaii (HW) samples can be found in Lear et al., 2002. The locations of the study sites are shown in Figure 1. The ranges of BWT, bottom water salinity, and $\Delta[\text{CO}_3^{-2}]$ covered by the study sites are shown in Appendix 1 and 2.

2.2 Carbonate geochemistry

Temperature and salinity profiles for the Norway, Gulf of Mexico, and Cape Hatteras sites are based on conductivity-temperature-depth (CTD) data collected during each cruise. For the New Zealand site, CTD data recovered temperature only, and salinity data is taken from the same source as the carbonate chemistry data. Total dissolved inorganic carbon (TCO₂) and total alkalinity (TAlk) data for Norway come from the nearest TTO (station 143; Brewer et al., 1986: http://gcmd.nasa.gov/records/GCMD_CDIAC_NDP4.html). For the Gulf of Mexico, Cape Hatteras, and New Zealand sites TCO₂ and TAlk data come from the nearest WOCE stations (A05 S97, Millero et al., 2000; A22 S40, Johnson et al., 2003; P15 S71, Feely et al., 1996, respectively; <http://cdiac.ornl.gov/>). In situ carbonate ion

concentrations were calculated from TCO₂ and TAlk using the CO2SYS program available online (Lewis and Wallace, 1998). Carbonate saturation with respect to calcite was calculated using the formula:

$$\Delta[\text{CO}_3^{-2}]_{\text{calcite}} = [\text{CO}_3^{-2}]_{\text{in situ}} - [\text{CO}_3^{-2}]_{\text{saturated}}$$

Where $[\text{CO}_3^{-2}]_{\text{saturated}} = 90\exp[0.16(Z-4)]$, where Z = water depth in kilometers (Broecker and Peng, 1982), as the CO2SYS program does not calculate carbonate saturation.

Temperature, salinity, and carbonate saturation profiles for these four sites are shown in Figure 7.

For the sites from earlier studies, temperature and salinity profiles come from conductivity-temperature-depth (CTD) data collected near the coring sites during each cruise (Slowey, 1990; Rosenthal et al., 2007). Total alkalinity and TCO₂ for the Hawaii site comes from the WOCE station nearest the coring sites (P15Na S68:

<http://cdiac.ornl.gov/>). TCO₂ and total alkalinity were determined for the Indonesia station on water samples collected during the cruise. Analyses were done by Dr. Chris Sabine at the NOAA/PMEL laboratory (Seattle, WA) following WOCE protocols (Rosenthal et al., 2007).

2.3 Analytical Protocols

After recovery, core tops from the Norwegian Sea, Cape Hatteras, New Zealand, and Indonesia sites were stored at 4°C until processing. Back in the laboratory, samples were preserved with a 4% formalin-seawater solution buffered with sodium borate, then processed in Rose Bengal stain (1 g/L of 4% formalin-seawater solution) for at least one

week to identify residual protoplasm and separate “recently alive” (stained) from unstained foraminifera that have been dead for an appreciable amount of time (Corliss and Emerson, 1990). Hawaiian samples were preserved shipboard with 3.8% formalin solution buffered with Borax to pH~8, and later stained in the laboratory. Gulf of Mexico samples were not stained for live specimens, due to their long storage time and lack of refrigeration before processing. Sediments were wet sieved through 63µm mesh and the wet coarse fraction was picked for stained specimens. Residual sediments were rinsed with deionized water, oven dried at 60°C, and subsequently picked for dead specimens. Both stained and unstained specimens were picked from the >150µm fraction for calcitic benthic foraminifera species (*Planulina wuellerstorfi*, *Cibicidoides pachyderma*, *Oridorsalis umbonatus*, and *Uvigerina spp.*).

Four to fifteen foraminiferal tests from the >150 µm size fraction were crushed, and then cleaned using standard protocol to remove clays, organic matter, and metal oxides (Boyle and Keigwin, 1985; Barker et al., 2003). The cleaned tests were dissolved in trace metal clean 0.065N HNO₃ (Optima®) and 100uL of dissolved sample was diluted with 300uL trace metal clean 0.5N HNO₃ to obtain a Ca concentration of 3±1mmol/L. Samples from Cape Hatteras and New Zealand were cleaned and dissolved using reagents prepared with boron-free water – double distilled water was passed over an anion exchange resin (Aldrich, amberlite IRA-743) to remove boron.

Samples were analyzed by (Thermo Element Sector Field Inductively Coupled Plasma Mass Spectrometer (SF-ICP-MS) operated in low resolution ($m/\Delta m = 300$) following the method outlined in (Rosenthal et al., 1999) and modified in (Lear et al.,

2002; Andreassen et al., 2006). Direct determination of elemental ratios from intensity ratios is significantly affected by the sample Ca concentration of the solute. In order to correct for this matrix effect, six standard solutions with identical elemental ratios but variable Ca concentrations, which covered the range of Ca concentrations of the samples, were included in each run. These solutions allow us to quantify and correct for the effects of variable Ca concentrations in sample solutions on the accuracy of Mg/Ca measurements (matrix effects) based on the ratio of Ca concentrations (Rosenthal et al., 1999). The corrections are typically $<0.1\text{mmol/mol}$ Mg/Ca. A discussion of matrix effects on the accuracy of Mg/Ca and Sr/Ca measurements in foraminifera can be found in Andreassen et al. (2006).

Instrument precision was determined by repeat analysis of three consistency standards over the course of this study. The long-term precision of the consistency standard with Mg/Ca of 1.24mmol/mol was $\pm 0.63\%$, the precisions of the consistency standards with Mg/Ca of 3.32mmol/mol and 7.5mmol/mol were $\pm 0.5\%$ and $\pm 0.53\%$, respectively. Note in Figure 8 the variability in the long term precision falls within 2sd across all analyses. Core top Mg/Ca data for all sites can be found in Appendix 1.

Replicate analysis ($n=3$) showed an uncertainty of $\pm 0.06\text{mmol/mol}$. As this uncertainty is within the magnitude of the analytical error, sample reproducibility is good (see Table 5).

III. Results

3.1 *Live vs. dead samples*

For foraminiferal tests containing cytoplasm (stained), referred to as “live,” (more accurately, both those that were alive upon collection and those recently living) we generally assume 1) the tests were precipitated under current bottom water conditions, and 2) the tests are recent enough to be free of post depositional alteration. If “dead” (unstained) test trace metal composition is not significantly different from that of the “live” specimen, we assume the data from all tests is reliably recent and free of post depositional alteration. Figure 9A shows Mg/Ca for live tests versus Mg/Ca for dead tests from the same sample for *P. wuellerstorfi*. A 1:1 line is shown for reference. Mg/Ca for live versus dead tests for *C. pachyderma* is shown in Figure 9B. *P. wuellerstorfi* from Norway and Hawaii samples plot fairly close to a 1:1 line, as do *C. pachyderma* samples from Cape Hatteras and Indonesia.

3.2 *Homothermal depth transects*

3.2.1 *Mg/Ca in P. wuellerstorfi*

Mg/Ca ratios in *P. wuellerstorfi* tests from the Norwegian Sea core tops cover over 2000m of water depth, but just 0.2°C temperature change (Figure 7), and exhibit variability of 0.32mmol/mol in Mg/Ca. There is no significant trend in the Mg/Ca data with depth at this site (Figure 10); a linear regression through the data gives a negligible slope (10^{-5} order of magnitude) and $R^2 = 0.34$.

As in other studies discussing the carbonate ion effect (e.g. Rosenthal et al., 2006; Elderfield et al., 2006), we will use carbonate ion saturation ($\Delta[\text{CO}_3^{2-}]$). Comparison to the transect carbonate saturation data, which ranges from 14.9 to 61.9 $\mu\text{mol/kg}$, also shows a trend of low significance ($R^2 = 0.33$), which fails to explain the 0.32 mmol/mol range in Mg/Ca (Figure 12).

The carbonate ion sensitivity determined by Elderfield et al. (2006) would theoretically account for the magnitude of the variability we see in this case. If we calculate the amount of change in Mg/Ca we would expect to see at this site based on the change in $\Delta[\text{CO}_3^{2-}]$ and the published carbonate sensitivity, we get:

$$\text{Mg/Ca} = 0.0086 * \Delta[\text{CO}_3^{2-}] \quad (\text{Elderfield et al., 2006})$$

$$\text{Range of } \Delta[\text{CO}_3^{2-}] = 61.9 - 14.9 = 47 \quad (\text{this study, Norwegian Sea})$$

$$0.0087 * 47 = \pm 0.41 \text{ mmol/mol Mg/Ca} \quad (\text{expected Mg/Ca}_{\Delta\text{CO}_3}, \text{ Norwegian Sea})$$

If up to 0.41 mmol/mol variability in the Mg/Ca were due to carbonate, scatter due to natural variability or analytical uncertainty would be completely lost in this site. However, the data do not show a trend significantly different from scatter ($R^2 = 0.33$). While the magnitude of the signal is close to that expected from the published relationship of Mg/Ca to $\Delta[\text{CO}_3^{2-}]$ (Elderfield et al., 2006), there is no directional trend in this data.

Gulf of Mexico samples of *P. wuellerstorfi* cover over 2000m of water depth, but only 0.1°C of temperature change (Figure 7A), and 33.6µmol/kg range in carbonate saturation (Figure 7C). Mg/Ca values show 0.42mmol/mol variability. There is no significant trend in the Mg/Ca data with depth at this site (Figure 14; $R^2 = 0.03$).

$\Delta[\text{CO}_3^{-2}]$ values in the Gulf of Mexico are comparable to, but slightly higher than those in the Norwegian Sea transect across a similar sample of depths. Gulf of Mexico $\Delta[\text{CO}_3^{-2}]$ values range from 29.7 to 71.0µmol/kg, and shows no significant influence on Mg/Ca (Figure 16; $R^2 = 0.03$).

In this case of little temperature variability with a broad $\Delta[\text{CO}_3^{-2}]$ change, the carbonate ion sensitivity expected from Elderfield et al. (2006) accounts for less (with respect to Norway) of the observed Mg/Ca variability (Mg/Ca_{ΔCO₃} of 0.36mmol/mol calculated, versus 0.42mmol/mol observed). The observed variability occurs as scatter across the entire data set, and not in a systematic way quantifiable in terms of either depth or $\Delta[\text{CO}_3^{-2}]$.

The Norway and Gulf of Mexico data sets provide examples of Mg/Ca data free of temperature controls and with changing $\Delta[\text{CO}_3^{-2}]$. No resolvable trends are observed despite a change in bottom water carbonate chemistry. This suggests that in saturated waters ($\Delta[\text{CO}_3^{-2}] > 10\mu\text{mol/kg}$), bottom water $\Delta[\text{CO}_3^{-2}]$ does not exert a significant influence over the Mg/Ca content of *P. wuellerstorfi* test calcite. It is important to note that in addition to having two homothermal data sets confirming a lack of significant carbonate chemistry influence on Mg/Ca, both data sets are from relatively low temperatures in the context of global calibration (e.g. 0-20°C, Lear et al., 2002). While

more recent calibrations use linear relationships (e.g., Elderfield et al., 2006; Marchitto et al., 2007), in early Mg/Ca-temperature calibrations the exponential fit predicts small changes in foraminiferal Mg/Ca at the cold end ($<4^{\circ}\text{C}$). This suggests the effects of any non-temperature processes should be relatively more pronounced, especially in the Norwegian Sea.

This leaves the question of what is causing the observed variability in Mg/Ca. Variability in both of the homothermal transects exceeds what we would expect to see for a single species at a single site and temperature. If this variability were scaled to temperature using the original 10% change in Mg/Ca per degree calibration, the scatter in our data would correspond to 3 to 4°C temperature change.

This large amount of variability both in stained and unstained samples could be the result of any of several factors: 1) a second order carbonate ion variability in the pore water that we have not captured that influences even an epibenthic species such as *P. wuellerstorfi* (Zeebe, 2007); 2) other environmental factors (possibly affecting growth or calcification rate) are affecting benthic foraminiferal Mg/Ca; and/or 3) measuring a large number of samples from a single site increases the possibility of capturing vital effects and natural intraspecific variability.

In order to further investigate the behavior of benthic shell chemistry at these particular sites, we examine additional species from the same transects.

3.2.2 Mg/Ca in *Oridorsalis umbonatus*

In contrast to *P. wuellerstorfi*, Mg/Ca data for *O. umbonatus* (Figure 18) show a linear trend with depth, but note that the slope of this relationship is extremely small and the significance is low (slope = 0.0001; $R^2 = 0.59$). The relationship between Mg/Ca and $\Delta[\text{CO}_3^{-2}]$ in *O. umbonatus* is inconclusive ($R^2 = 0.34$) in the current data set (Figure 19). *O. umbonatus* in the Gulf of Mexico samples are of insufficient mass for ICP-MS analysis.

P. wuellerstorfi and *O. umbonatus* are two of the more commonly used benthic species in multi-species Mg/Ca downcore records; note that both show little or no variability with depth and carbonate saturation under homothermal conditions in saturated waters (Figures 10, 12, 14, 16, 18, 19).

3.3 Global calibration sites

3.3.1 Mg/Ca in *P. wuellerstorfi*

The Cape Hatteras samples cover a water depth range of 830 to 3979 m. BWT ranges from 2.2 to 5.9°C. $\Delta[\text{CO}_3^{-2}]$ and salinity cover ranges of 17.4 to 48.7 $\mu\text{mol/mol}$, and 34.88 to 34.93, respectively (Figure 7: A, B, and C respectively). *P. wuellerstorfi* in the Cape Hatteras samples shows 0.72mmol/mol variability in Mg/Ca (Figure 20).

There were not a significant number of live benthic foraminifera to run for ICP-MS analysis so it was not possible to compare stained and unstained tests for this site.

Likewise, as we have no ^{14}C ages for these core tops it is difficult to assert that they are modern age. Nonetheless based on companion cores we are confident that they represent

late Quaternary age. The Cape Hatteras data show a large amount of scatter throughout the ranges of depth and temperature covered (Figure 20A). While showing a slight decrease in Mg/Ca with increasing depth, data from this site do not show a clear slope with temperature (Figure 20B). No relationship with $\Delta[\text{CO}_3^{-2}]$ is seen (Figure 22; $R^2 = 0.003$).

The New Zealand samples correspond to a water depth range of 663 to 4375m. Bottom water temperature and salinity range from 1.2 to 4.9°C and 34.29 to 34.71, respectively (Figure 7). The $\Delta[\text{CO}_3^{-2}]$ range is -14.9 to 57.2 $\mu\text{mol/kg}$ (Table 4; Figure 7C). Live *P. wuellerstorfi* are not present. Mg/Ca exhibits variability of 1.25mmol/mol and decreases with decreasing temperature (Figure 24B). The slope of that temperature relationship, is about 0.3mmol/mol/°C ($R^2 = 0.52$). Mg/Ca in New Zealand follows the general thermocline structure with depth. Mg/Ca also shows a decrease with decreasing $\Delta[\text{CO}_3^{-2}]$ (Figure 26), but as temperature and $\Delta[\text{CO}_3^{-2}]$ both decrease with depth, some of this relationship is undoubtedly due to temperature.

Mg/Ca ratios in the Indonesia data decrease linearly with temperature from 2.09mmol/mol at 8°C to 1.09mmol/mol at 3.5°C (Lear et al., 2002) (Figure 28B). While the Hawaii data do not have as strong a linear relationship, they fall in line with the overall linear relationship between Mg/Ca and temperature for the combined Cape Hatteras, New Zealand, Hawaii, and Indonesia sites (Figure 29).

The New Zealand samples cover cold temperature and undersaturated bottom water. We were unable to obtain enough calcite for measurement ($>100\mu\text{mol}$) in many of

the undersaturated core tops, so we have few ($n=3$) measurements in undersaturated conditions. The data we do have agrees reasonably well with the other sites (Figure 29).

3.3.2 Mg/Ca in *C. pachyderma* and *O. umbonatus*

C. pachyderma in the Cape Hatteras samples show a Mg/Ca range of 0.65mmol/mol. There is a scatter throughout the ranges of depth and temperature covered (Figure 30A, 30B). The data show a decrease in Mg/Ca with increasing depth, and a slope with temperature of about 0.1mmol/mol/°C (Figure 30B; $R^2 = 0.23$). A relationship with $\Delta[\text{CO}_3^{-2}]$ is seen, but the trend is not strong ($R^2 = 0.42$) and Mg/Ca decreases with increasing $\Delta[\text{CO}_3^{-2}]$, opposite of the expected relationship (Figure 31).

Cape Hatteras *O. umbonatus* samples show a Mg/Ca range of 1.62mmol/mol. Mg/Ca decreases with increasing temperature, reverse the expected relationship (Figure 32B). Mg/Ca in Cape Hatteras *O. umbonatus* also decreases with increasing $\Delta[\text{CO}_3^{-2}]$ (Figure 32C). This species does not provide reliable results at this site, for purposes of core-top calibration. New Zealand *O. umbonatus* samples show a Mg/Ca range of 1.03mmol/mol. There are, as expected, Mg/Ca decreases with increasing depth, and increases with increasing temperature and $\Delta[\text{CO}_3^{-2}]$ (Figure 33A, 33B, 33C).

IV. Discussion

4.1 Minimizing the temperature effect

By comparing *P. wuellerstorfi* data from the Gulf of Mexico, New Zealand, Cape Hatteras, Indonesia, and Hawaii sites from a set of narrow temperature ranges (1.2-2.2°C; 1-3°C; 3.5-4.5°C) we minimize the effect of temperature on Mg/Ca to better assess carbonate ion control. The 1.2-2.2°C subset of the data suggests that the carbonate ion effect becomes significant between slightly saturated ($\Delta[\text{CO}_3^{2-}] = 3\mu\text{mol/kg}$) and undersaturated ($\Delta[\text{CO}_3^{2-}] = -15\mu\text{mol/kg}$) waters (see Figure 34). The precise threshold at which the carbonate ion effect becomes significant cannot be determined, due to a lack of data in between 3 and -15 $\mu\text{mol/kg}$. Data from the 1-3°C subset support the presence of a threshold (Figure 35). The data from 3.5-4.5°C suggests part of this slope is likely due to temperature and the decrease in Mg/Ca with $\Delta[\text{CO}_3^{2-}]$ seems to intensify as $\Delta[\text{CO}_3^{2-}]$ approaches zero (Figure 36). In contrast to the colder data, this saturated data set indicates there may be carbonate ion control on Mg/Ca in waters with $\Delta[\text{CO}_3^{2-}]$ as high as 20 $\mu\text{mol/mol}$. Data from *C. pachyderma* for the same sites for two temperature ranges (3.5-4.5°C and 7.5-9.5°C) show no significant relationships with $\Delta[\text{CO}_3^{2-}]$ (Figure 37, 38; $R^2 = 0.014$ and 0.0008, respectively). Data for the 7.5-9.5°C range are all from sites where $\Delta[\text{CO}_3^{2-}]$ is well above 20 $\mu\text{mol/kg}$; data for the 3.5-4.5°C range are inconclusive with respect to a carbonate ion effect in the 3-20 $\mu\text{mol/kg}$ range. Thus it appears from the results in this study that the carbonate ion effect occurs primarily in undersaturated waters and there is little or no significant carbonate ion effect in waters with $\Delta[\text{CO}_3^{2-}] > 3$. This is consistent with the results in the homothermal depth transects. From these

results it is reasonable to assume Mg/Ca at sites where bottom water saturation is greater than $3\mu\text{mol/kg}$ is controlled only by temperature.

4.2 Two part global calibration equation

Disregarding the data points that correspond to $\Delta[\text{CO}_3^{-2}] < 3\mu\text{mol/kg}$ leaves a global core top data set for which Mg/Ca is controlled predominantly by temperature . Adding back in the homothermal transects shown to be free of carbonate ion control, I can now begin to build a global core top Mg-temperature calibration (See Figure 39). The linear regression through these data (Norwegian Sea, Gulf of Mexico, Cape Hatteras, New Zealand, Indonesia, and Hawaii) where $\Delta[\text{CO}_3^{-2}] > 3\mu\text{mol/kg}$, returns a temperature dependence of Mg on T where:

$$(1) \text{ Mg/Ca} = 1.08 + 0.077 (\text{BWT}) \quad (R^2 = 0.49)$$

This equation should hold true wherever $\Delta[\text{CO}_3^{-2}] > 3\mu\text{mol/kg}$

For sites where $\Delta[\text{CO}_3^{-2}] < 3\mu\text{mol/kg}$, the Mg- $\Delta[\text{CO}_3^{-2}]$ relationship obtained in the New Zealand data (Figure 40) is used to construct an equation for Mg/Ca controlled by both temperature and carbonate chemistry:

$$(2) \text{ Mg/Ca}_{\Delta\text{CO}_3} = 0.97 + 0.012(\Delta[\text{CO}_3^{-2}]) \quad (R^2 = 0.49)$$

This sensitivity to $\Delta[\text{CO}_3^{-2}]$ is large compared to Elderfield et al. (2006), most likely due to the exclusion of the relatively high Mg Norwegian Sea data. Elderfield et al. (2006) assumed all sites below a temperature threshold (3°C) are affected by carbonate saturation. In this study the homothermal Norwegian Sea data strongly suggest

foraminifera in saturated bottom waters below 3°C (at -0.9°C) are not experiencing a significant saturation effect. The slope of the Mg/Ca- $\Delta[\text{CO}_3^{-2}]$ relationship is sensitive to the method used to calibrate the data.

Combining equations (1) and (2) gives:

$$(3) \text{ Mg/Ca} = 1.04 + 0.077(\text{BWT}) + 0.012(\Delta[\text{CO}_3^{-2}])$$

Which describes Mg/Ca as a function of both BWT and $\Delta[\text{CO}_3^{-2}]$ where $\Delta[\text{CO}_3^{-2}] < 3\mu\text{mol/kg}$. While this equation may be applicable for our core top data, the real test is how well it performs downcore.

If the equation is a good fit to the core top data, $\text{Mg/Ca}_{\text{estimated}}$ will be close to our measured values for Mg/Ca. $\text{Mg/Ca}_{\text{estimated}}$ is calculated by plugging our measured BWT and $\Delta[\text{CO}_3^{-2}]$ into equation 1 where $\Delta[\text{CO}_3^{-2}] > 3\mu\text{mol/kg}$, and equation 3 ($\text{Mg/Ca} = 1.04 + 0.077*\text{BWT} + 0.012*\Delta[\text{CO}_3^{-2}]$) where $\Delta[\text{CO}_3^{-2}]$ is $< 3\mu\text{mol/kg}$. Figure 41 shows Mg/Ca estimated using equations (1) and (3) versus measured Mg/Ca. Estimated Mg/Ca returns slightly high values for Mg/Ca, relative to the actual data. It should be noted that while estimated Mg/Ca is high, the data plots along the slope of the 1:1 relationship. A simple linear regression through this core top data without the carbonate saturation term (such as equation 1) results in an overall worse fit to the data (Figure 41B).

4.3 Application of a two part linear calibration to a downcore record

In order to apply this calibration downcore, assumptions must be made about past changes in bottom water carbonate chemistry. The downcore record by Martin et al. (2002) was constructed using core M16772 (Eastern Atlantic, 1°21'S 11°58'W; 3912 m),

which in the present time is predominantly bathed by North Atlantic Deep Water (NADW). As a simple exercise, I will use values from Broecker and Clark (2001) to estimate a few changes in $\Delta[\text{CO}_3^{-2}]$ over time at this site.

Modern value: NADW $[\text{CO}_3^{-2}] \sim 112 \mu\text{mol/kg}$ (Broecker & Clark 2001)

$[\text{CO}_3^{-2}]_{\text{saturation}} = 90e^{(0.16*(z-4))}$ where z = water depth in km.

$$\Delta[\text{CO}_3^{-2}] = [\text{CO}_3^{-2}]_{\text{in situ}} - [\text{CO}_3^{-2}]_{\text{saturation}} = 112 - 88.7 = 23.3 \mu\text{mol/kg}$$

Broadly, (even though the data comes from the opposite side of the Atlantic basin from this downcore record) I will use the statement by Broecker and Clark (2001) that at around 4km (just a bit deeper than core M16772), $[\text{CO}_3^{-2}]_{\text{in situ}}$ was about $23 \mu\text{mol/kg}$ lower in the glacial than today, bringing us to:

$$\Delta[\text{CO}_3^{-2}] = [\text{CO}_3^{-2}]_{\text{in situ}} - [\text{CO}_3^{-2}]_{\text{saturation}} = 89 - 88.7 = 0.3 \mu\text{mol/kg}$$

Even more broadly simplified, between the modern value and the glacial value linear interpolation is used to gradually decrease the $\Delta[\text{CO}_3^{-2}]$ between the two end values.

For times when $\Delta[\text{CO}_3^{-2}]$ in the record $> 3 \mu\text{mol/kg}$, temperature will be calculated using equation (1). Wherever $\Delta[\text{CO}_3^{-2}] \leq 3 \mu\text{mol/kg}$, equation (3) is used. These two conditions are applied to the Mg/Ca data from Martin et al. (2002) to calculate a BWT record based on measured Mg/Ca and our estimated $\Delta[\text{CO}_3^{-2}]$ (Figure 42). Bottom water temperature reconstructed using this equation is quite cold (-5°C in the glacial). It also appears this equation would give very large amplitude climate variability when used downcore. The original paleoclimate reconstruction finds a glacial-interglacial

temperature change of about 4°C (Martin et al., 2002), while equation (3), for the same time period, results in a ΔT of 7°C. This illustrates the difficulty of balancing an equation that fits core top data well with an equation that gives plausible results when applied downcore.

4.4 Comparison to published calibrations

Our *Planulina wuellerstorfi* data fall along a line with the *P. wuellerstorfi* data from Elderfield et al., 2006 (Figure 43). The major differences in calibration equations are the result of methodology – including different subsets of similar data result in different regressions. Marchitto et al. 2007 data for *Cibicidoides pachyderma* lacks temperature overlap with our *C. pachyderma* data, yet can be seen to fall in line with our data (Figure 44). Difficulty in comparing linear regressions in different publications occurs due to lack of overlap between data sets, effectively examining different sections of an overall calibration curve ranging from -1 to 20°C.

Taking the data as a whole, combining both *Planulina* and *Cibicidoides* measurements from saturated waters ($\Delta[\text{CO}_3^{2-}] > 3$) from these three sources (Figure 45), gives a regression of:

$$(4) \text{ Mg/Ca} = 0.87 + 0.122 \cdot \text{BWT} \quad (R^2 = 0.61)$$

Notably, this regression fits well through all data with the exception of the very cold Norwegian Sea *P. wuellerstorfi* data (BWT = -1°C).

Our Norwegian Sea data is similar to the Nordic Sea data given in Elderfield et al. (2006). This suggests that the high Mg/Ca values at this site are not an anomaly.

Preliminary results in benthic ostracod Mg/Ca (Sosdian, personal communication) also indicate higher than expected Mg/Ca in the Norwegian Sea site. Elderfield et al. (2006) explains high Mg at this site as a product of high $\Delta[\text{CO}_3^{-2}]$. However, recall that a number of samples from this site fall in the $\Delta[\text{CO}_3^{-2}]$ range of 20-30 $\mu\text{mol/kg}$ (Figure 12). This is not particularly high relative to other sites in this study. If the samples from the highest carbonate saturation levels at this site were affected by high $\Delta[\text{CO}_3^{-2}]$, that does not explain why the samples from bottom water with lower saturation are so high relative to in situ BWT. Until the mechanism affecting the results from this site can be better determined, or this end of the calibration confirmed in another site with comparable bottom water temperature, it may be wise to leave this site out of the global calibration.

Now evaluate the method which will result in the most useful calibration by comparing the compiled core top data regression in this study to other regressions. Recall that application of our two part equation with Mg/Ca a function of T and $\Delta[\text{CO}_3^{-2}]$ was not successful, in that it resulted in unlikely BWT estimates. Application of equation 5 (below, Elderfield et al., 2007) similarly shows offsets in temperatures and large amplitude of temperature change throughout the record. (See Figure 46) Applying these types of equations, for Mg/Ca as a function of two properties, downcore seems to give inconsistent and often unrealistic results.

$$(1) \text{ Mg/Ca} = 1.04 + 0.077T \text{ (this study, } \Delta[\text{CO}_3^{-2}] > 3 \text{ waters)}$$

$$(4) \text{ Mg/Ca} = 0.87 + 0.122T \text{ (this study, compiled core top data, } \Delta[\text{CO}_3^{-2}] > 0)$$

$$(5) \text{ Mg/Ca} = 0.82 + 0.056T + 0.0087\Delta[\text{CO}_3^{-2}] \text{ (Elderfield et al., 2006, BWT} > 3^\circ\text{C)}$$

$$(6) \text{ Mg/Ca} = 1.20 + 0.116T \text{ (Marchitto et al., 2007)}$$

Using our core top data covering a temperature range of -1° to 9°C , gave a temperature sensitivity for Mg/Ca of $0.077/^{\circ}\text{C}$. Marchitto et al. (2007) used data across the temperature range of 6° to 18°C . Elderfield et al. (2006) covered a similar range to our data, -1° to 7°C . It is possible that the various recently published calibration equations simply represent linear segments of an overall, more complex relationship across the broad temperature range of the ocean. While the goal of this project was to combine global data and establish a calibration that works at all temperatures, it appears that conditions in the individual study locations, such as the high Mg values seen in the Norwegian Sea and scatter seen in the Cape Hatteras site, suggest that not all core top locations may conform to a single Mg/Ca-BWT pattern. It may be necessary to evaluate the slope derived from only the core top data covering the temperature range seen in the downcore record of interest to determine an appropriate calibration on a case by case basis. As an example, if considering only the subset of data from this study from 0° to 6°C , excluding the anomalously high Norwegian Sea data, (Figure 47):

$$(7) \text{ Mg/Ca} = 0.679 + 0.173T \quad (\text{linear fit, } R^2 = 0.588)$$

$$(8) \text{ Mg/Ca} = 0.753e^{0.145T} \quad (\text{exponential fit, } R^2 = 0.556)$$

Contrast these equations to the low temperature sensitivities obtained from either the Elderfield et al. (2006) equation or the full core top data set from this site. Applying a temperature sensitivity of around 0.065 (equation 1) gives unrealistically large amplitudes ($\pm 8^{\circ}\text{C}$) for bottom water temperature across glacial-interglacial cycles (see Figure 42; 46).

V. Summary

Mg/Ca measurements in benthic species *Planulina wuellerstorfi* and *Cibicidoides pachyderma* across homothermal, homohaline depth transects in saturated Norwegian Sea and Gulf of Mexico waters show insignificant correlation between Mg/Ca and $\Delta[\text{CO}_3^{-2}]$. This suggests that the influence of carbonate saturation on benthic foraminiferal Mg/Ca is insignificant in saturated waters, and cannot be explained using a simple linear relationship across the cold end of the calibration. At the cold end of the calibration, the exponential fit of earlier calibrations predicts small changes in foraminiferal Mg/Ca. The effects of any non temperature processes should be relatively more pronounced at colder temperatures, yet we still see no significant carbonate ion effect in the Norwegian Sea data. Benthic foraminiferal data from this site and others, as well as preliminary ostracod data, suggest that the Norwegian Sea calcite Mg/Ca may be responding to something other than temperature and $\Delta[\text{CO}_3^{-2}]$, as it is unexpectedly high relative to other study sites. Core top measurements for *P. wuellerstorfi* from five sites throughout the Atlantic and the Pacific (Norwegian Sea, Gulf of Mexico, Cape Hatteras, New Zealand, and Indonesia) show significant scatter not associated with temperature or $\Delta[\text{CO}_3^{-2}]$, leading to a linear calibration with a low temperature sensitivity. When applied downcore, this low temperature sensitivity results in cold BWT reconstructions with large glacial-interglacial variability. High temperature sensitivity and more realistic application results are obtained when combining species (*P. wuellerstorfi* and *C. pachyderma*) and forming an equation using data that covers the entire available temperature range. Alternatively, better temperature reconstructions result when a specific calibration equation based on only the data from the temperature range covered by the downcore record is employed.

One possible effect that should be investigated is the influence of pore water chemistry on benthic test composition. It has been shown that in some locations pore water chemistry may have more of an effect on benthic calcite formation than bottom water chemistry. Modeled respiration driven dissolution can lead to significant differences between properties in the bottom water and in the top few centimeters of sediment, even for a moderate rate of organic matter deposition. Chemical concentrations are frequently assumed to be equal between bottom water and the sediment-water interface; however models demonstrate that they can be quite different. If this is the case, the chemical composition of benthic foraminiferal tests, even for epibenthic species, will not reflect bottom water chemistry (Zeebe, 2007).

In summary, the direct test for carbonate ion effect in homothermal transects is a good indication that the problem is more complex than previously thought. Additionally, application tests of these linear calibrations with a saturation term downcore illustrates the importance of calibrating with an eye towards application, as well as testing any new calibration on previously published records.

VI. References

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VII. Tables

Table 1: Core locations and hydrographic properties, Norwegian Sea.

Core	depth (m)	BWT (°C)	Salinity	[CO ₃ ⁻²]* (μmol/kg)	ΔCO ₃ ** (μmol/kg)	Latitude	Longitude
MC-14	965	-0.6	34.9	100.1	44.6	62° 29' 28" N	1° 10' 48" E
MC-11	1285	-0.7	34.91	100.9	42.49	63° 1' 4" N	0° 28' 59" E
MC-50	1906	-0.8	34.91	99.5	34.79	63° 27' 10" N	1° 13' 55" E
MC-48	2402	-0.9	34.91	99.2	29.04	64° 0' 25" N	0° 26' 6" E
MC-21	2640	-0.9	34.91	98.8	25.9	64° 1' 37" N	1° 7' 25" W
MC-45	2799	-0.9	34.91	97.6	22.76	64° 20' 20" N	0° 26' 3" W
MC-24	3036	-0.8	34.91	96.0	18.25	64° 18' 8" N	2° 20' 24" W
MC-27	3341	-0.8	34.91	95.7	13.96	64° 30' 34" N	3° 30' 2" W

*water chemistry from TTO 004 Station 143 (phosphate, silicate, total alkalinity and TCO₂) used to calculate [CO₃⁻²] in CO2SYS.

** modern –not corrected for anthropogenic CO₂

Table 2: Gulf of Mexico hydrographic properties and sample locations.

Core	depth (m)	BWT (°C)	Salinity	[CO ₃ ⁻²]* (μmol/kg)	ΔCO ₃ ** (μmol/kg)	Latitude	Longitude
RW3-4	1330	4.4	34.97	113.6	54.9	27° 0' 16" N	95° 29' 51" W
MT4-4	1402	4.4	34.97	116.7	57.3	27° 49' 39" N	89° 9' 58" W
W4-5	1406	4.3	34.97	116.9	57.5	26° 43' 50" N	93° 19' 11" W
C4-5	1470	4.3	34.98	115	55	27° 27' 1" N	89° 45' 43" W
NB2-5	1530	4.3	34.98	113.2	52.6	27° 7' 58" N	92° 0' 1" W
RW4-2	1580	4.3	34.98	111.6	50.5	26° 44' 56" N	95° 14' 40" W
RW5-3	1620	4.3	34.98	111.1	49.6	26° 30' 1" N	95° 0' 0" W
NB3-2a	1875	4.3	34.98	111.7	47.6	26° 33' 16" N	91° 49' 30" W
NB4-2	2050	4.3	34.99	111.6	45.7	26° 14' 58" N	92° 23' 28" W
MT5-1	2275	4.3	34.99	111.4	43.1	27° 19' 34" N	88° 40' 10" W
S38-4	2630	4.3	34.99	107.5	35.2	28° 16' 47" N	87° 19' 39" W
MT6-5	2743	4.3	34.99	106.2	32.6	27° 0' 5" N	87° 59' 56" W
W5-4	2745	4.3	34.99	106.2	32.6	26° 16' 3" N	93° 19' 57" W
S40-3	2972	4.3	35	103.6	27.2	27° 50' 17" N	86° 45' 2" W
S41-1	2974	4.3	35	103.6	27.2	28° 0' 43" N	86° 34' 11" W
S39-2	3000	4.3	35	103.3	26.6	27° 29' 41" N	86° 59' 53" W

RW6-1	3015	4.3	35	103.1	26.2	26° 0' 8" N	94° 29' 22" W
W6-3	3150	4.3	35	102.5	23.9	24° 59' 45" N	93° 18' 33" W

*water chemistry from WOCE A05 Station 97 (phosphate, silicate, total alkalinity and TCO₂) used to calculate [CO₃⁻²] in CO2SYS.

**modern –not corrected for anthropogenic CO₂

Table 3: Core locations & hydrographic properties, Cape Hatteras (KN178)

Core	Water depth (m)	BWT (°C)	Salinity	[CO ₃ ⁻²]* (μmol/kg)	ΔCO ₃ ** (μmol/kg)	Latitude	Longitude
MC-20	1815	3.6	34.9	112.2	48.7	36°01.70 N	74°30.50 W
MC-67	1956	3.5	34.9	112.0	47.1	36°50.92 N	74°19.49 W
MC-46	2000	3.5	34.9	112.0	46.7	35°45.70 N	74°26.50 W
MC-47	2000	3.5	34.9	112.0	46.7	35°45.70 N	74°26.50 W
MC-16	2214	3.4	34.9	111.7	44.1	35°57.97 N	74°17.90 W
MC-12	2573	3.1	34.9	111.5	39.9	35°54.95 N	74°06.94 W
MC-14	2602	3.0	34.9	111.6	39.6	35°55.87 N	74°06.16 W
MC-8	2997	2.5	34.9	110.8	34.2	35°51.46 N	73°52.06 W
MC-74	3022	2.5	34.9	110.5	33.6	38°22.39 N	71°01.95 W
MC-76	3065	2.4	34.9	110.0	32.5	39°06.30 N	68°48.01 W
MC-7	3361	2.2	34.8	108.3	27.1	35°49.032 N	73°35.61 W
MC-5	3382	2.2	34.8	108.4	26.9	35°49.46 N	73°34.89 W
MC-4	3865	2.2	34.8	106.5	18.4	36° 07.40N	072°16.79W
MC-1	3979	2.2	34.8	107.1	17.4	36°07.21 N	72°17.52 W

* water chemistry from WOCE A22 Station 40 (phosphate, silicate, total alkalinity and TCO₂) used to calculate [CO₃⁻²] in CO2SYS.

** modern –not corrected for anthropogenic CO₂

Table 4: Core locations & hydrographic properties, New Zealand

Core	Water depth (m)	BWT (°C)	Salinity	[CO ₃ ⁻²]* (μmol/kg)	ΔCO ₃ ** (μmol/kg)	Latitude	Longitude
MC-76	1165	3.2	34.38	79.5	22.3	36°57.50 S	176°35.50 E
MC-133	1407	2.7	34.47	77.8	18.4	36°24.01 S	176°34.05 E
MC-82	1623	2.5	34.54	77.8	16.3	36°44.23 S	176°38.30 E
MC-22	1682	2.4	34.56	78.2	16.1	42°27.72 S	177°50.16 W
MC-92	1818	2.3	34.60	79.2	15.7	36°57.90 S	177°26.39 E
MC-102	2055	2.1	34.66	79.8	13.9	36°51.98 S	177°20.92 E
MC-118	2252	2.0	34.69	83.8	15.7	36°22.63 S	177°26.75 E
MC-26	2418	1.9	34.71	82.3	12.4	42°04.47 S	177°37.56 W
MC-106	2472	1.9	34.72	82.5	12.0	36°44.00 S	177°35.00 E
MC-114	3295	1.2	34.73	82.9	2.5	36°23.5 S	177°19.0 E
MC-38	4375	1.2	34.71	80.7	-14.9	39°56.47 S	176°13.43 W

* water chemistry from WOCE P15S Station 71 (phosphate, silicate, total alkalinity and TCO₂) used to calculate [CO₃⁻²] in CO2SYS.

** modern –not corrected for anthropogenic CO₂

Table 5: Replicate analyses A) Individual samples, split in three before cleaning and analysis. B) The same sample, re-run individually. Standard deviations of the splits are not significantly different from the standard deviations of the replicates; sample reproducibility is good.

A)

site	Core	Sample	Depth (m)	BWT(°C)	Mg/Ca	SD (of splits)	RSD (%)
Gulf of Mexico	MT5-1	split 1	2275	4.4	2.399	0.009	0.37
"	"	split 2	"	"	2.387		
"	"	split 3	"	"	1.640*		
		AVG			2.393		
"	"	original run	"	"	1.676		
Gulf of Mexico	NB2-5	split 1	1530	4.3	1.681	0.068	4.25
"	"	split 2	"	"	1.556		
"	"	split 3	"	"	1.573		
"	"	AVG	"	"	1.603		
"	"	original run	"	"	1.476		
Norwegian Sea	MC-45	split 1	2799	-0.9	1.048	0.076	7.91
"	"	split 2	"	"	0.898		
"	"	split 3	"	"	0.947		
"	"	AVG	"	"	0.964		
"	"	original run	"	"	1.075		
Norwegian Sea	MC-21	split 1	2640	-0.9	0.847	0.049	5.39
"	"	split 2	"	"	0.929		
"	"	split 3	"	"	0.934		
"	"	AVG	"	"	0.903		
"	"	original run	"	"	1.015		

* not included in calculation, assumed a flier

B)

site	Core	Depth	BWT	Mg/Ca	SD of replicates	RSD (%)
Norway	MC-21	2640	-0.9	1.025	0.024	2.37
				1.014		
				1.061		
Norway	MC-45	2799	-0.9	0.949	0.063	6.22
				1.013		
				1.075		
Norway	MC-27	3341	-0.8	0.979	0.113	10.47
				1.203		
				1.062		
Norway	MC-50	1906	-0.9	1.210	0.044	3.83
				1.118		
				1.153		
				1.116		

VIII. Figures

Figure 1: Deep Atlantic and Pacific core tops fall outside of the expected Mg/Ca-BWT relationship (after Martin et al., 2002).

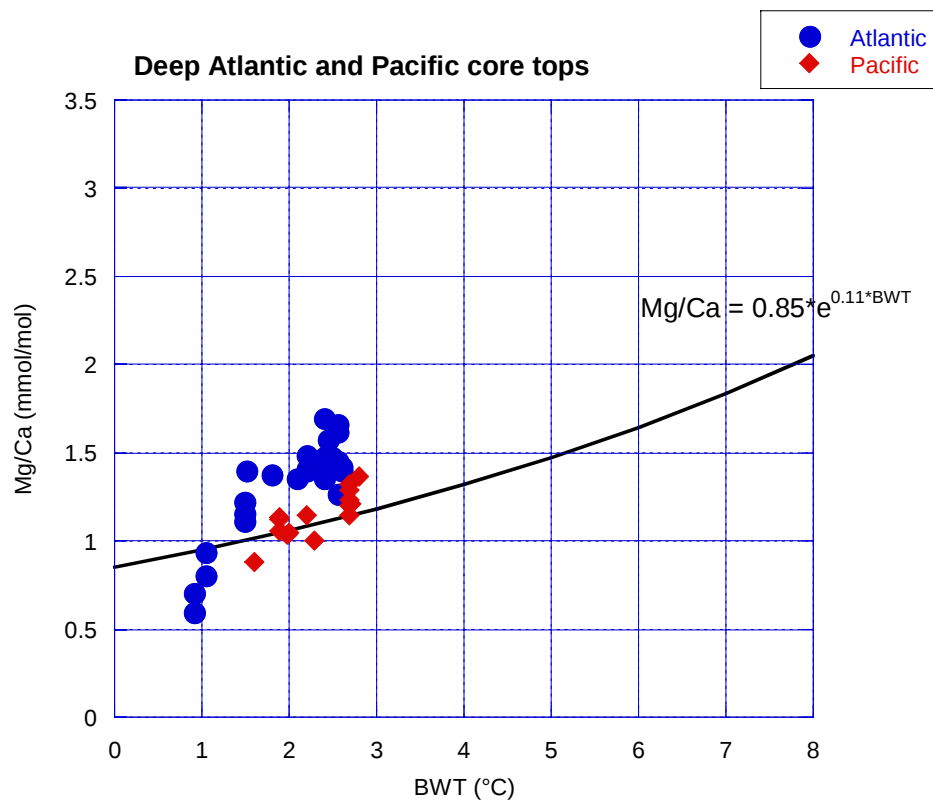


Figure 2: Locations of core top sites used in this study.



Figure 3: Norwegian Sea Cruise Track (KN177-2) and multi core locations. Shading shows water depth in meters.

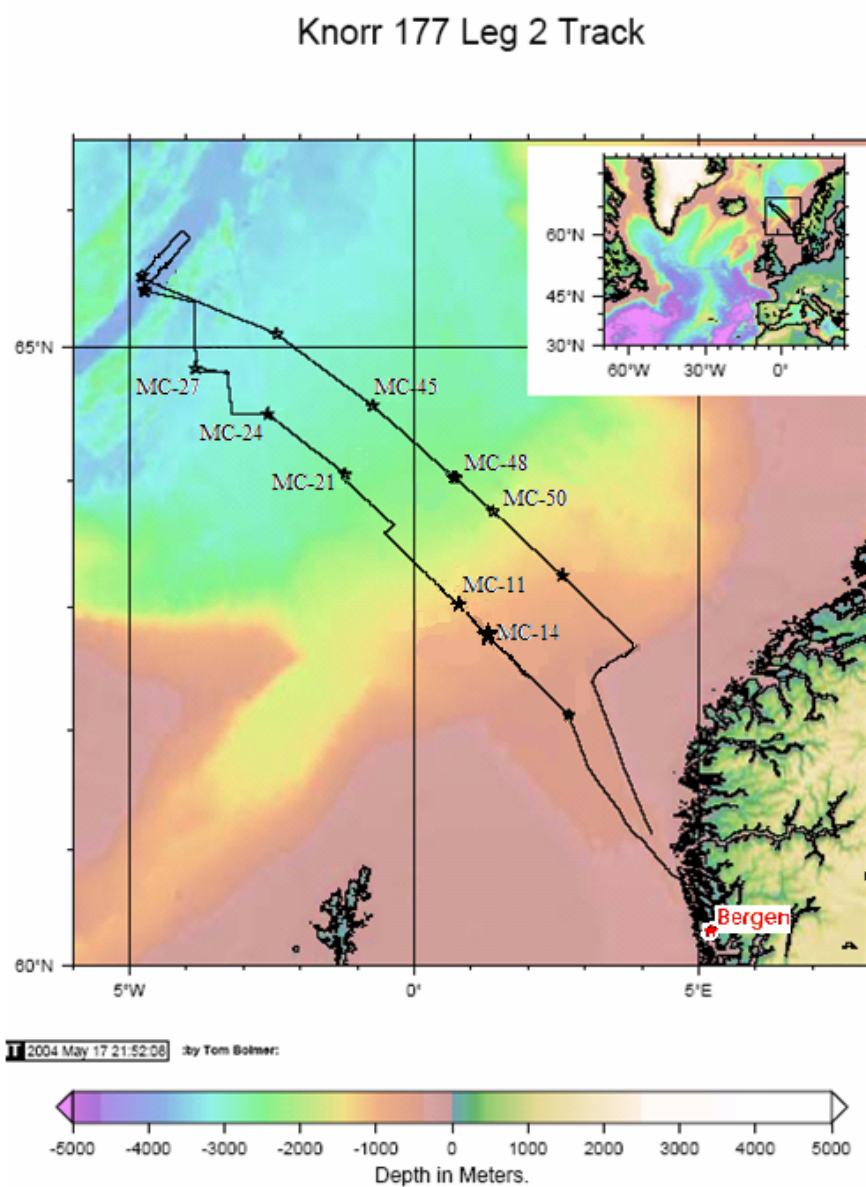


Figure 4: Gulf of Mexico box core locations.

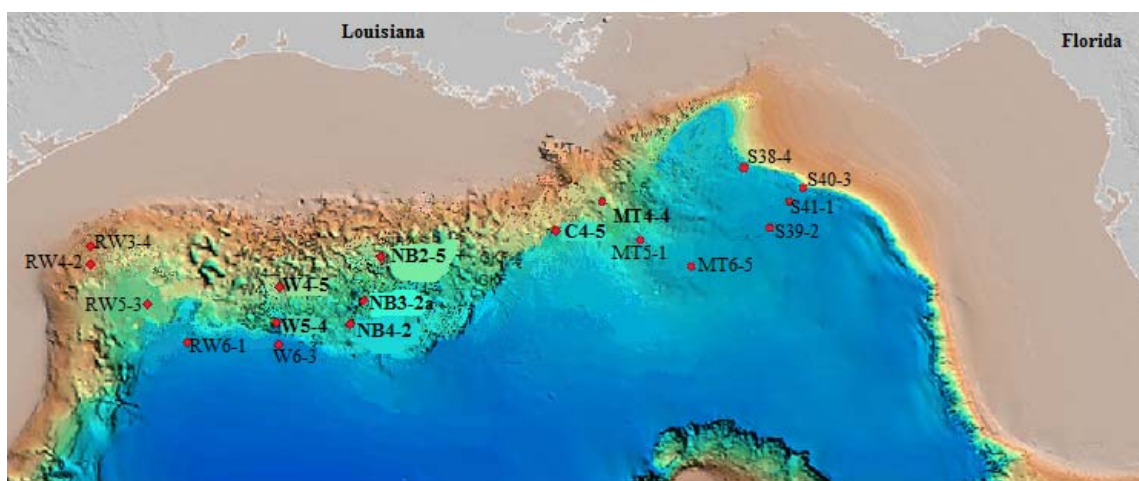


Figure 5: Cape Hatteras cruise track (KN178) and multi core locations.

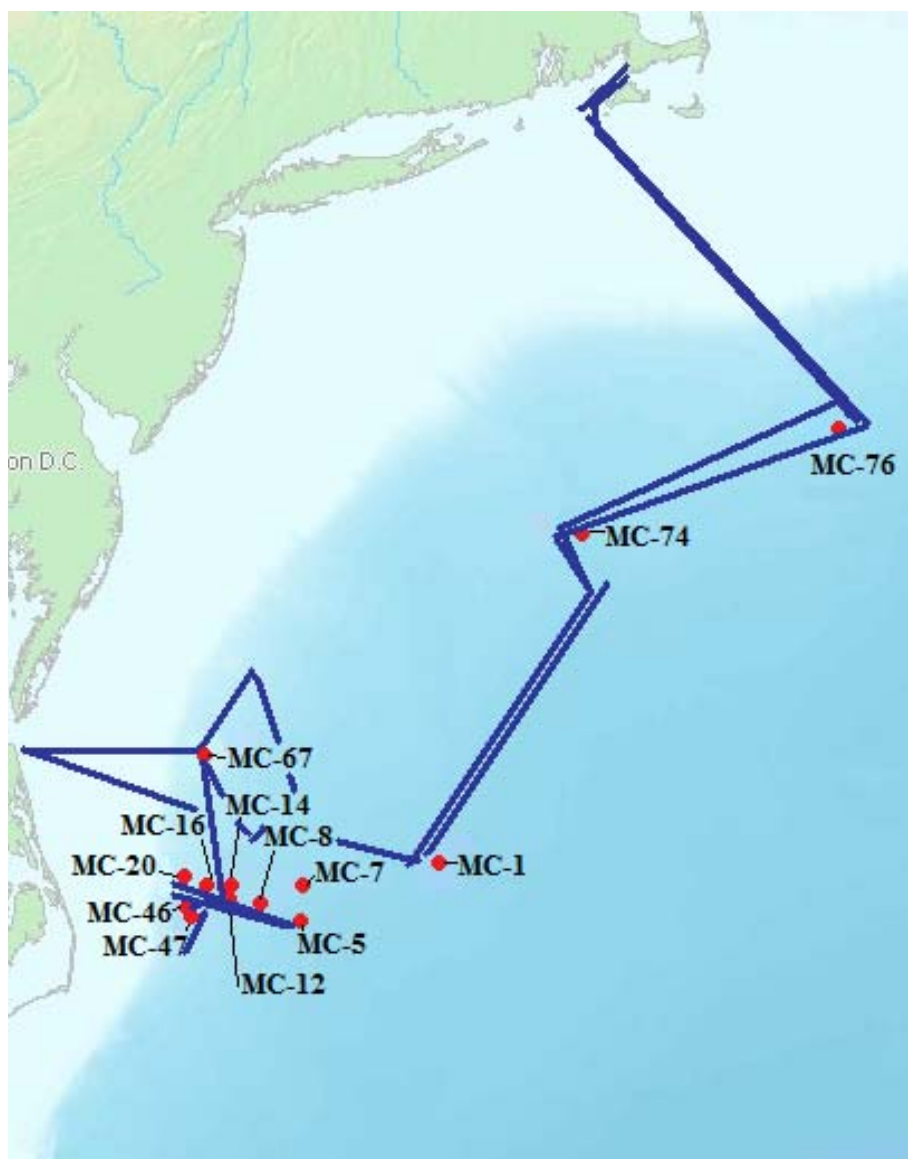


Figure 6: New Zealand Cruise Track (RR05-03) and multi core locations.

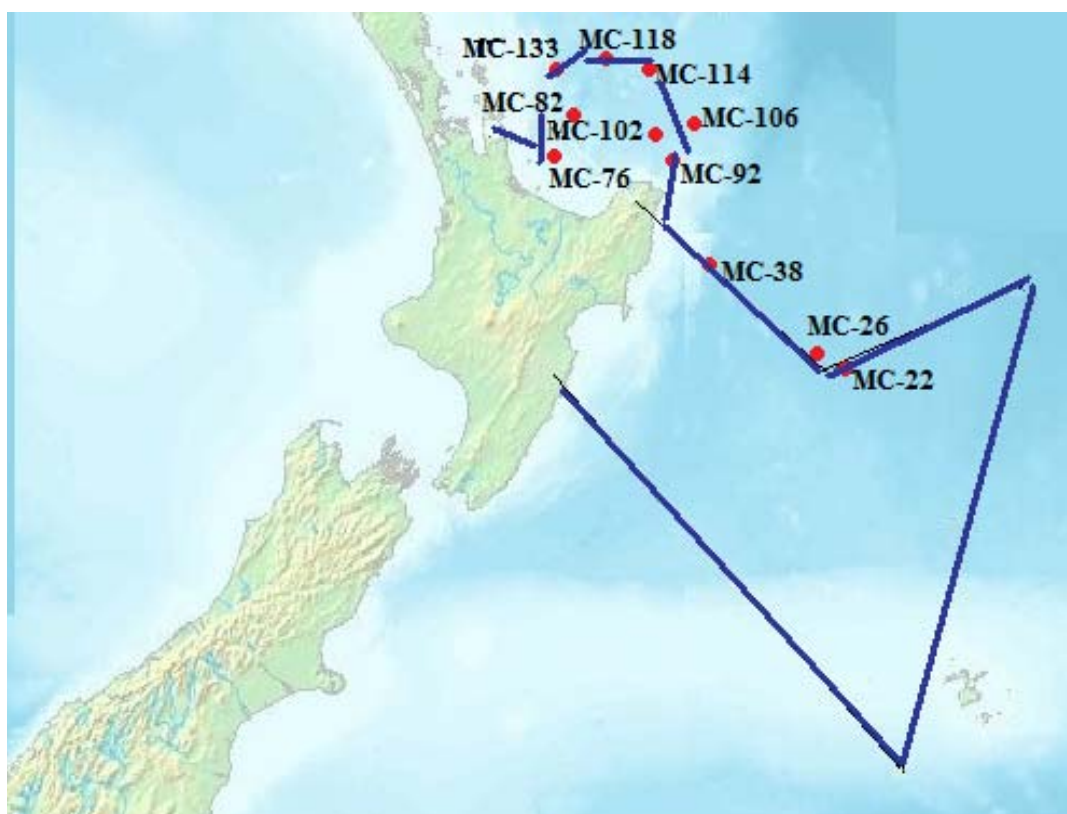
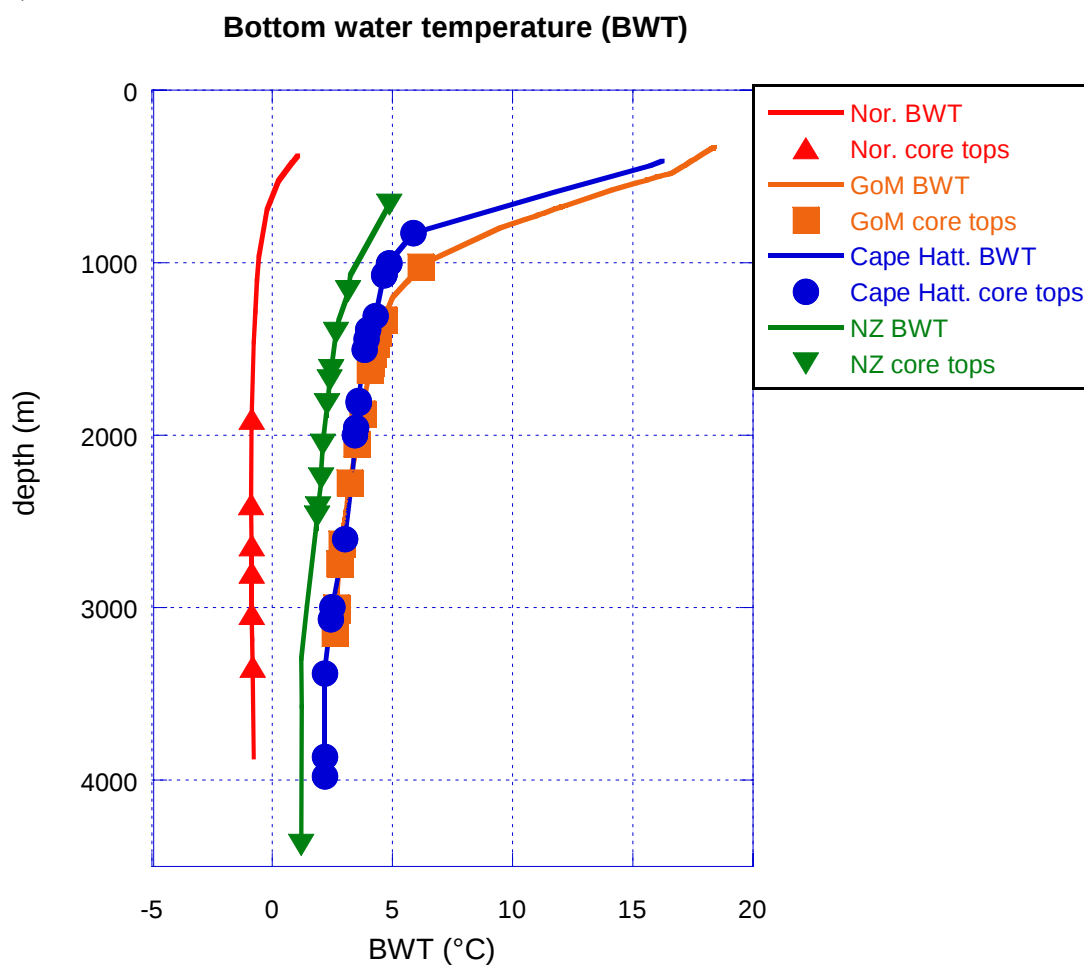
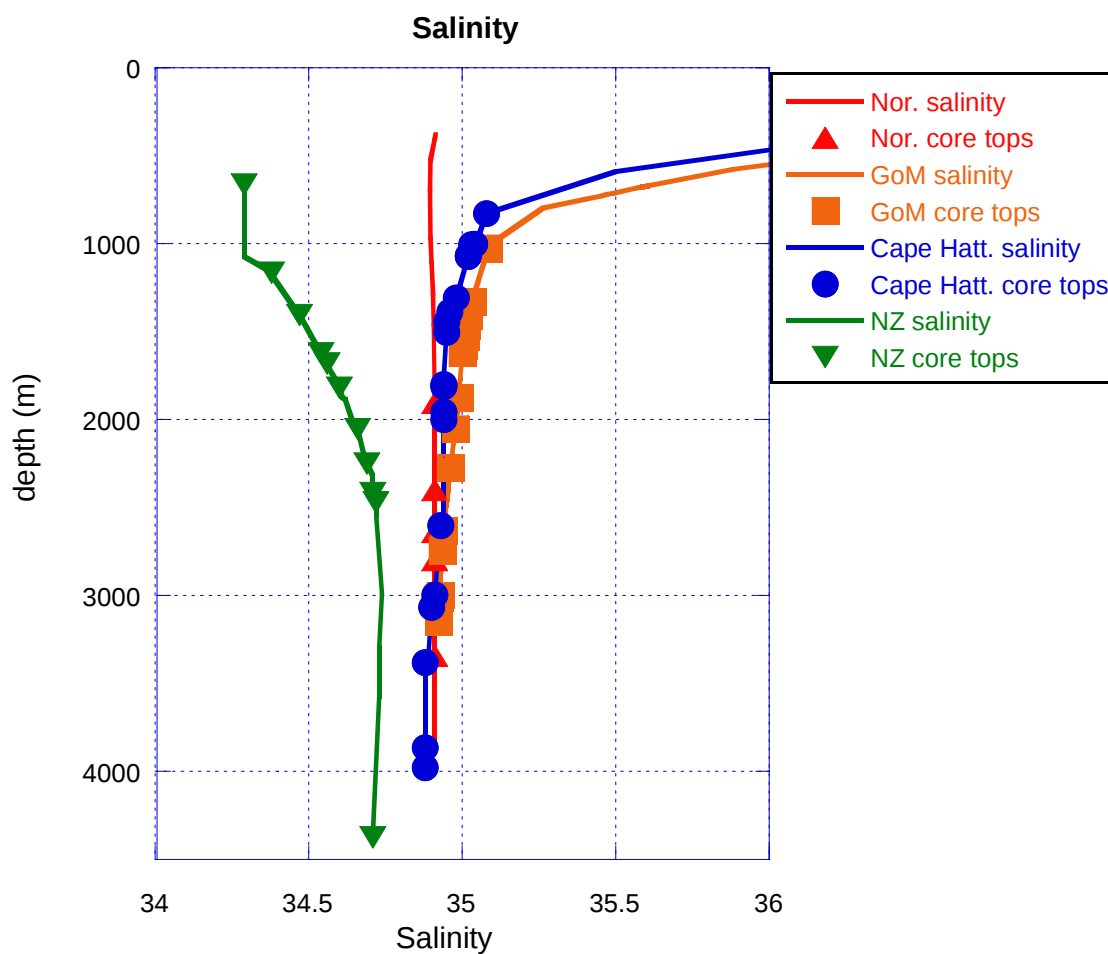


Figure 7: Hydrographic data and core top locations for this study's sites. A) Bottom water temperature versus depth. Data source: Norwegian Sea cruise, KN177-2 CTD-30; Gulf of Mexico cruise, DGoMB Station S1, CTD S2; Cape Hatteras cruise, KN178 CTD-11; New Zealand cruise, RR05-03, CTD on MC-7 deployment.

A)



B) Bottom water salinity versus depth. Data source: Norwegian Sea cruise, KN177-2 CTD-30; Gulf of Mexico cruise, DGoMB Station S1, CTD S2; Cape Hatteras cruise, KN178 CTD-11; New Zealand, WOCE P15S, Station 71.



C) Bottom water carbonate ion concentration and carbonate saturation, $\Delta[\text{CO}_3^{2-}]$ (calculated using CO2SYS). Data Source: Norwegian Sea water chemistry from KN177-2 CTD-30 and TTO 004 Station 143; Gulf of Mexico water chemistry from DGoMB Station 1 CTD S2 and WOCE A05 Station 97; Cape Hatteras water chemistry from KN178 CTD-11 and WOCE A22 Station 40; New Zealand water chemistry from WOCE P15S Station 71.

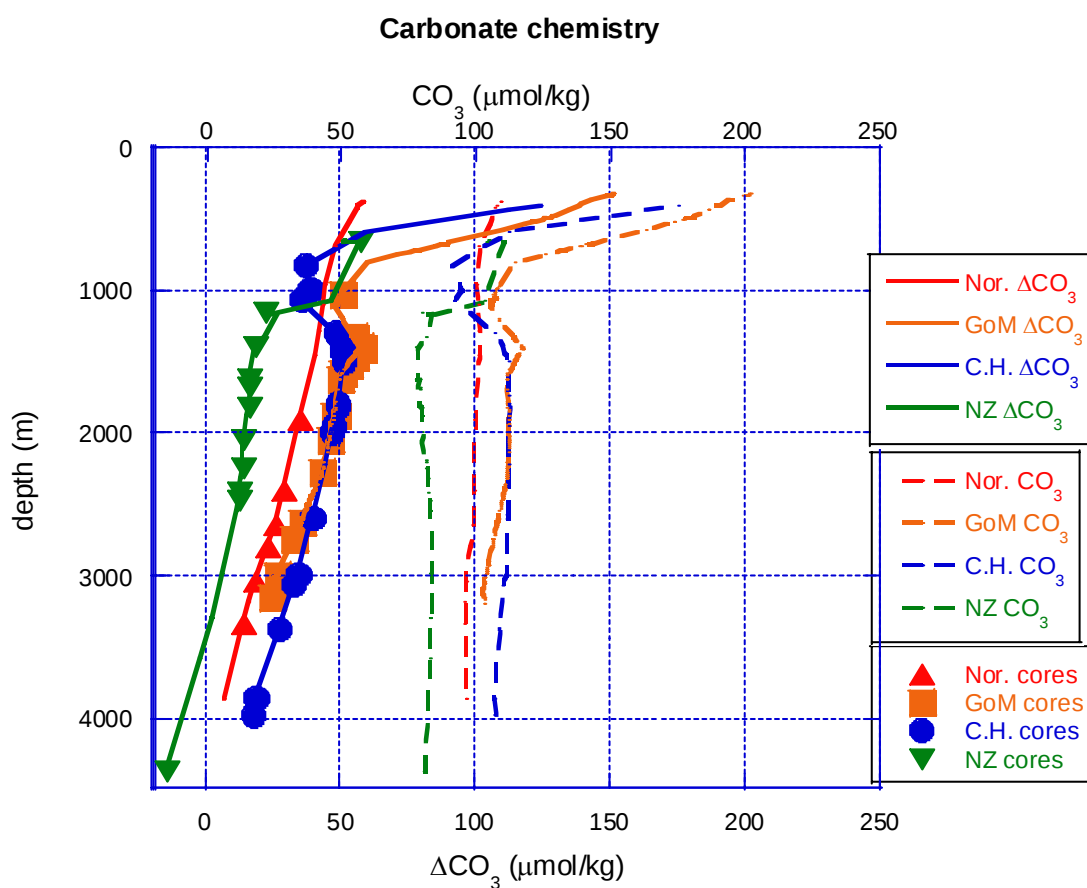
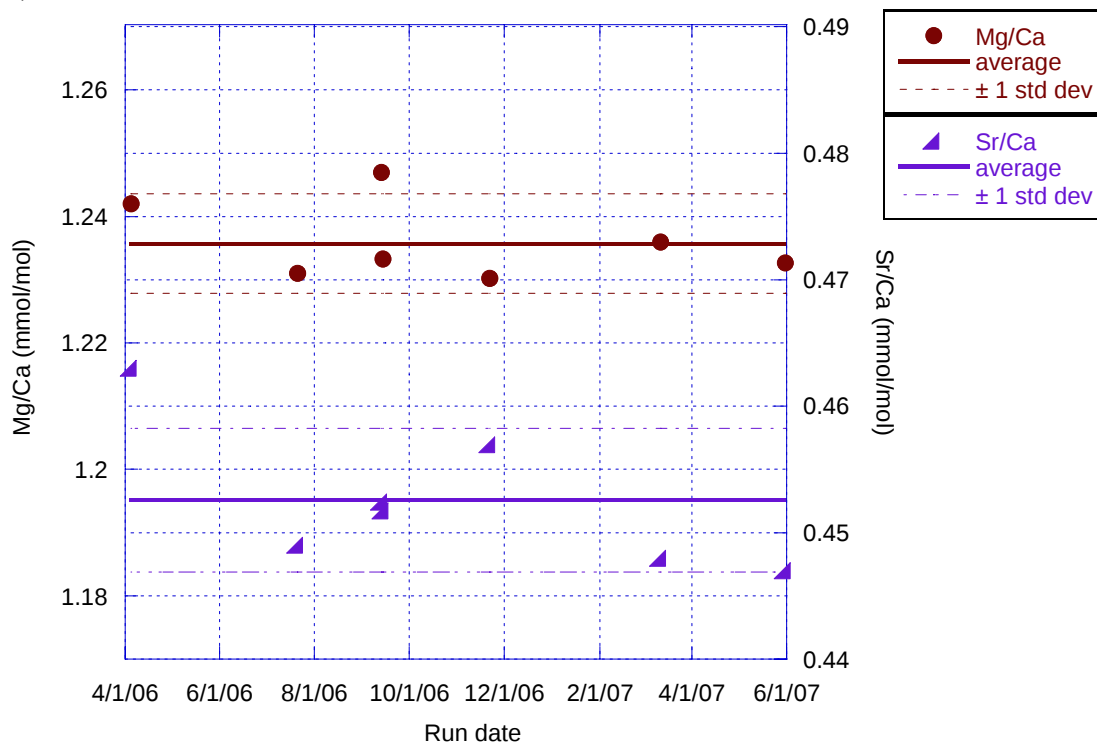
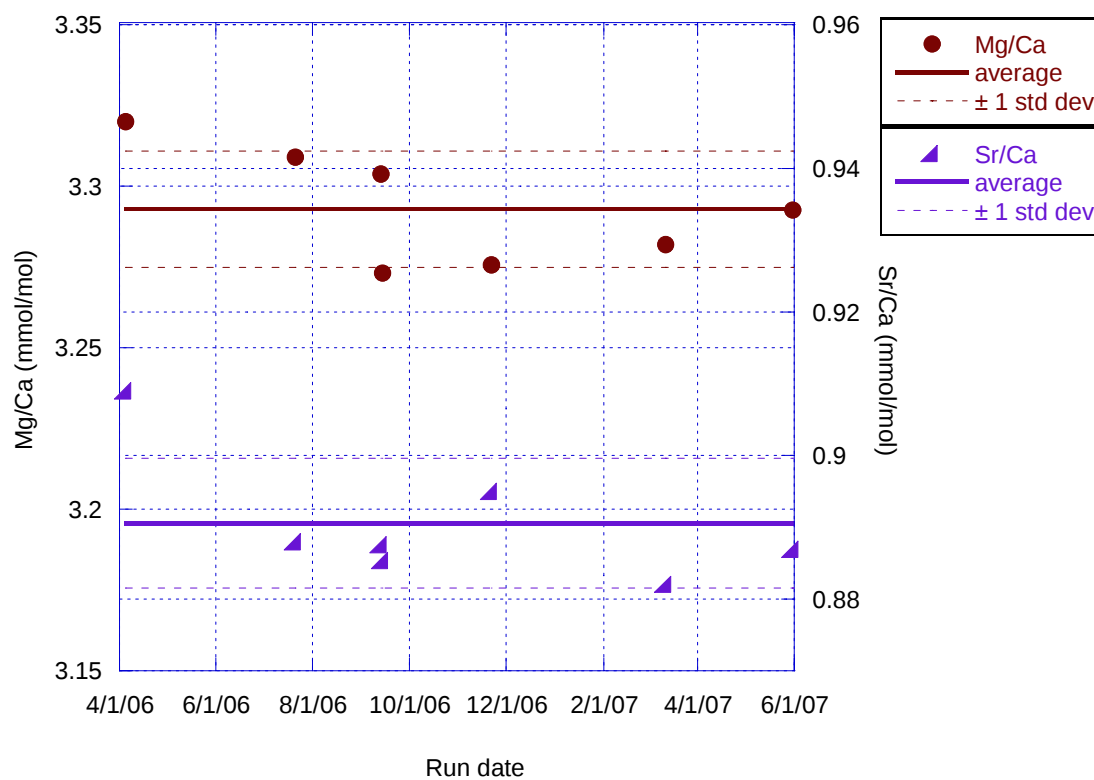


Figure 8: Consistency standard CSI, CSII and CSIII (A, B, and C; Mg/Ca = 1.24, 3.32, and 7.5mmol/mol, respectively) show good reproducibility (within 2SD) over time. Long term standard deviations for CSI (A) CSII (B) and CSIII(C) are 0.008, 0.018, and 0.039, respectively, for Mg/Ca and 0.006, 0.009, and 0.01, respectively, for Sr/Ca.

A)



B)



C)

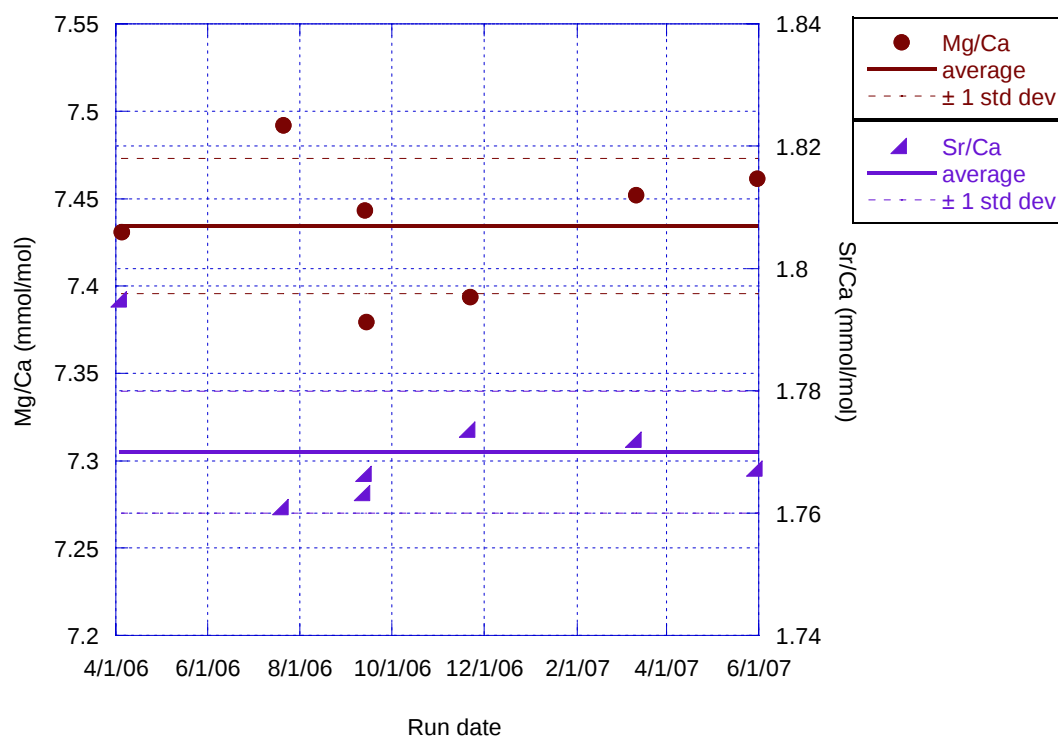
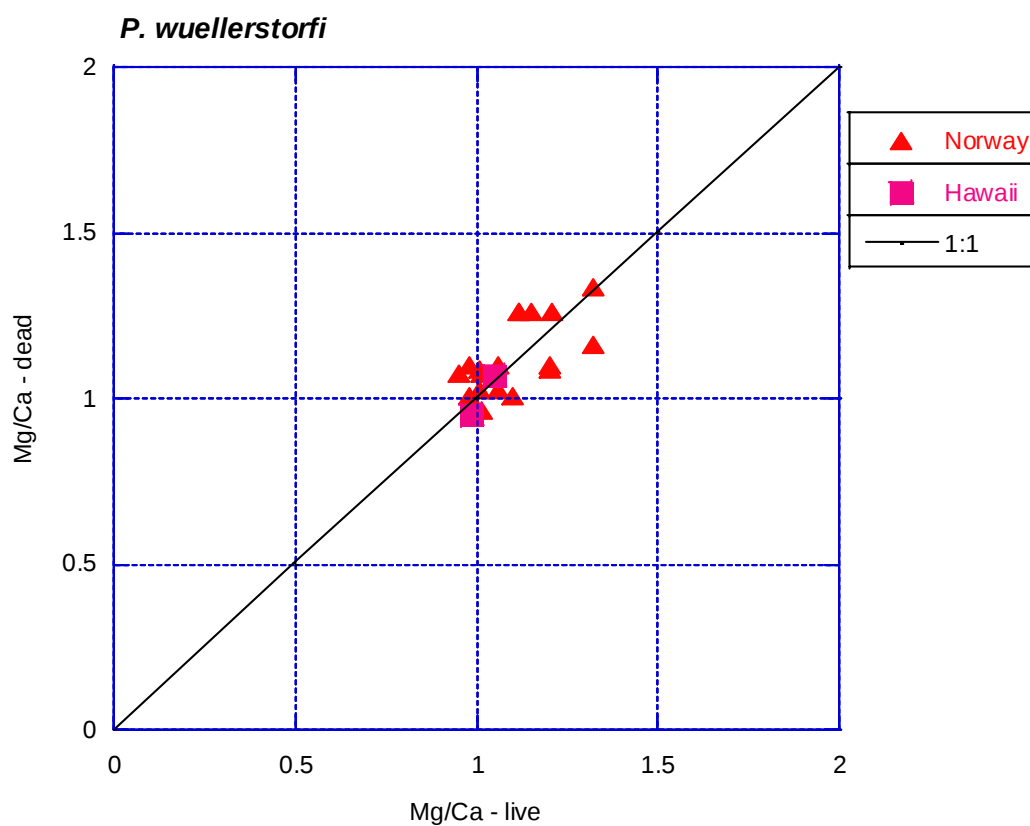


Figure 9: Mg/Ca in live (stained) versus dead (unstained) samples for A) *P. wuellerstorfi* and B) *C. pachyderma*. Live and dead shells from the same core are compared. Diagonal line shows 1:1 relationship.

A)



B)

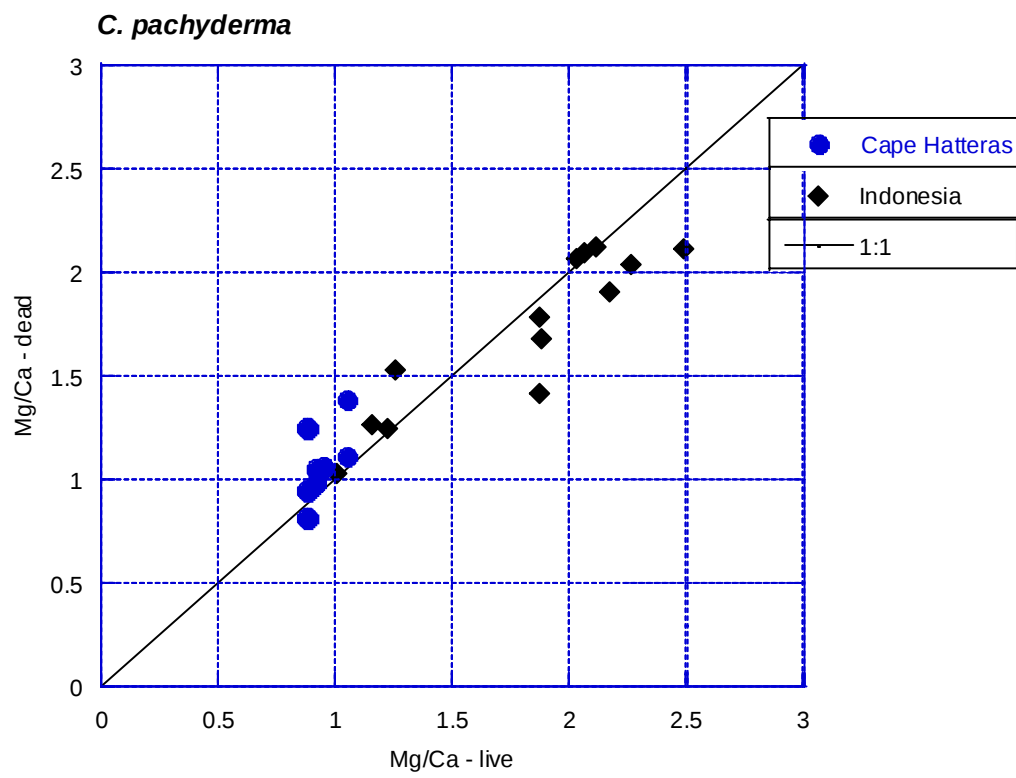


Figure 10: Norwegian Sea Mg/Ca data for live (stained) and dead (unstained) *P. wuellerstorfi*. Error bars show standard error.

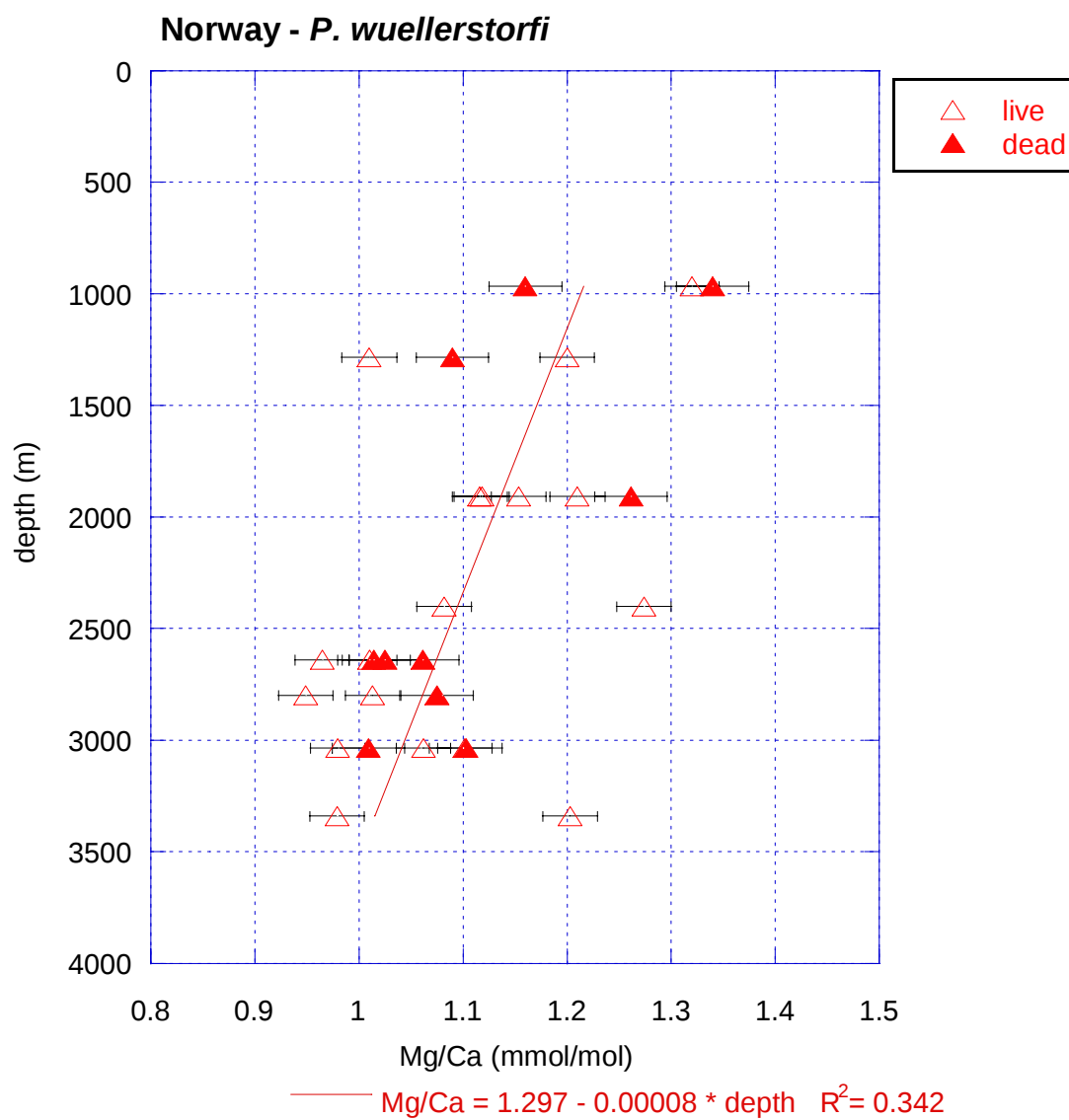


Figure 11: Norwegian Sea d18O data for live (stained) and dead (unstained) *P. wuellerstorfi*. Error bars show standard error.

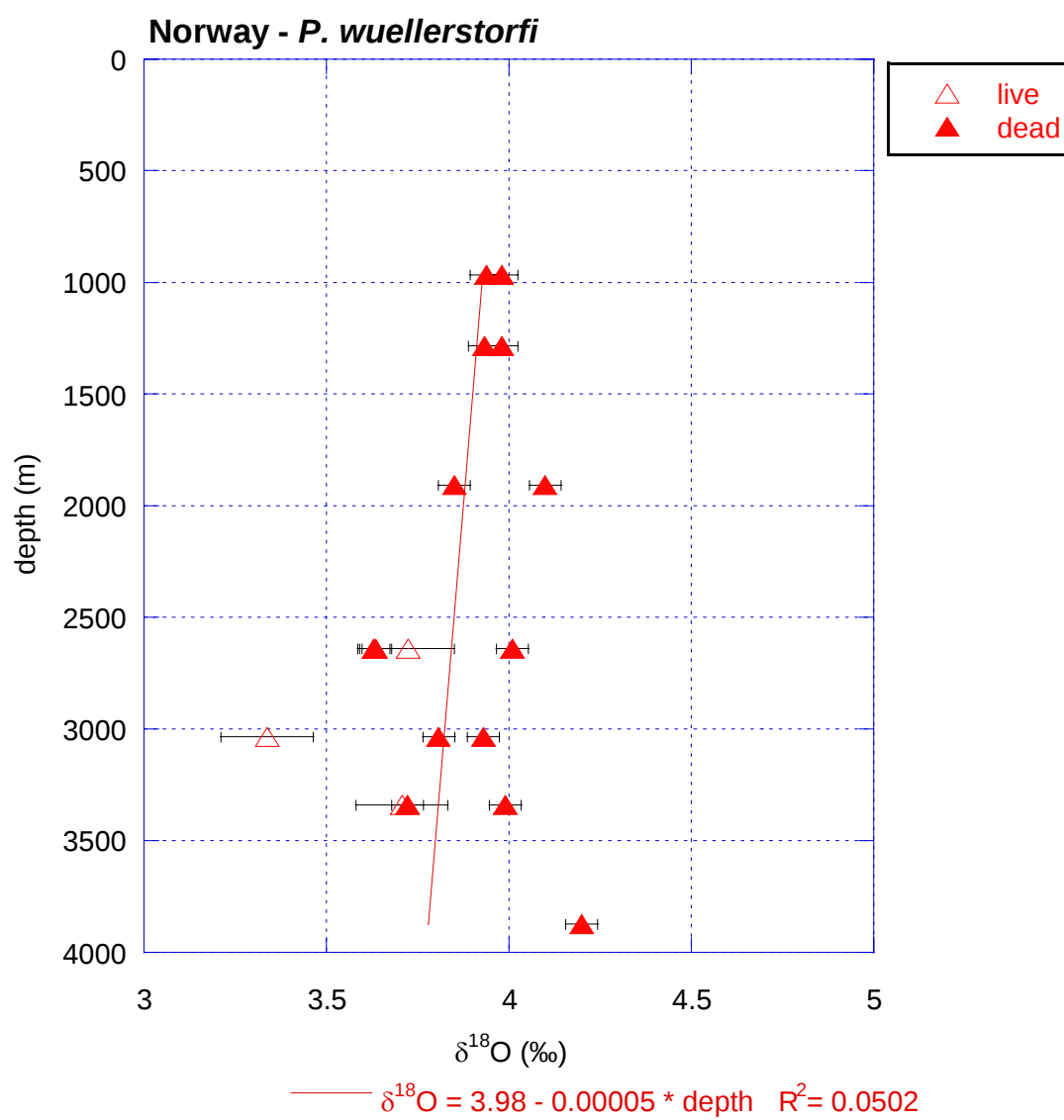


Figure 12: Norwegian Sea Mg/Ca for live (stained) and dead (unstained) *P. wuellerstorfi*. Error bars show standard error. $\Delta[\text{CO}_3^{-2}]$ vales are corrected to pre-industrial carbon. For correction details see Appendix 3. The blue line shows the expected slope of the Mg/Ca- $\Delta[\text{CO}_3^{-2}]$ relationship (from Elderfield et al., 2006). The red line shows the linear regression through all data (live and dead). Note the R^2 for this regression is low.

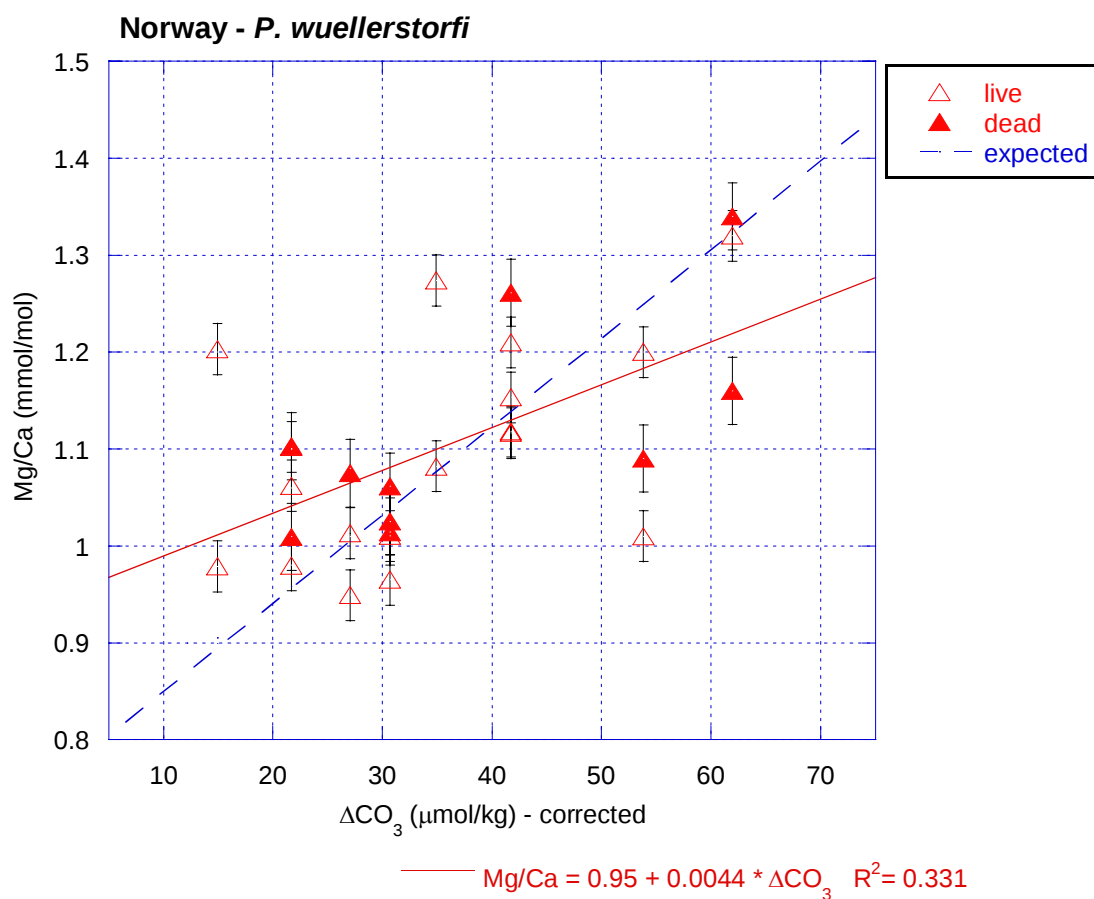
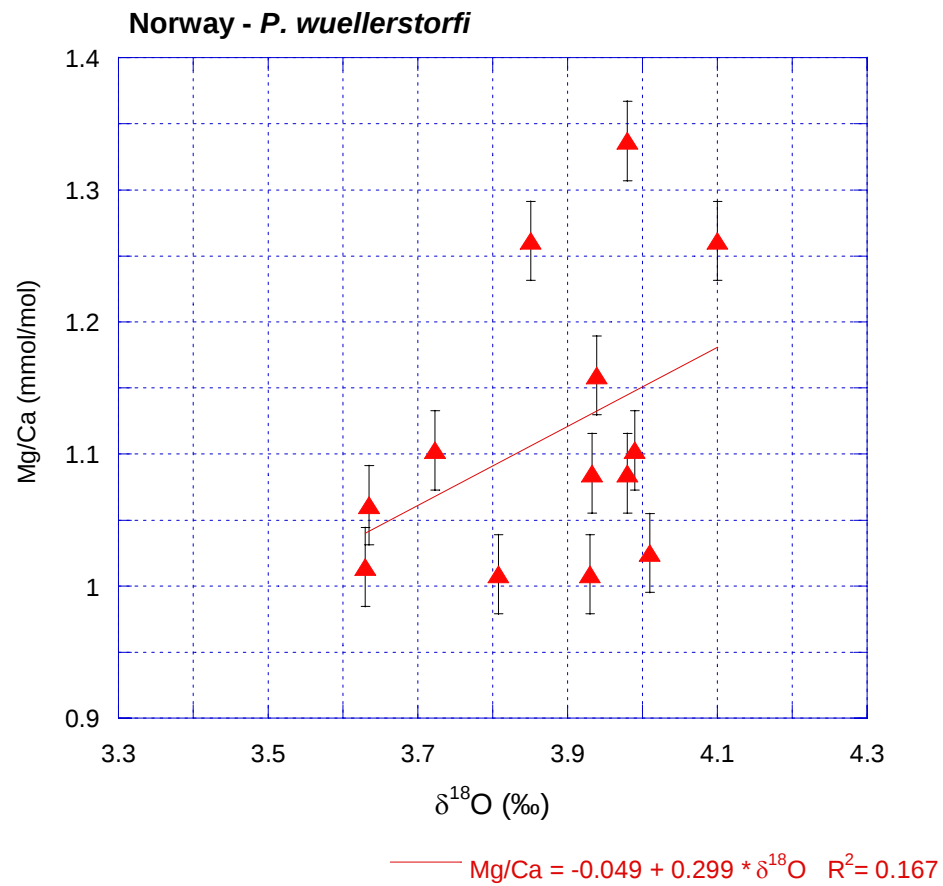


Figure 13: A) Oxygen isotope ($\delta^{18}\text{O}$) data for *P. wuellerstorfi*, Norwegian Sea. B) Carbon isotope ($\delta^{13}\text{C}$) data for *P. wuellerstorfi*. Error bars show standard error.

A)



B)

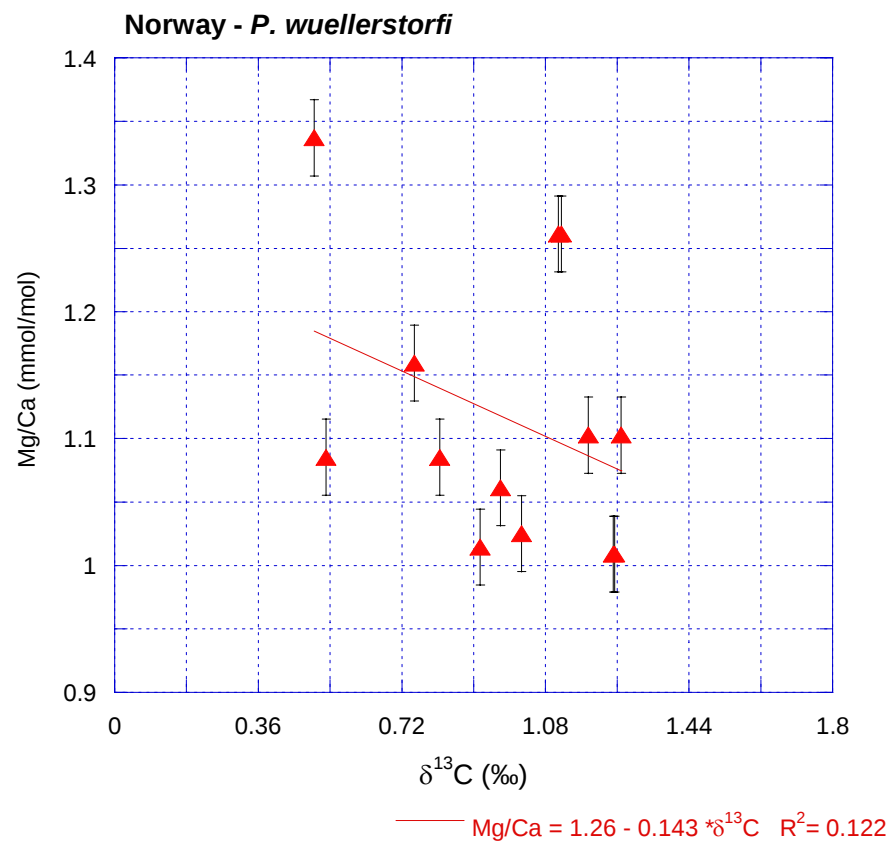


Figure 14: Gulf of Mexico Mg/Ca data for *P. wuellerstorfi*. Error bars show standard error. No live (stained) data are shown; samples were not stained due to long storage time before processing.

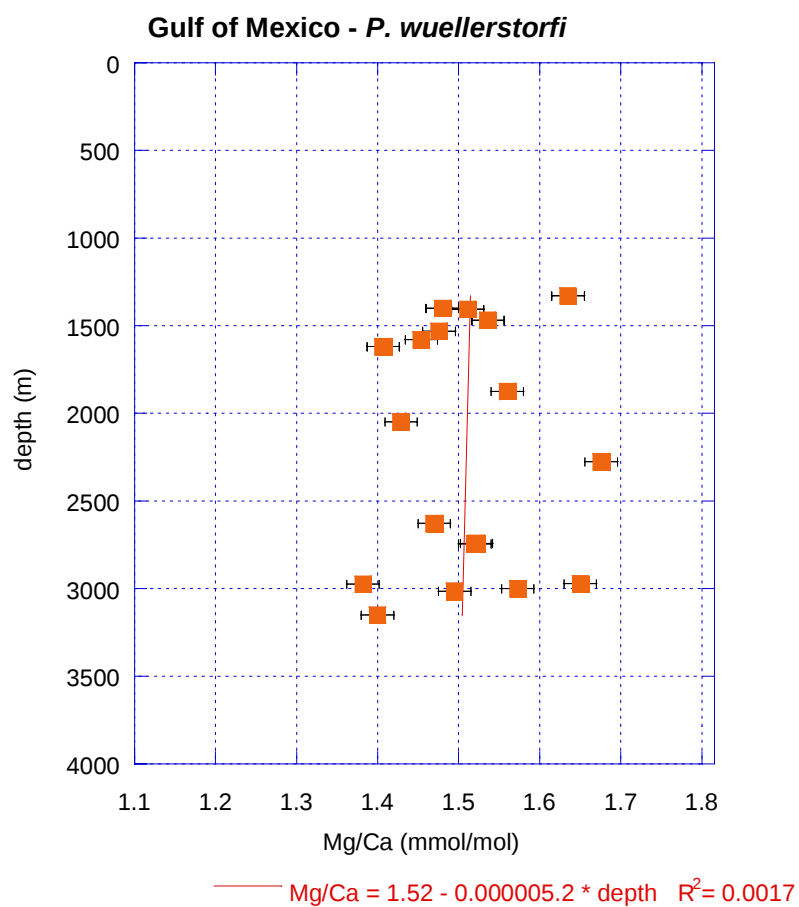


Figure 15: Gulf of Mexico $\delta^{18}\text{O}$ data for *P. wuellerstorfi*. Error bars show standard error.

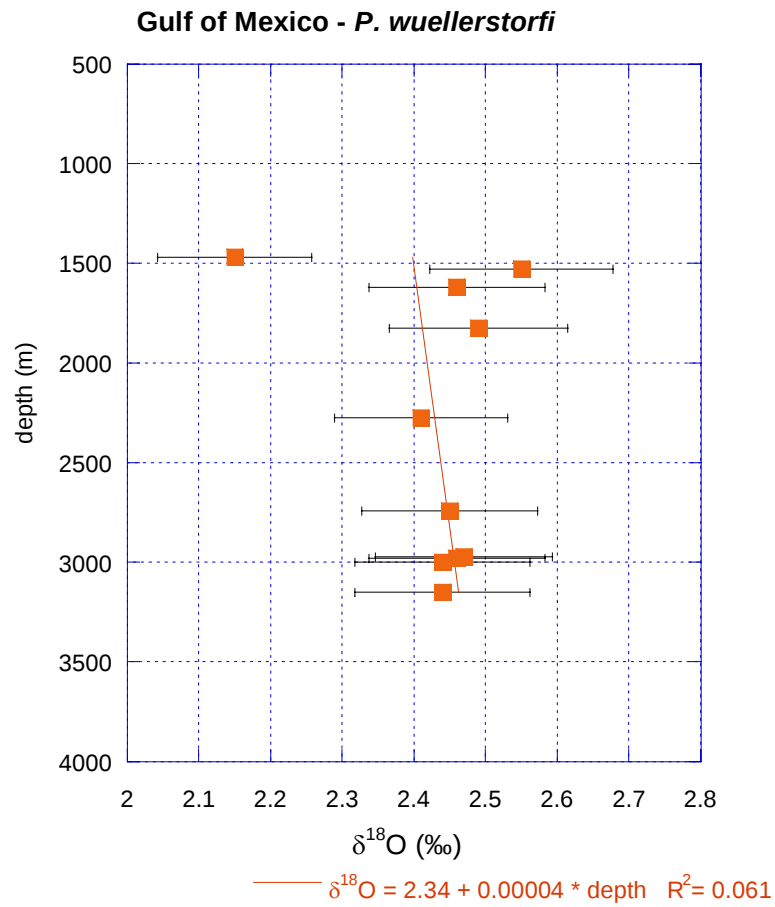


Figure 16: Gulf of Mexico Mg/Ca data for *P. wuellerstorfi*. Error bars show standard error. $\Delta[\text{CO}_3^{-2}]$ values are corrected to pre-industrial carbon. For correction details see Appendix 3. The blue line shows the expected slope of the Mg/Ca- $\Delta[\text{CO}_3^{-2}]$ relationship (from Elderfield et al., 2006). The orange line shows the linear regression. Note the R^2 for this regression is low.

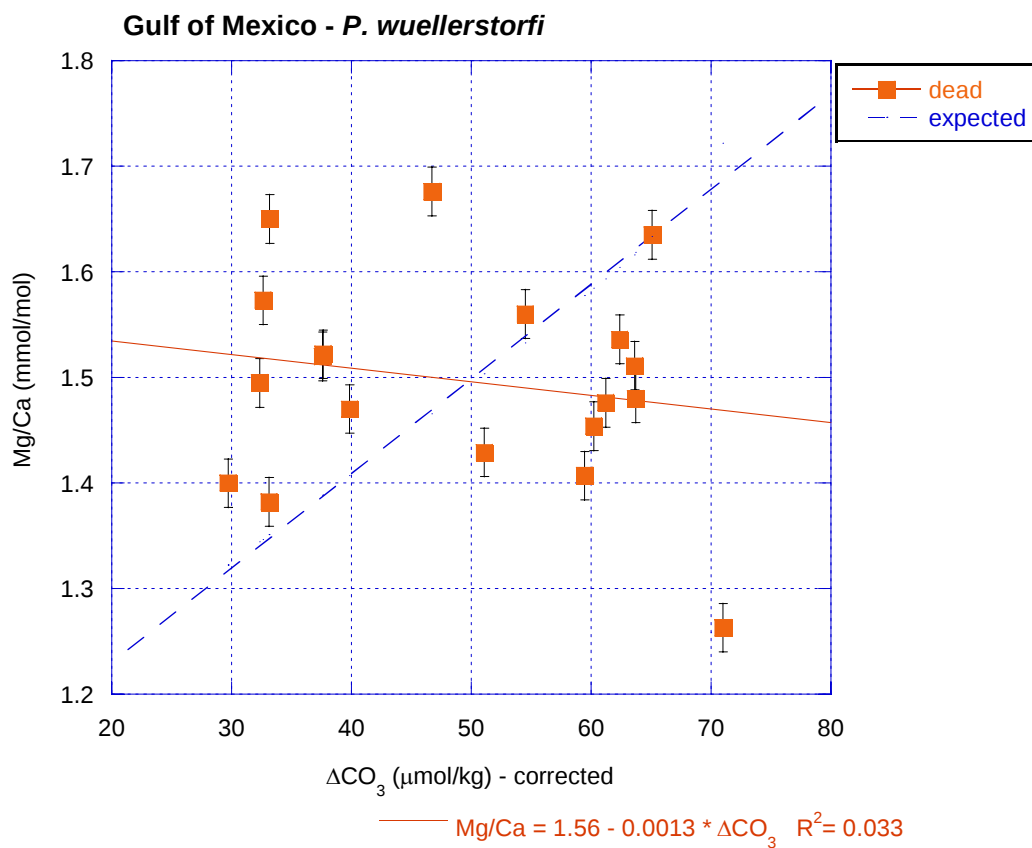
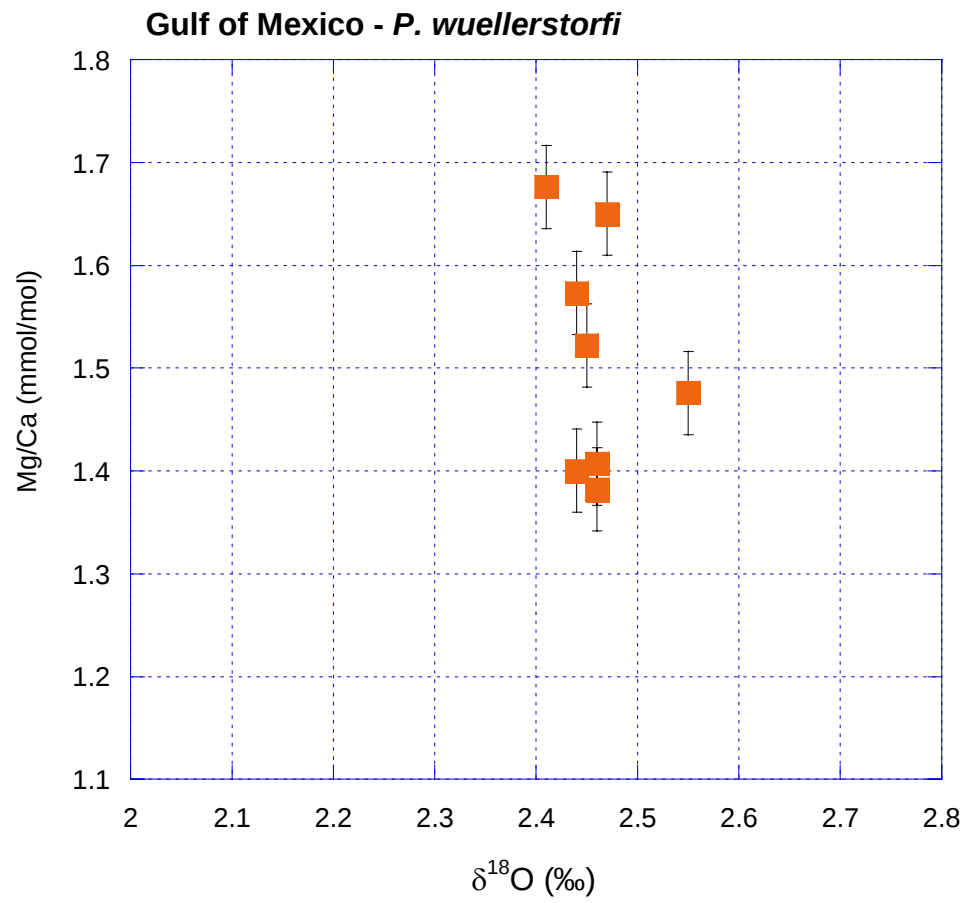


Figure 17: A) Oxygen isotope ($\delta^{18}\text{O}$) data for *P. wuellerstorfi*, Gulf of Mexico. B) Carbon isotope ($\delta^{13}\text{C}$) data for *P. wuellerstorfi*. Error bars show standard error.



B)

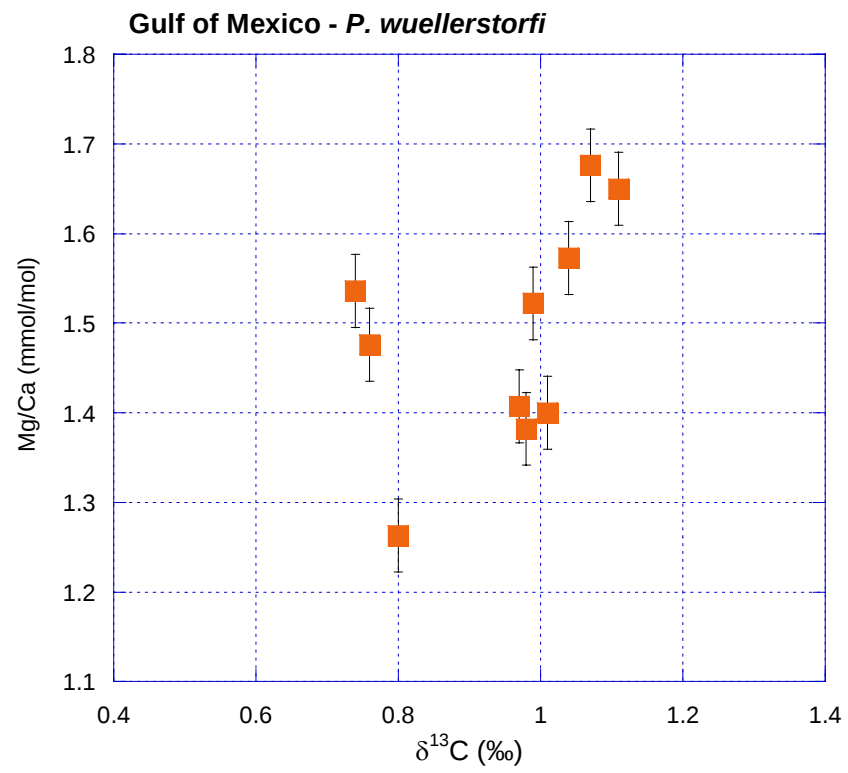


Figure 18: Norwegian Sea Mg/Ca for live (stained) and dead (unstained) *O. umbonatus*. Error bars show standard error.

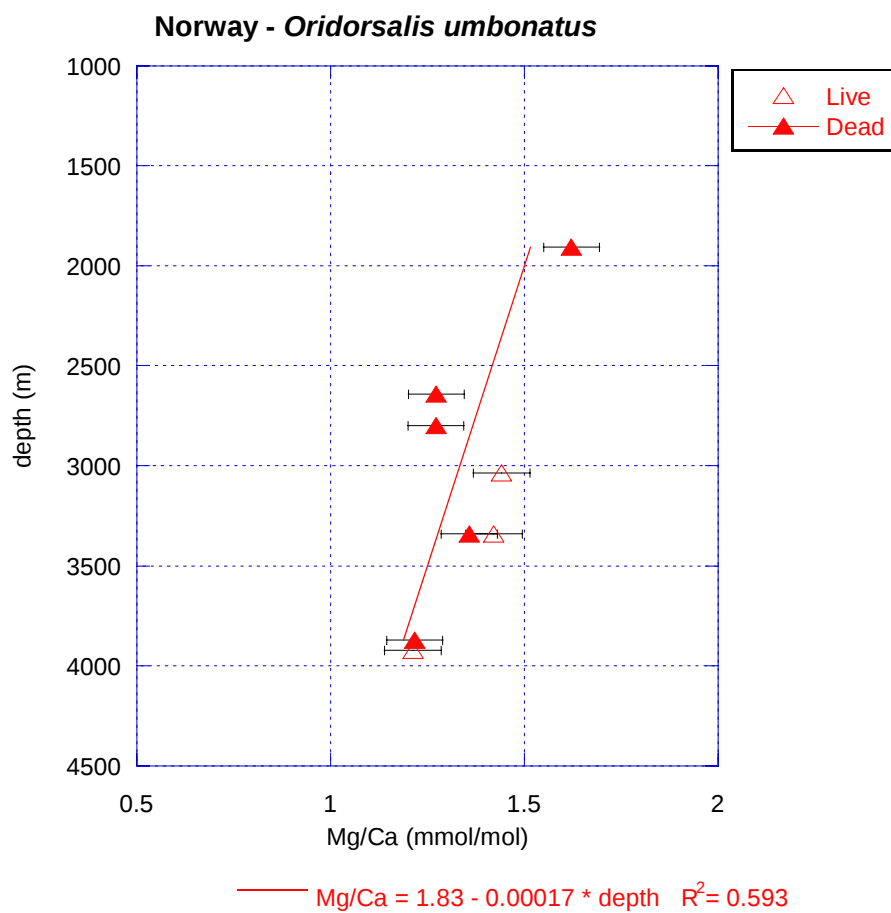


Figure 19: Mg/Ca in *O. umbonatus*, Norwegian sea. Error bars show standard error.

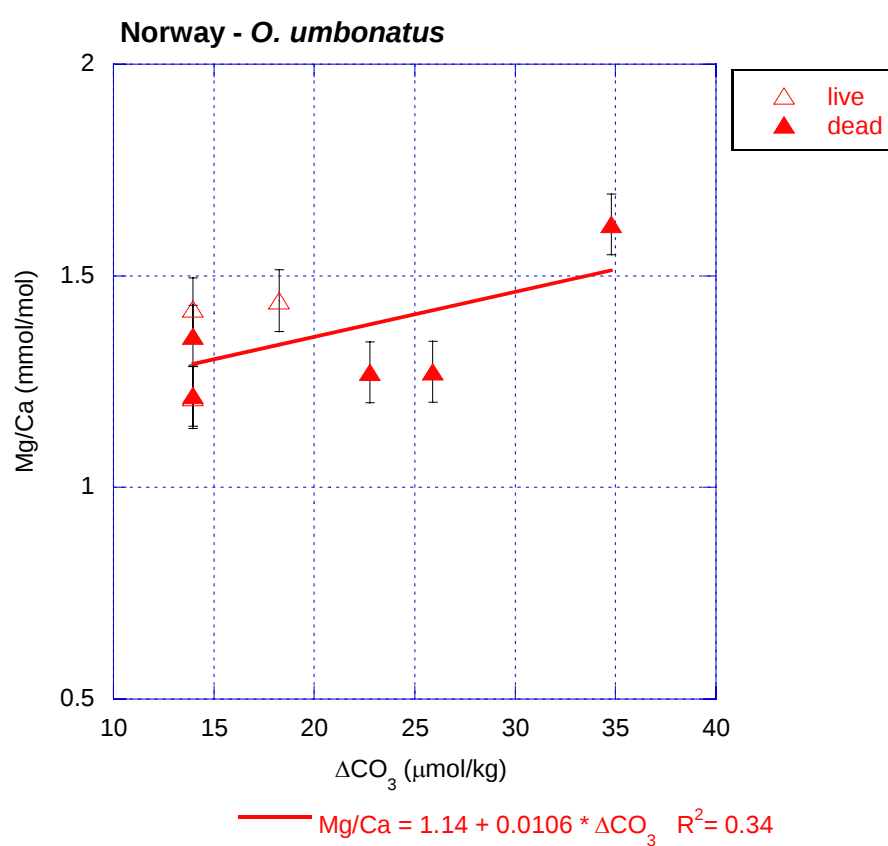
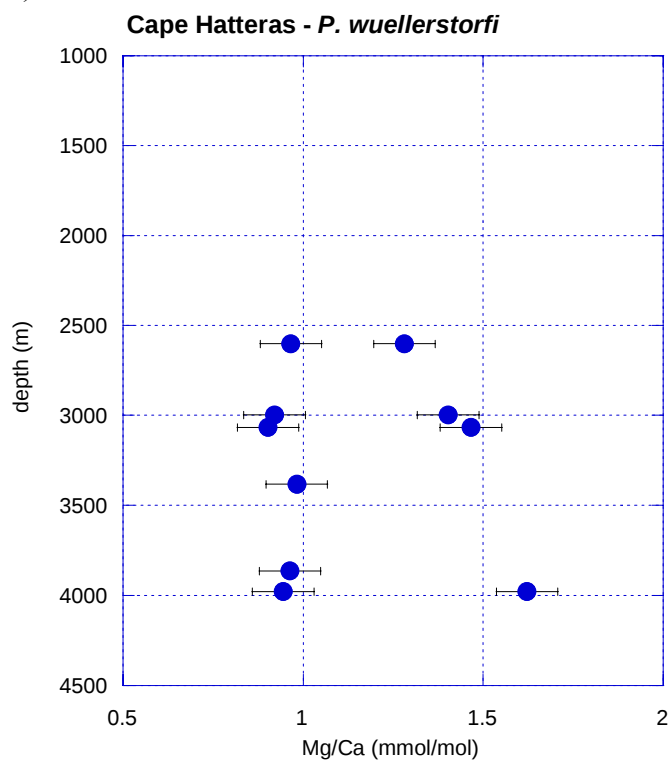


Figure 20: Cape Hatteras Mg/Ca data for *P. wuellerstorfi*. A) versus depth, and B) versus BWT. Numbers of live (stained) benthics are insufficient for ICP-MS analysis, and so live versus dead data are not shown. Error bars show standard error.

A)



B)

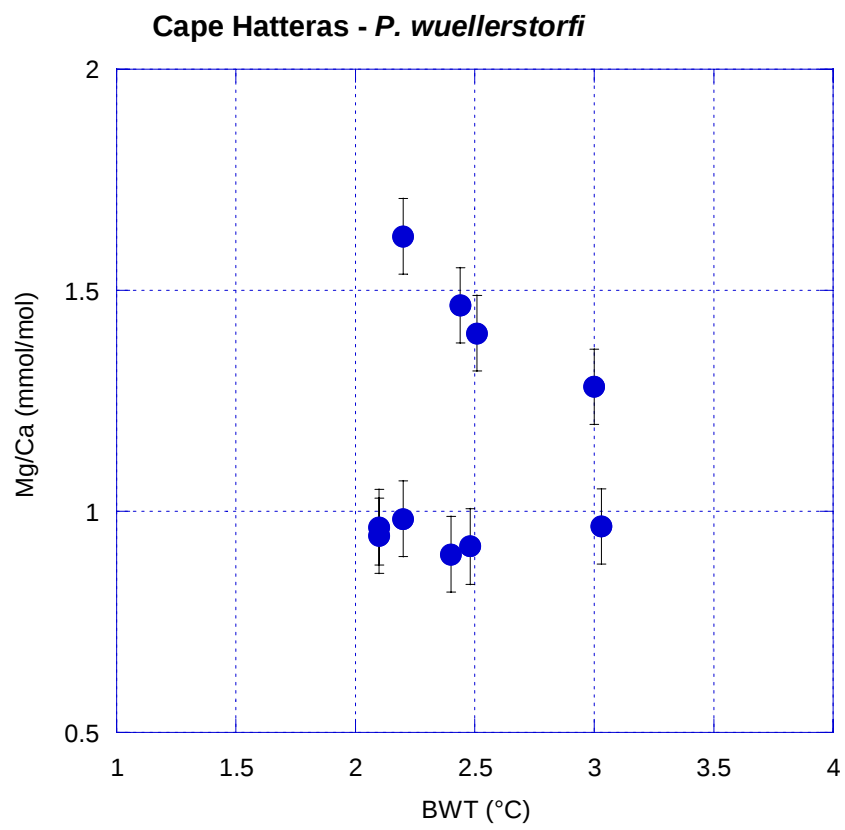


Figure 21: Oxygen isotope ($\delta^{18}\text{O}$) data in *P. wuellerstorfi* for Cape Hatteras.

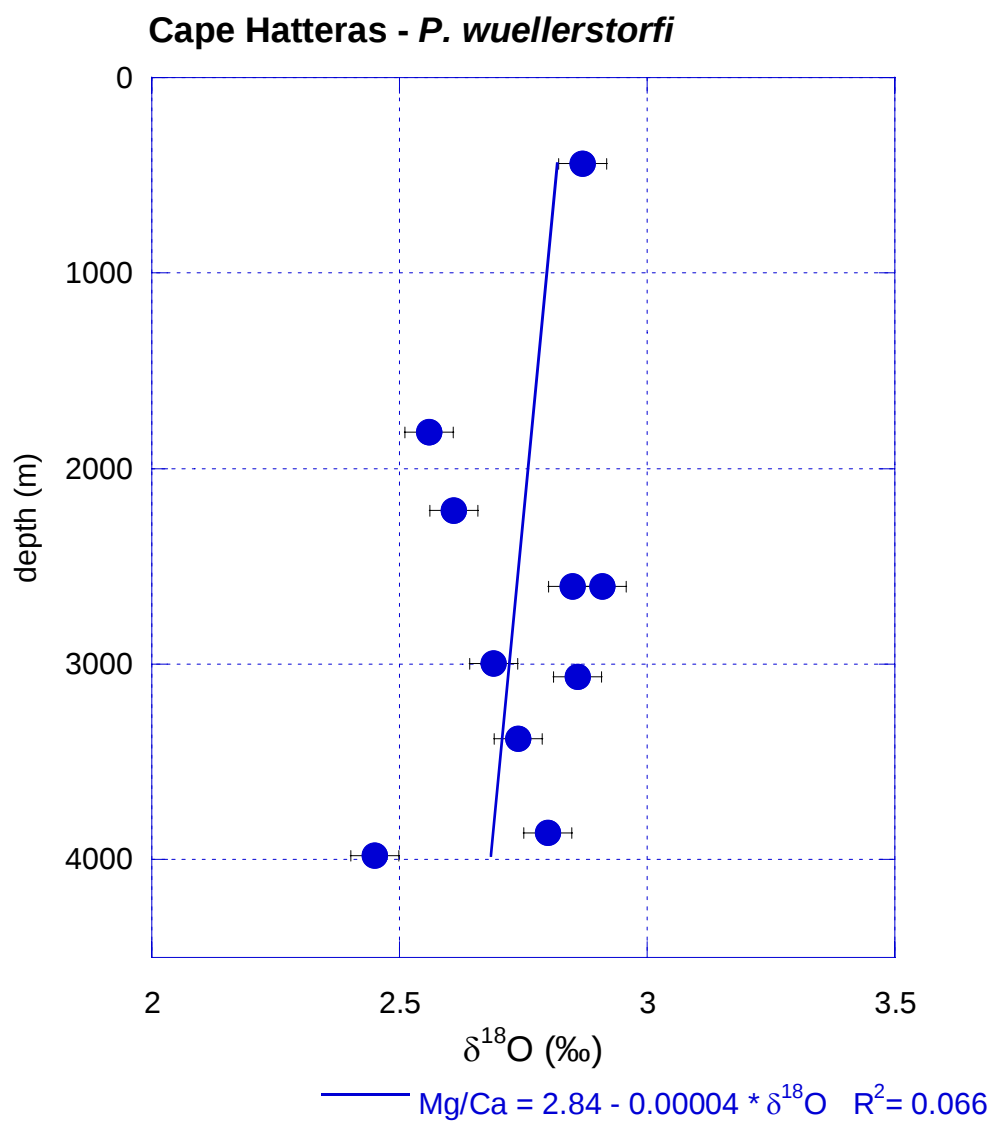


Figure 22: Cape Hatteras Mg/Ca data for *P. wuellerstorfi*. Error bars show standard error.

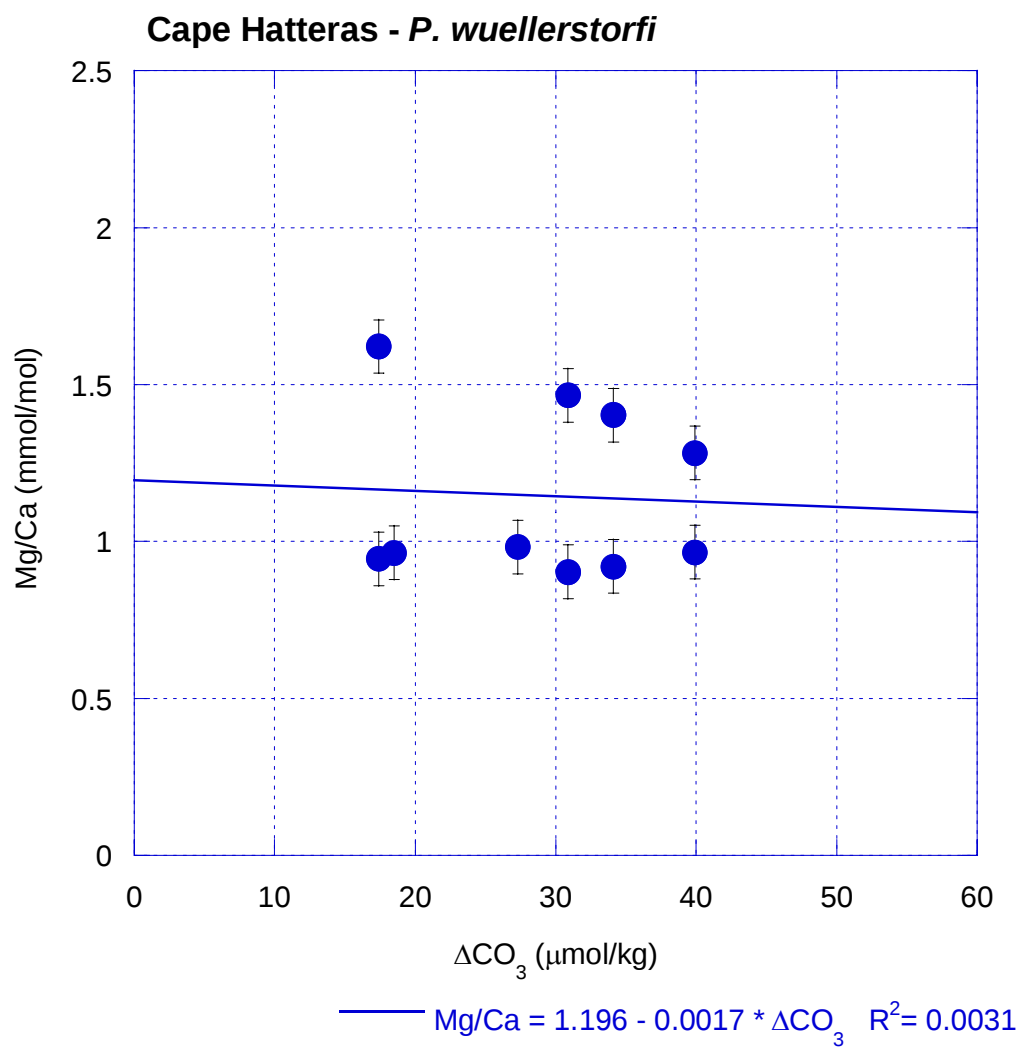
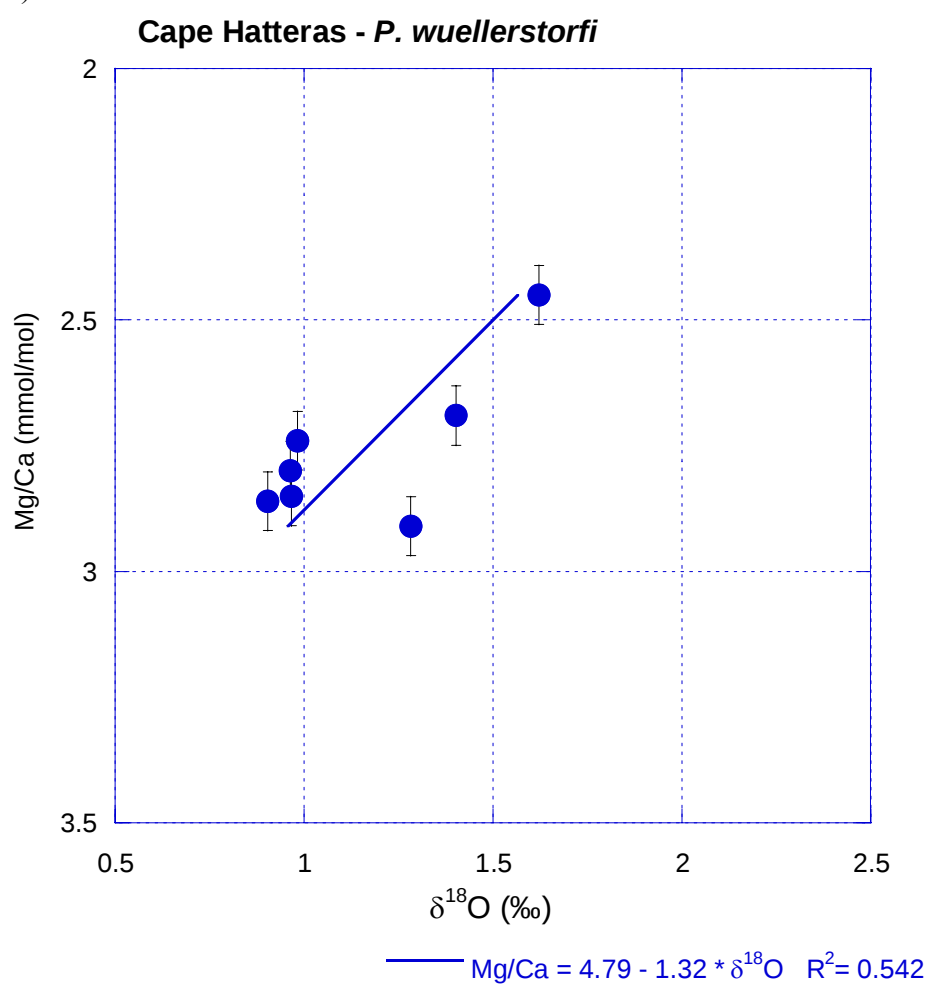


Figure 23: A) Oxygen isotope ($\delta^{18}\text{O}$) data for *P. wuellerstorfi*, Cape Hatteras. B) Carbon isotope ($\delta^{13}\text{C}$) data for *P. wuellerstorfi*. Error bars show standard error.

A)



B)

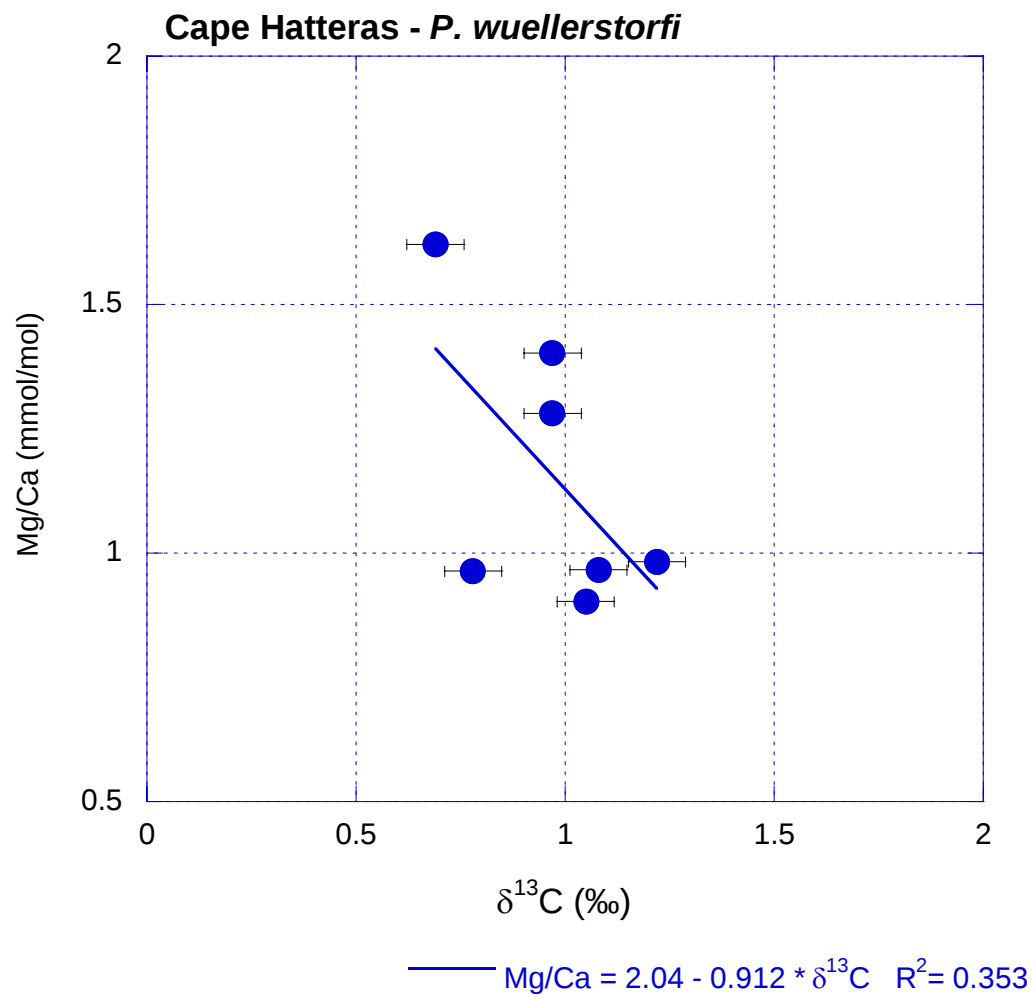
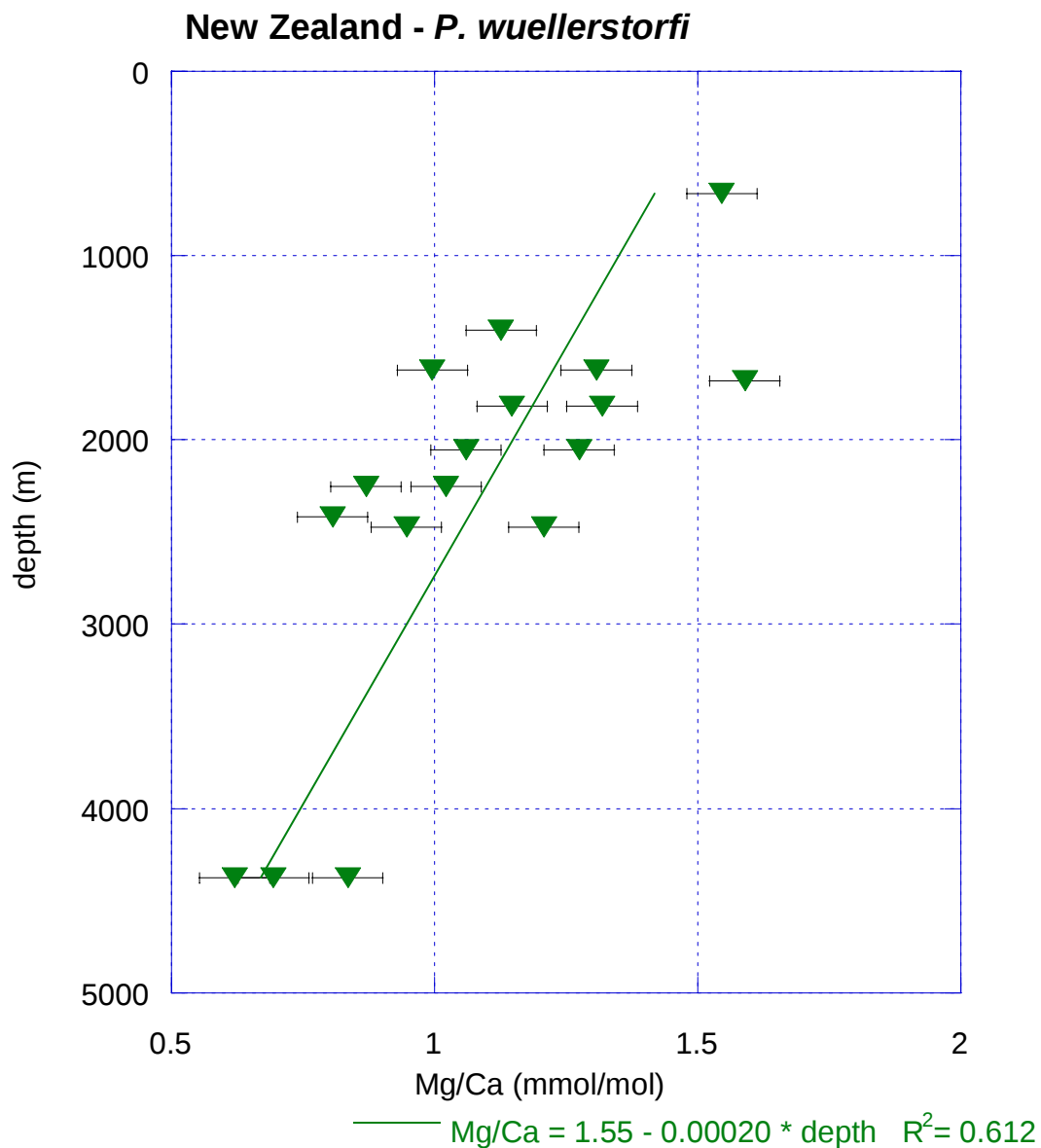


Figure 24: New Zealand Mg/Ca data *P. wuellerstorfi* vs. A) depth and B) BWT. Live versus dead data are not shown due to lack of live (stained) specimens. Error bars show standard error.

A)



B)

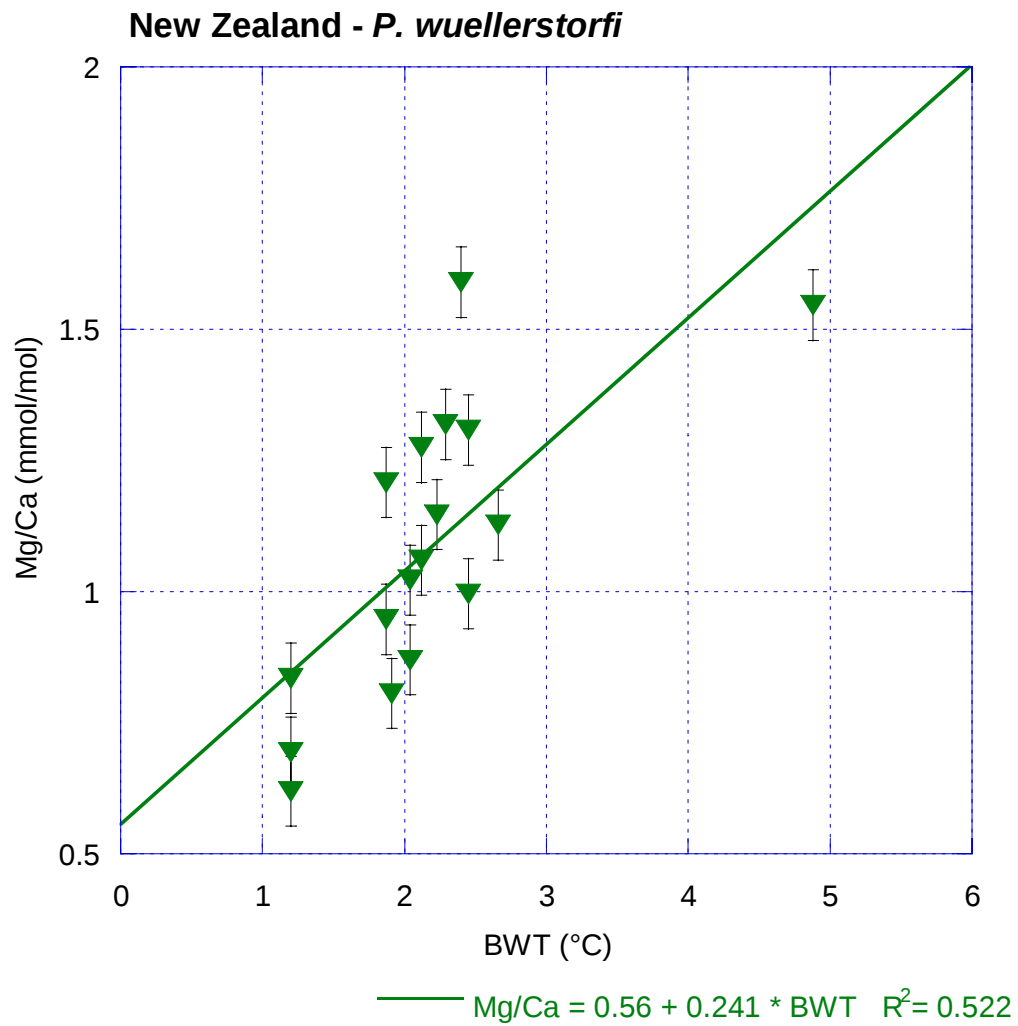


Figure 25: Oxygen isotope data for *P. wuellerstorfi* in New Zealand. Error bars show standard error.

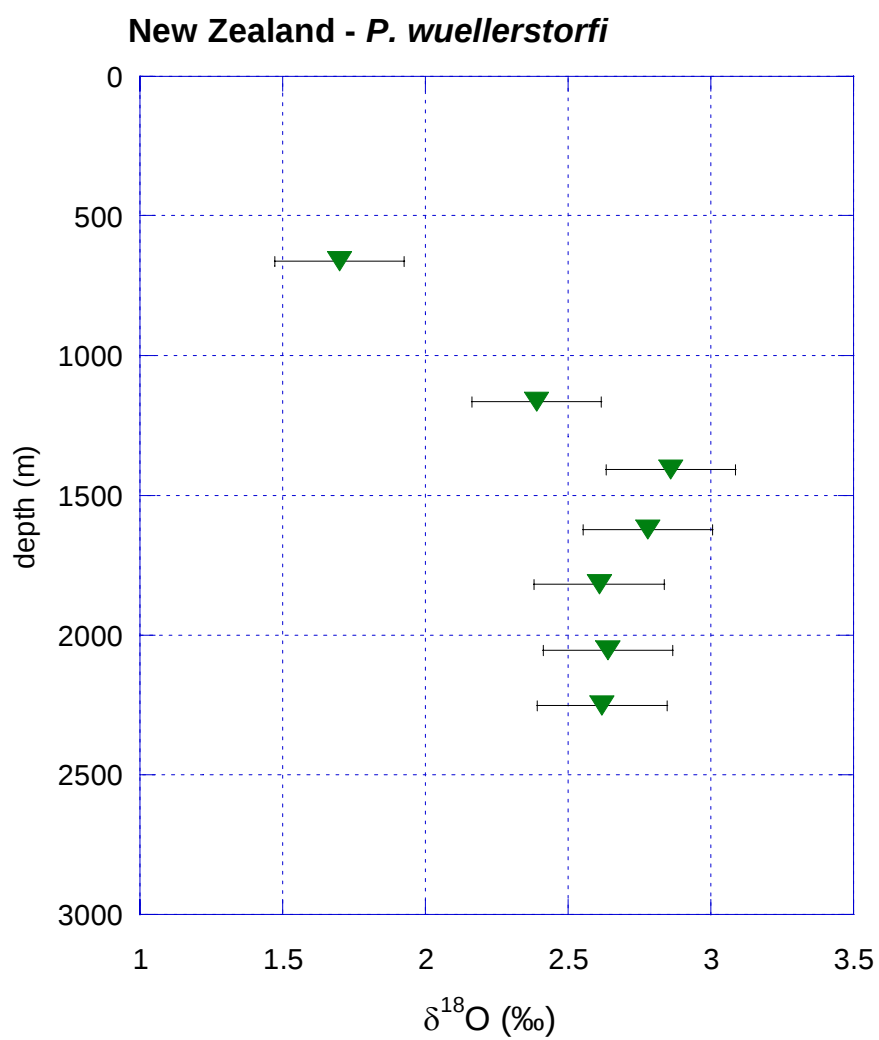


Figure 26: New Zealand Mg/Ca data *P. wuellerstorfi* vs $\Delta[\text{CO}_3^{-2}]$. Error bars show standard error.

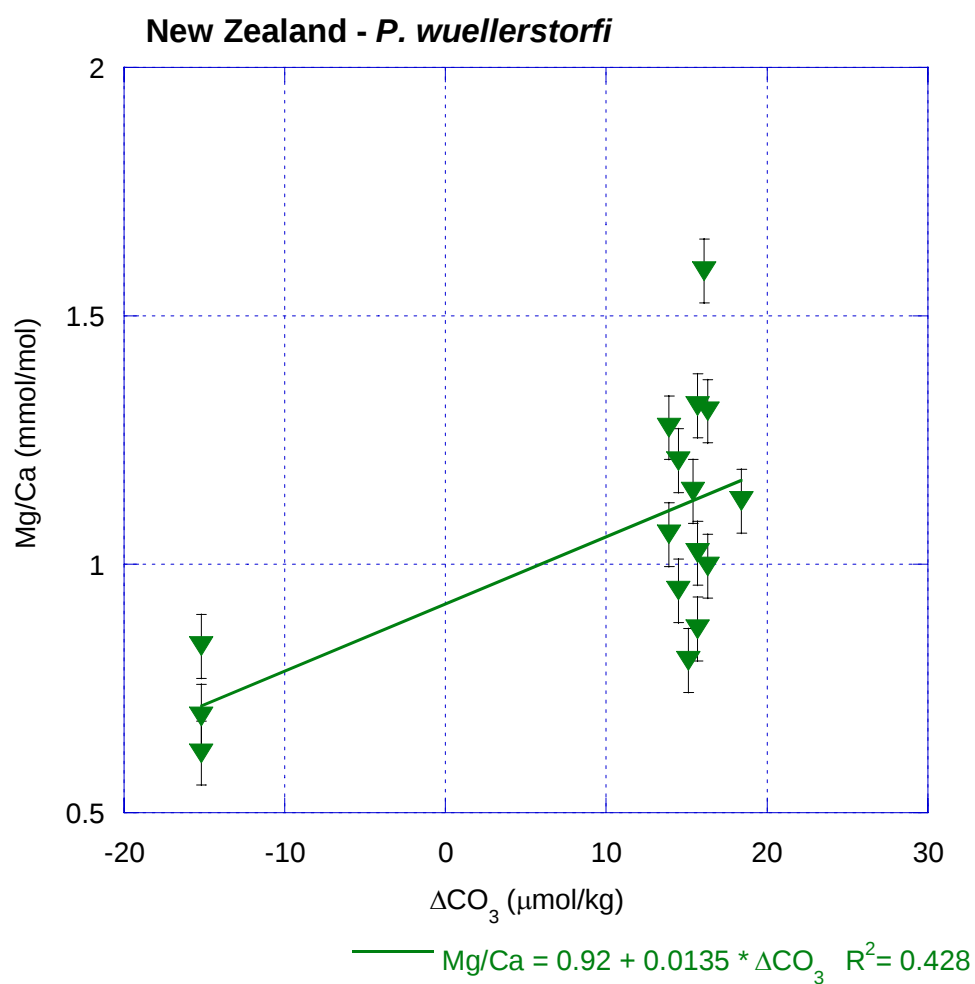
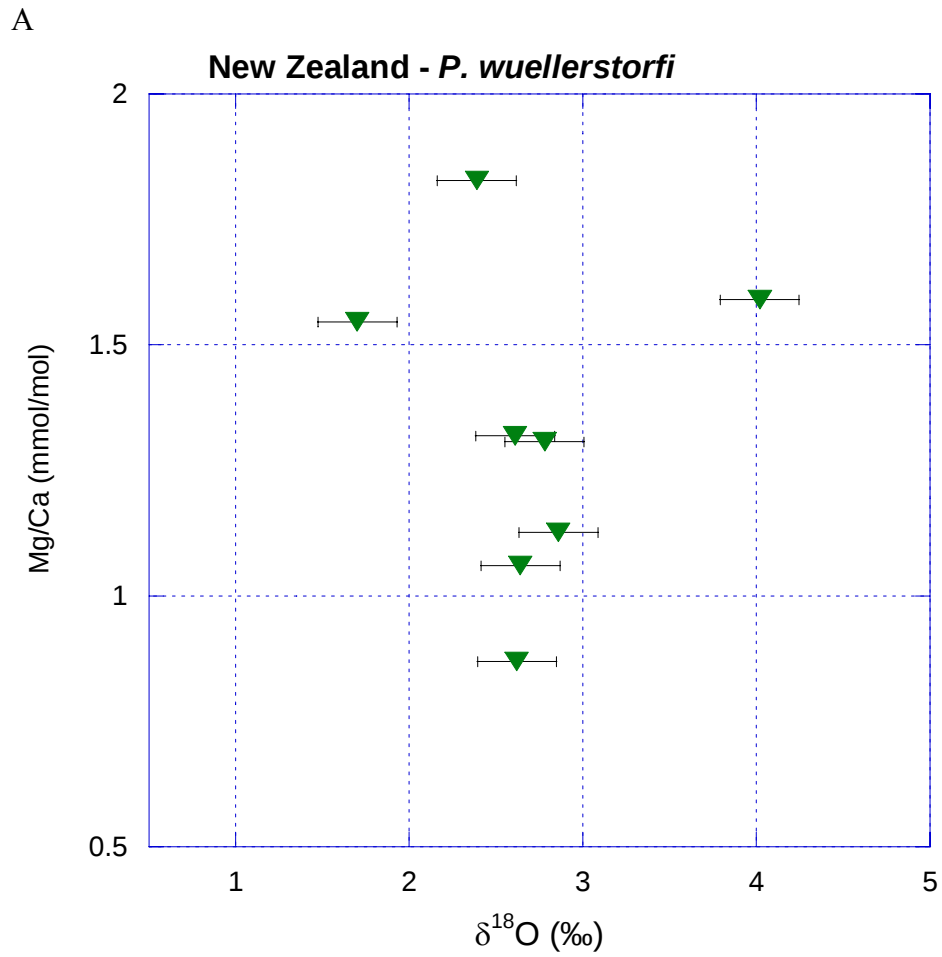


Figure 27: A) Oxygen isotope ($\delta^{18}\text{O}$) data for *P. wuellerstorfi*, New Zealand. B) Carbon isotope ($\delta^{13}\text{C}$) data for *P. wuellerstorfi*. Error bars show standard error.



B)

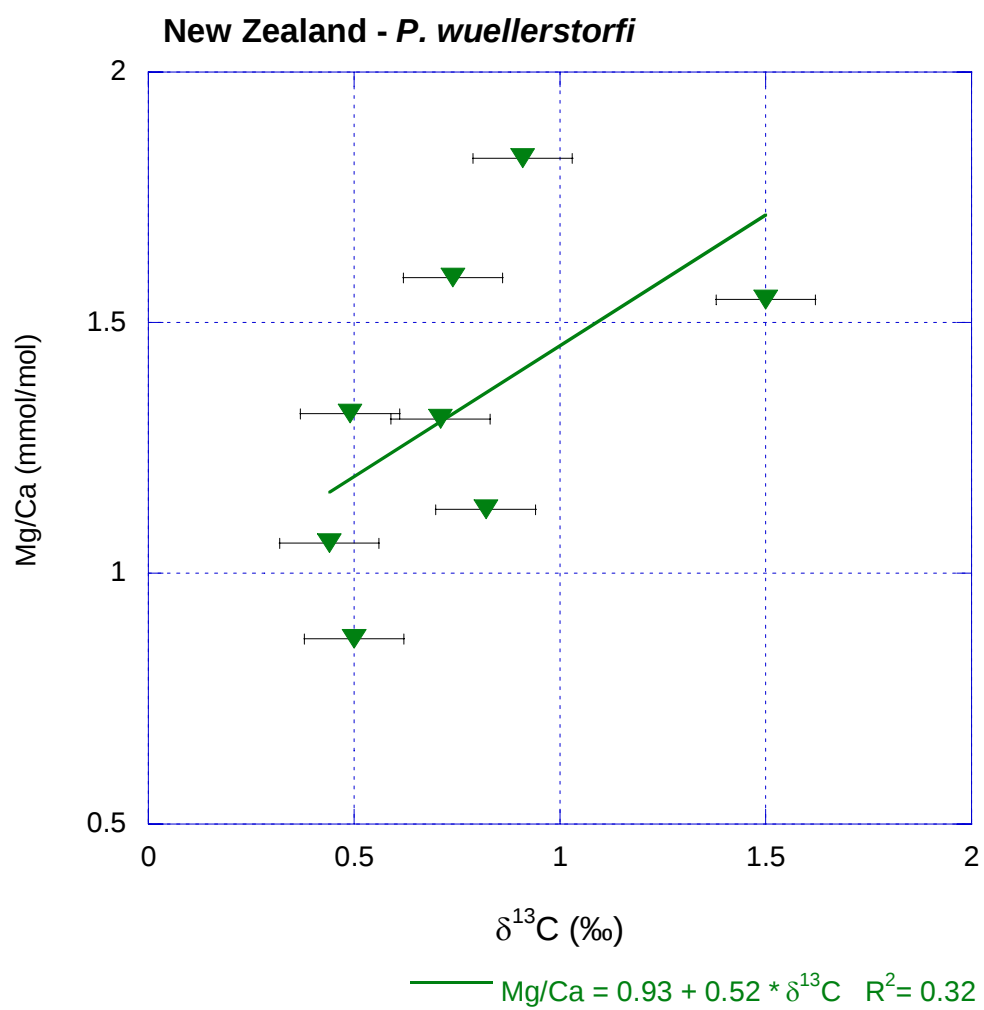
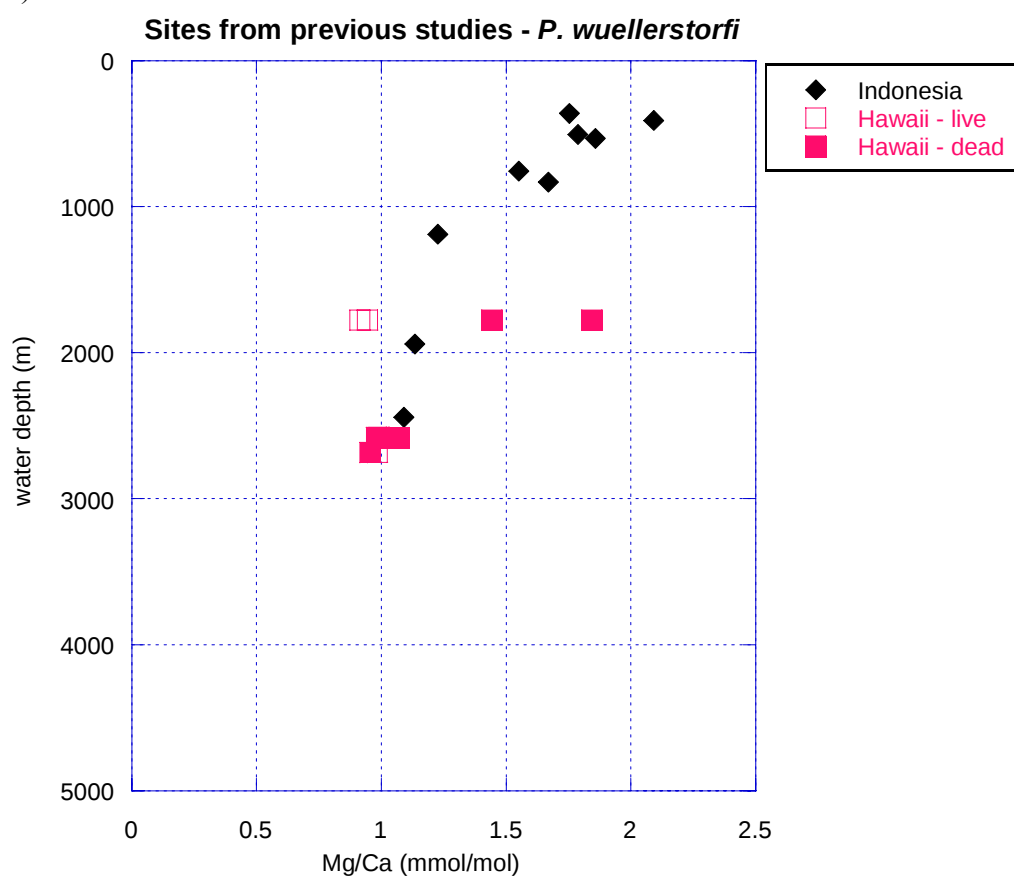


Figure 28: Mg/Ca in *P. wuellerstorfi* for sites (Indonesia, Hawaii) from previous studies vs A) depth and B) BWT. See Rosenthal et al., 1997 and Lear et al., 2002.

A)



B)

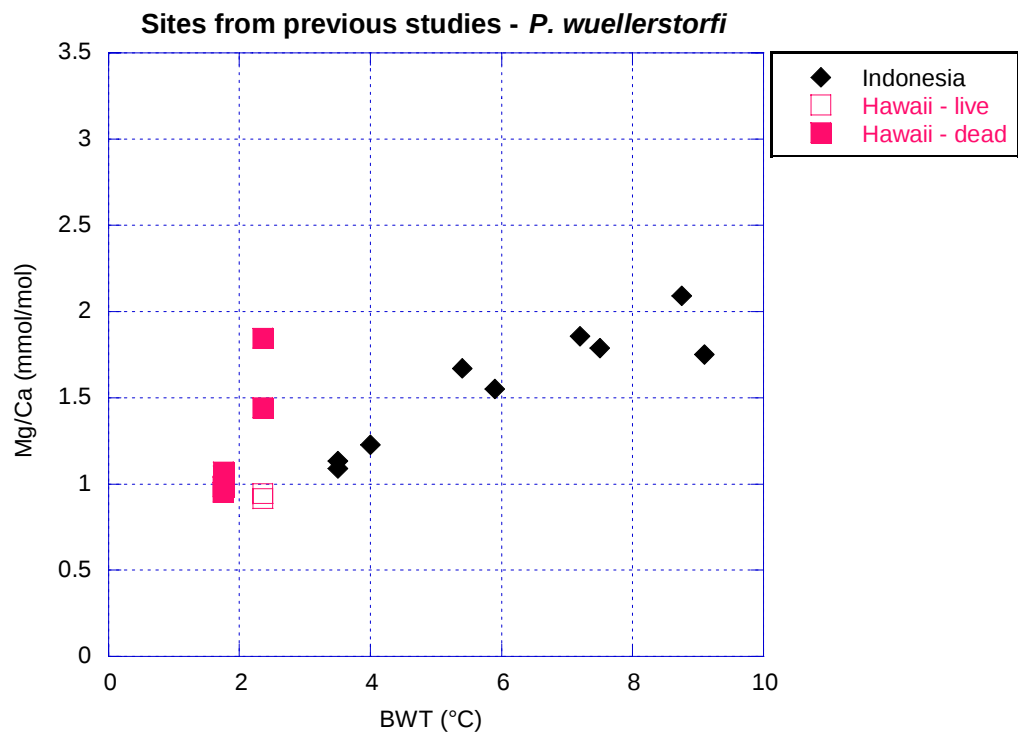


Figure 29: *P. wuellerstorfi* Global calibration Mg/Ca for Cape Hatteras, New Zealand, Indonesia, and Hawaii.

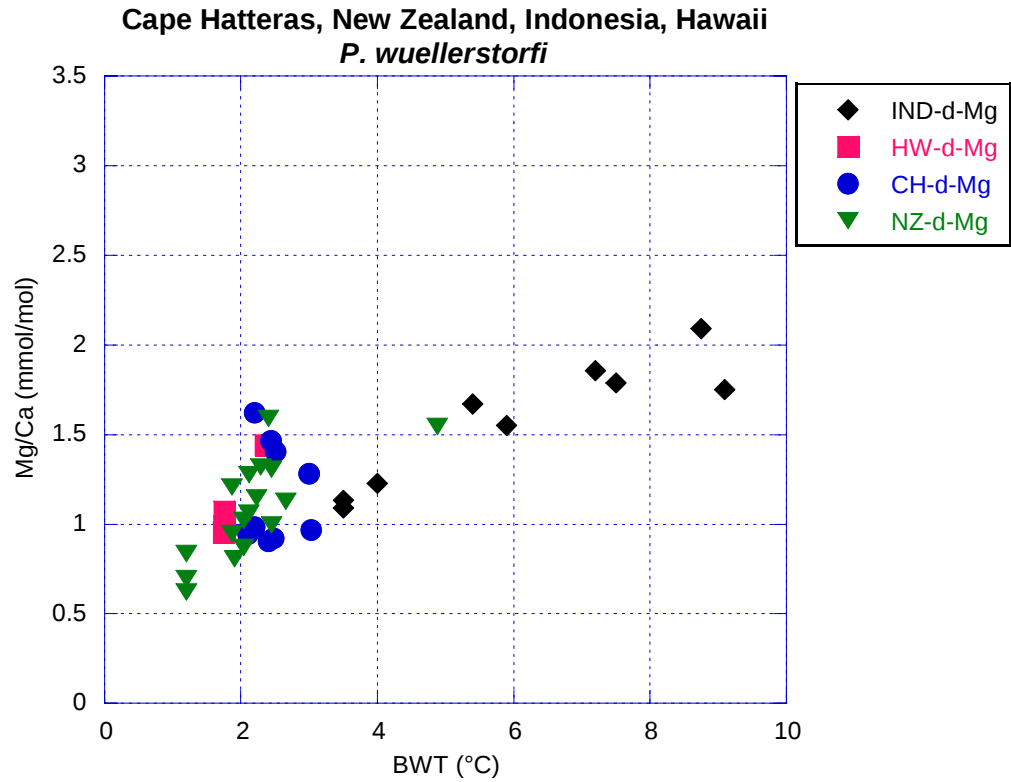
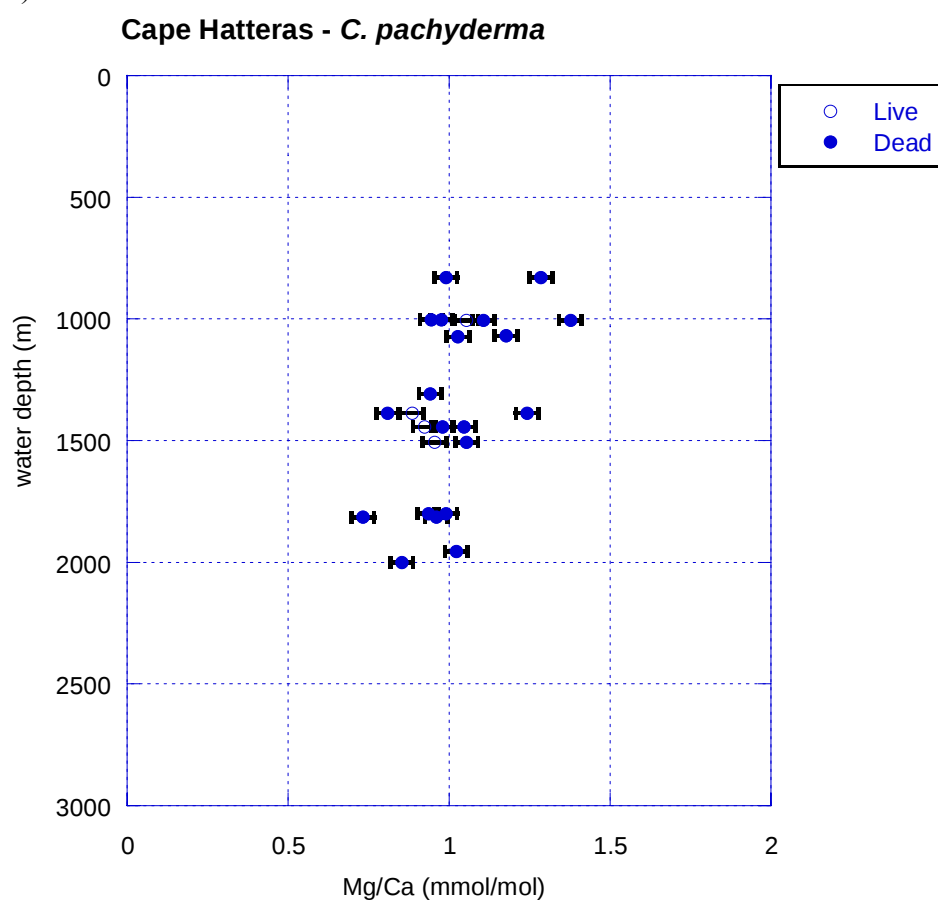


Figure 30: Mg/Ca in *C. pachyderma* from Cape Hatteras. Error bars show standard error. A) Mg/Ca with depth and B) Mg/Ca with BWT.

A)



B)

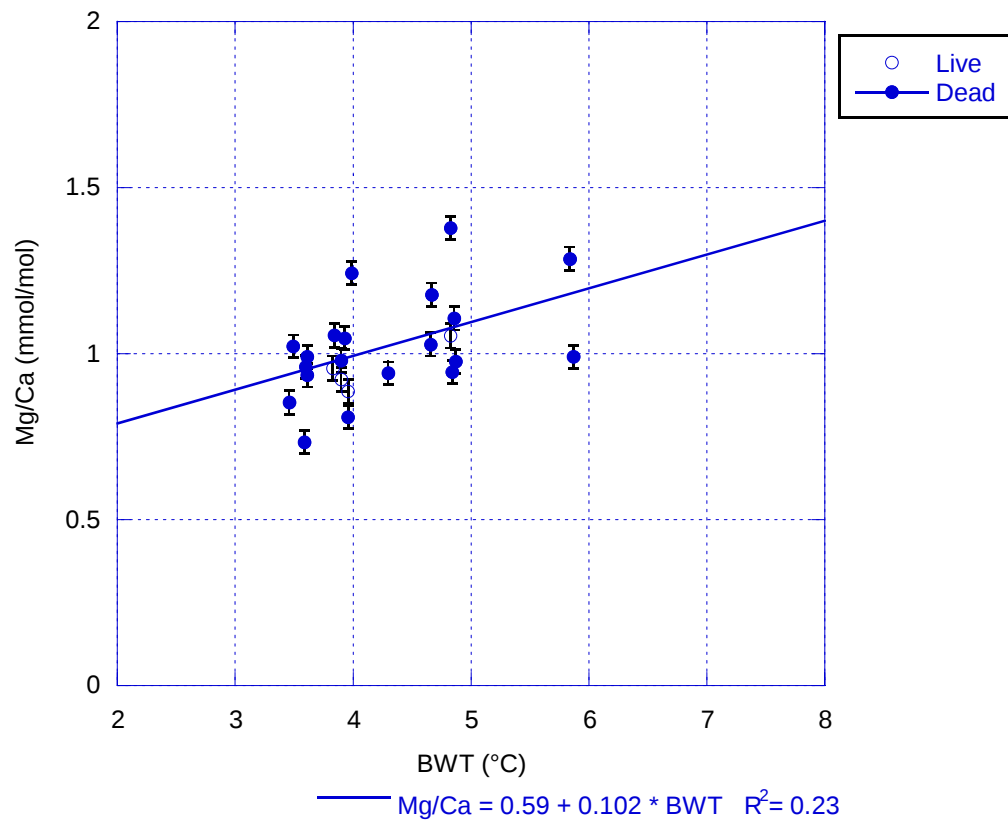
Cape Hatteras - *C. pachyderma*

Figure 31: Mg/Ca in *C. pachyderma* from Cape Hatteras. Error bars show standard error.

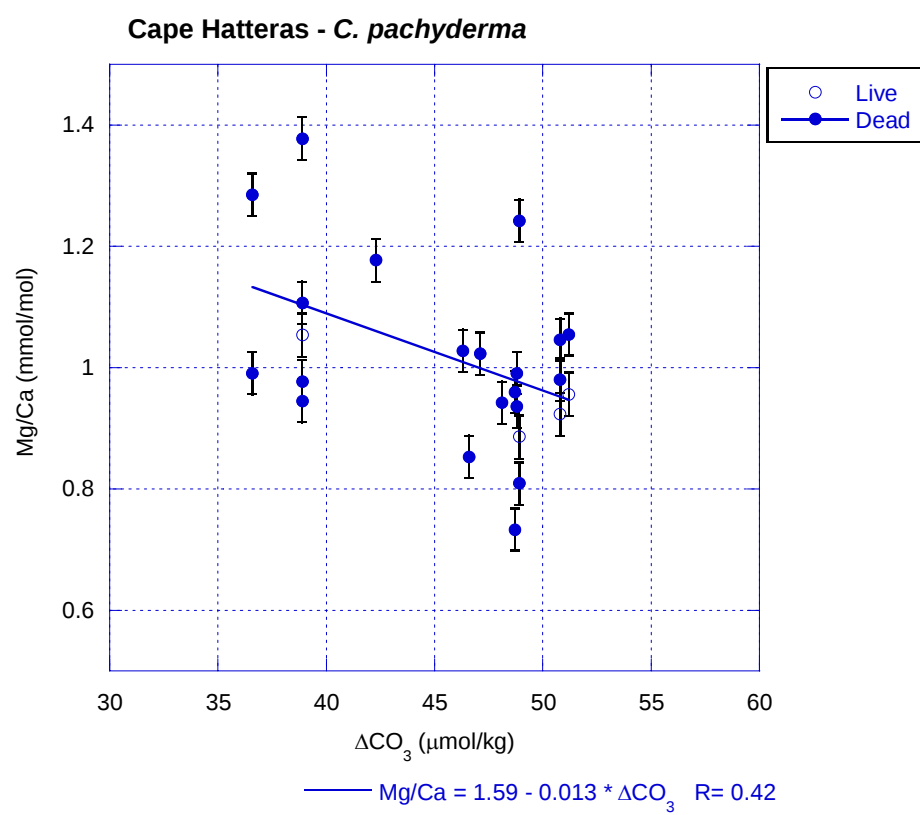
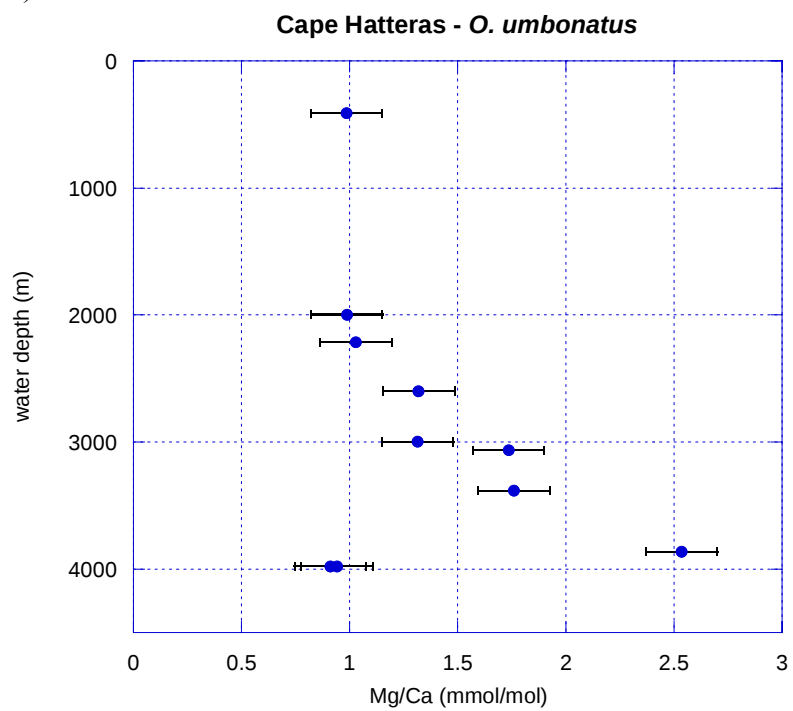
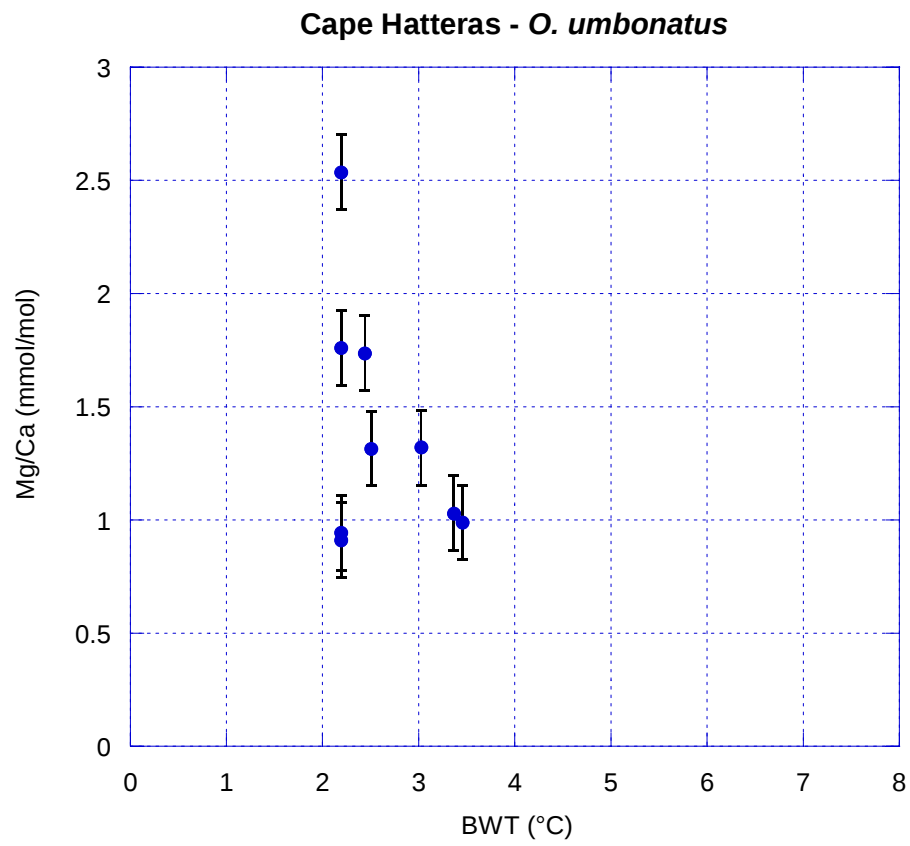


Figure 32: Cape Hatteras Mg/Ca in *O. umbonatus* from Cape Hatteras, vs A) depth, B) BWT, and C) carbonate. Error bars show standard error.

A)



B)



C)

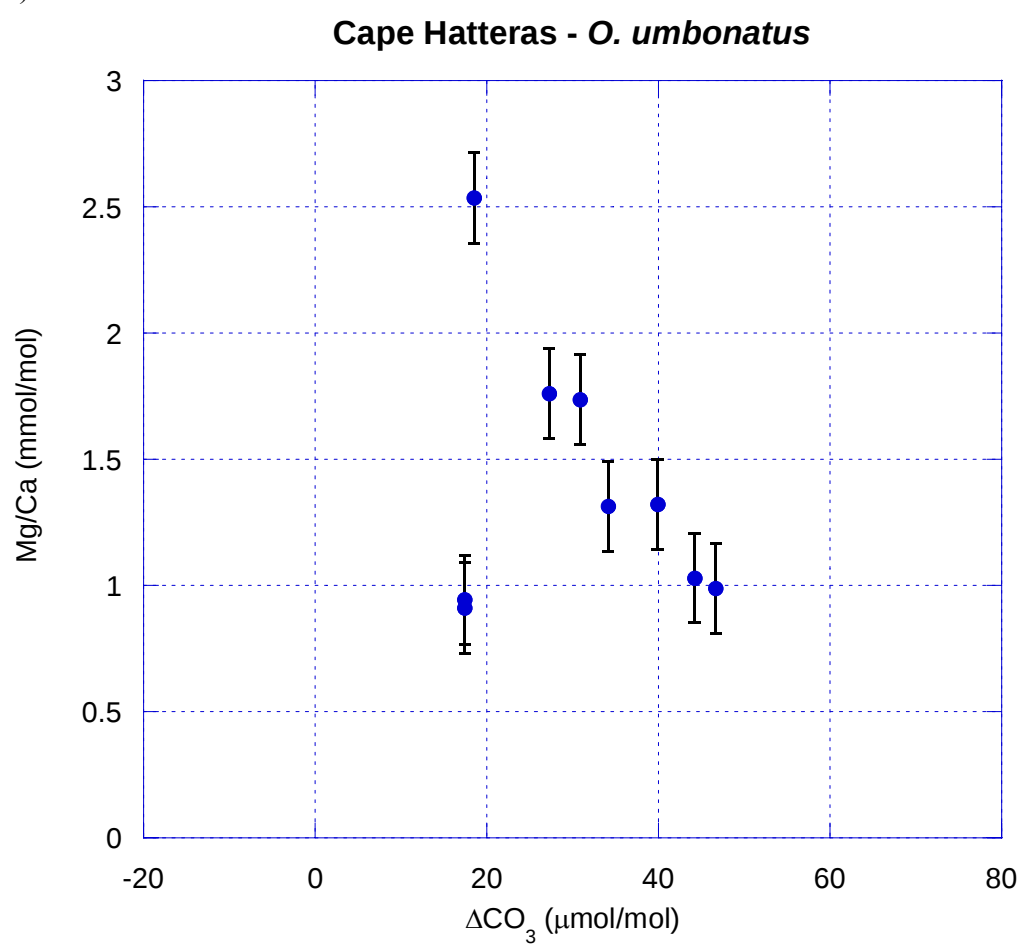
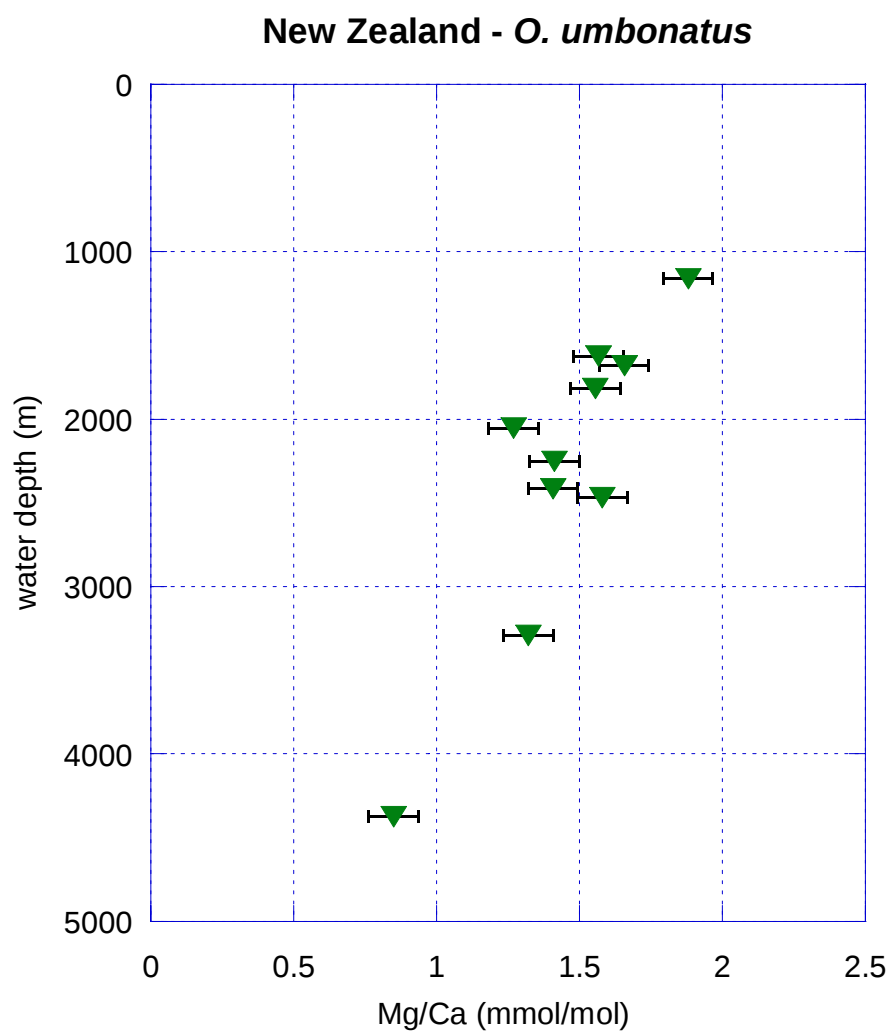
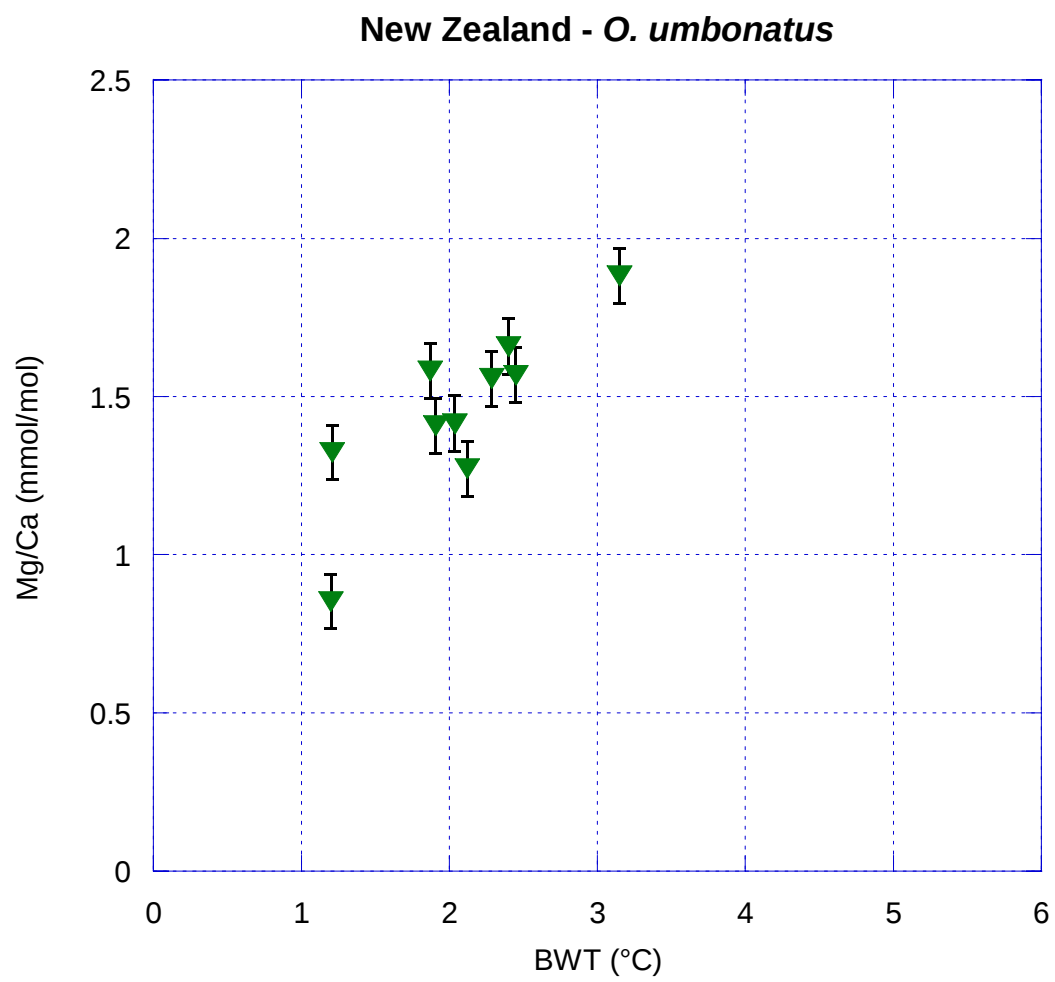


Figure 33: Mg/Ca in *O. umbonatus* from New Zealand vs A) depth, B) BWT, and C) carbonate. Error bars show standard error.

A)



B)



C)

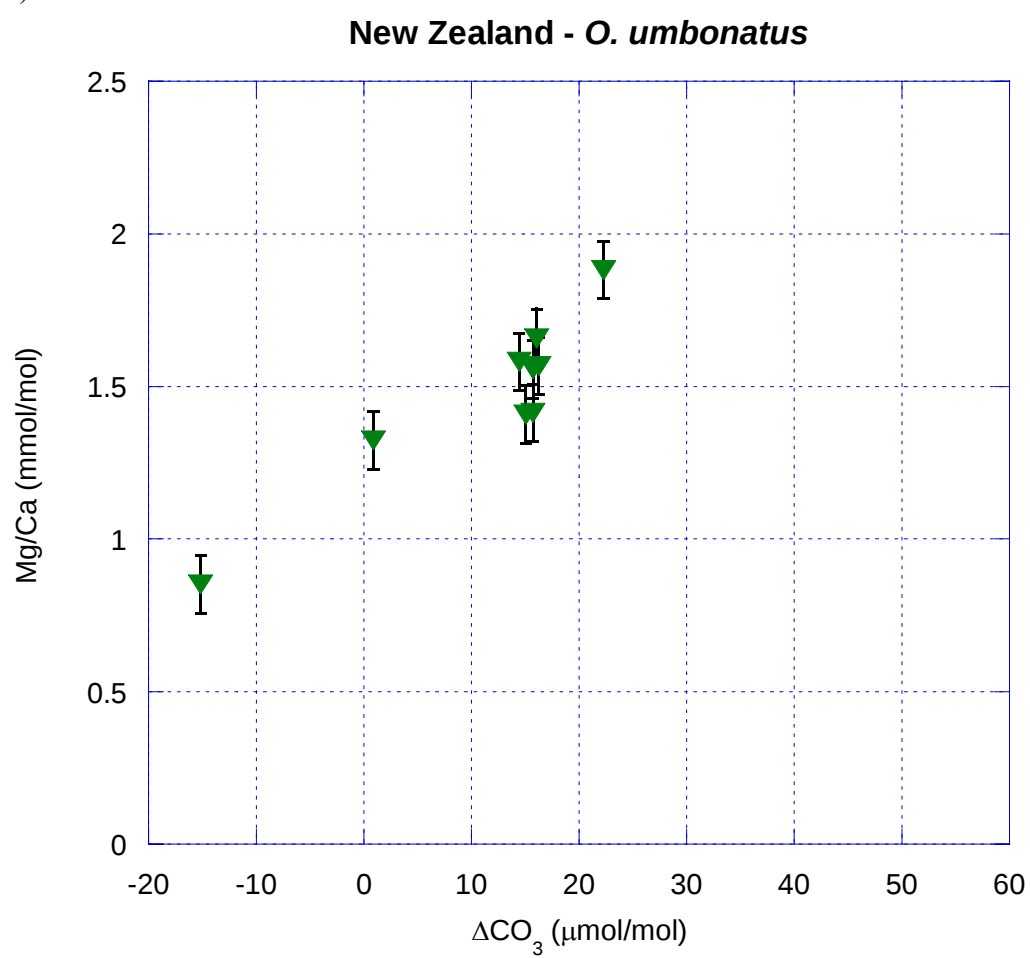


Figure 34: Data from the Gulf of Mexico, Cape Hatteras, New Zealand, Indonesia, and Hawaii sites between 1.2 and 2.2°C. Data are color coded by temperature.

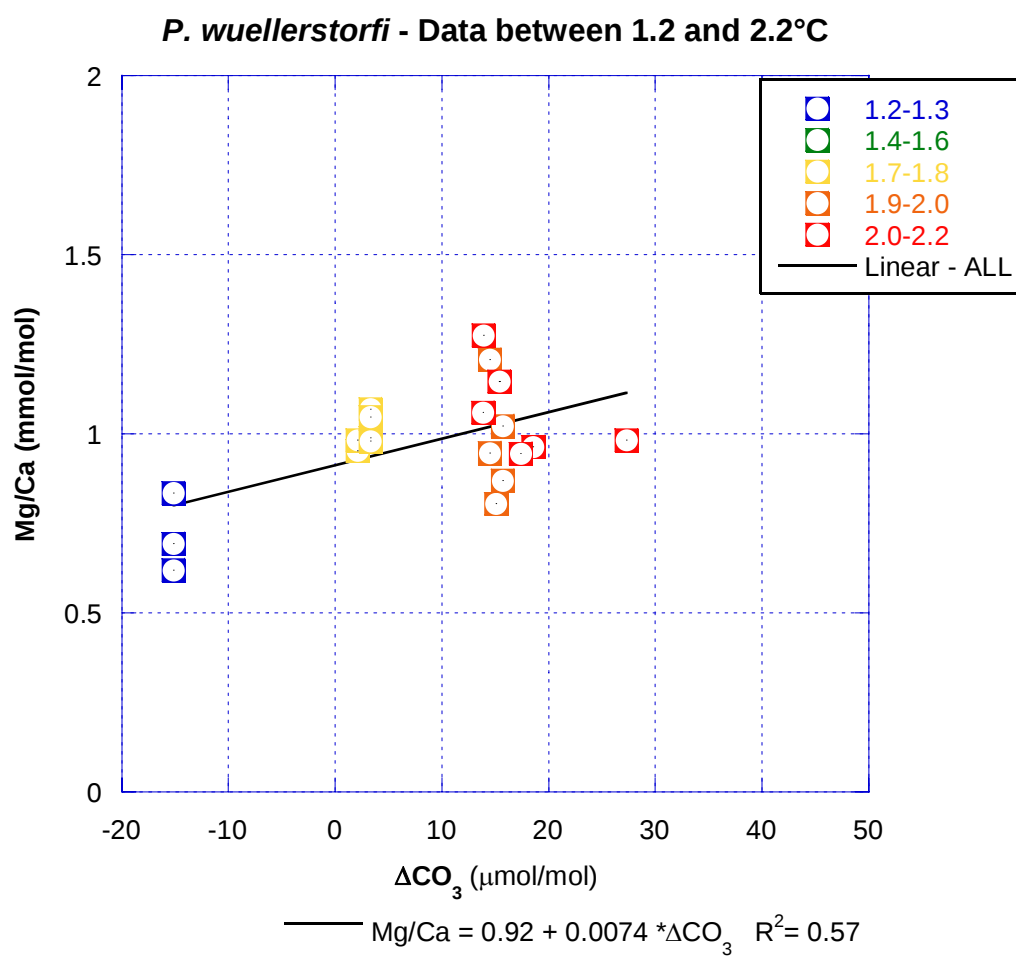


Figure 35: Data from the Gulf of Mexico, Cape Hatteras, New Zealand, Indonesia, and Hawaii sites between 1 and 3°C. Data are color coded by temperature.

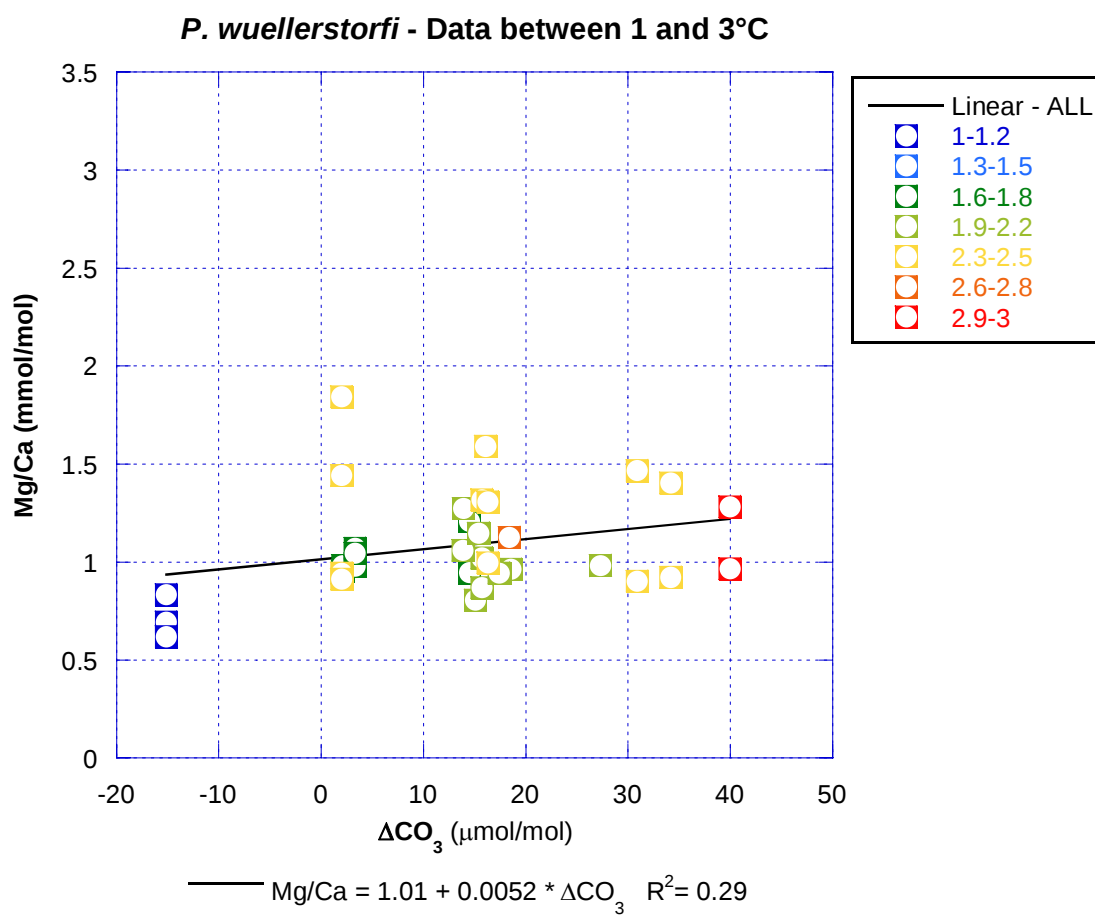


Figure 36: Data from the Gulf of Mexico, Cape Hatteras, New Zealand, Indonesia, and Hawaii sites between 3.5 and 4.5°C. Data are color coded by temperature.

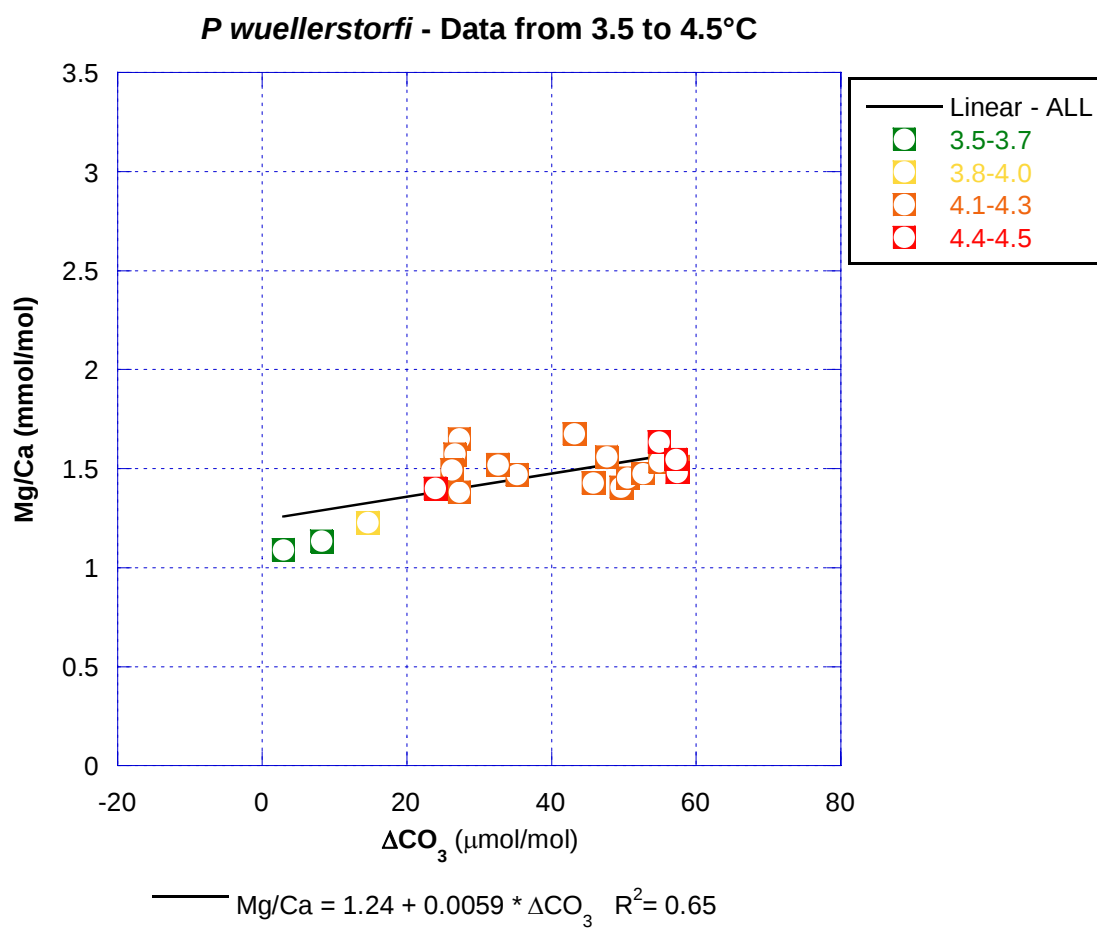


Figure 37: *C. pachyderma* data from the Gulf of Mexico, Cape Hatteras, New Zealand, Indonesia, and Hawaii sites between 3.5 and 4.5°C. Data are color coded by temperature.

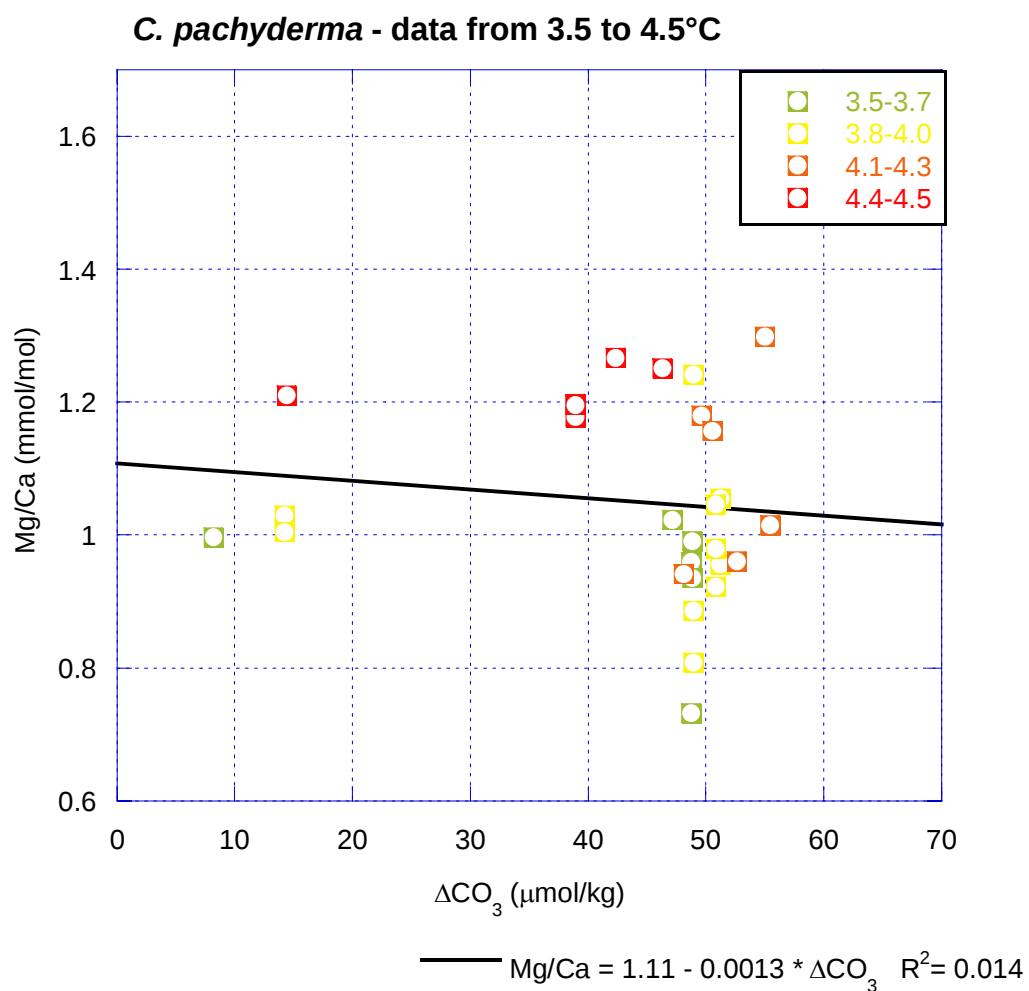


Figure 38: *C. pachyderma* data from the Gulf of Mexico, Cape Hatteras, New Zealand, Indonesia, and Hawaii sites between 7.5 and 9.5°C. Data are color coded by temperature.

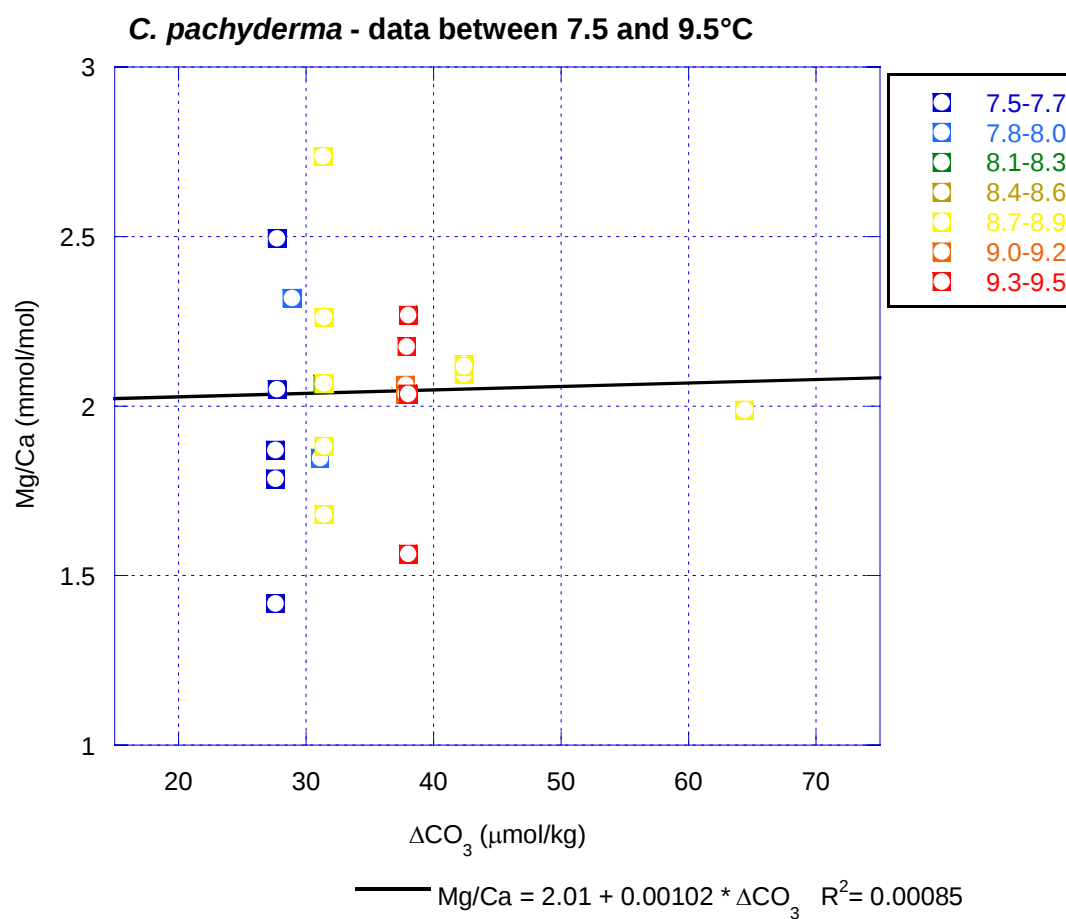


Figure 39: The linear regression through all data from this study with $\Delta\text{CO}_3 > 3\mu\text{mol/kg}$.

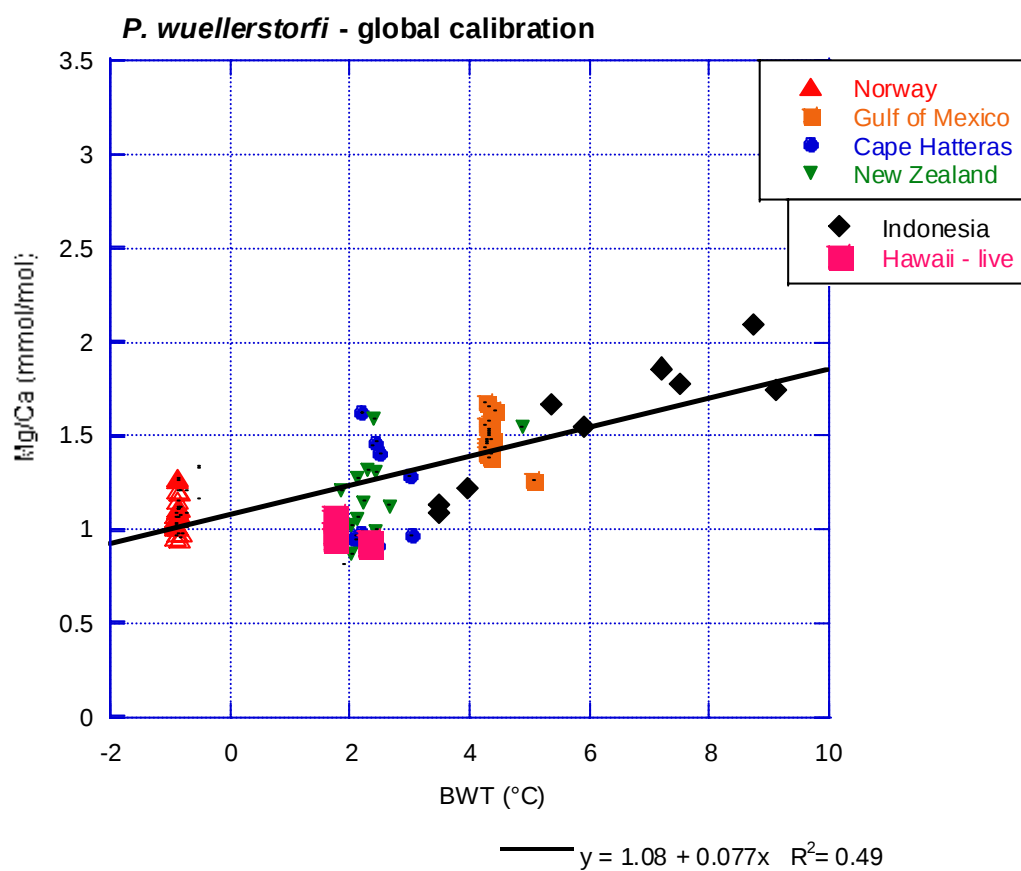


Figure 40: The Mg/Ca- ΔCO_3 relationship as determined from the New Zealand data.

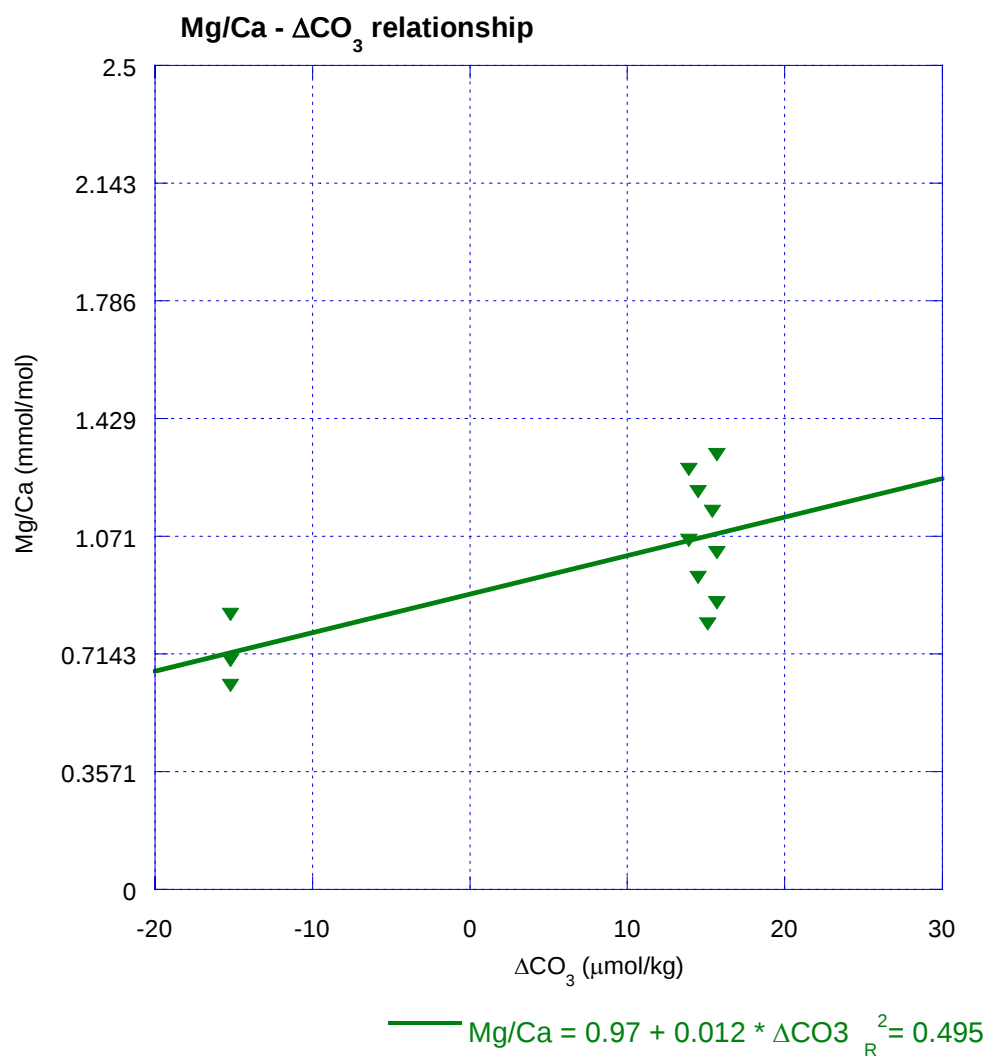


Figure 41: Estimated Mg/Ca versus measured Mg/Ca for the corresponding core. A) Estimated Mg/Ca is calculated by plugging measured BWT and $\Delta[\text{CO}_3^{2-}]$ data into equation 3 ($\text{Mg/Ca} = 1.04 + 0.077 \cdot \text{BWT} + 0.012 \cdot \Delta[\text{CO}_3^{2-}]$). Note that most estimated Mg/Ca is higher than the measured value for that core top. B) Estimated Mg/Ca is calculated by plugging measured BWT and $\Delta[\text{CO}_3^{2-}]$ data into equation 1 ($\text{Mg/Ca} = 1.08 + 0.077 \cdot \text{BWT}$).

A)



B)

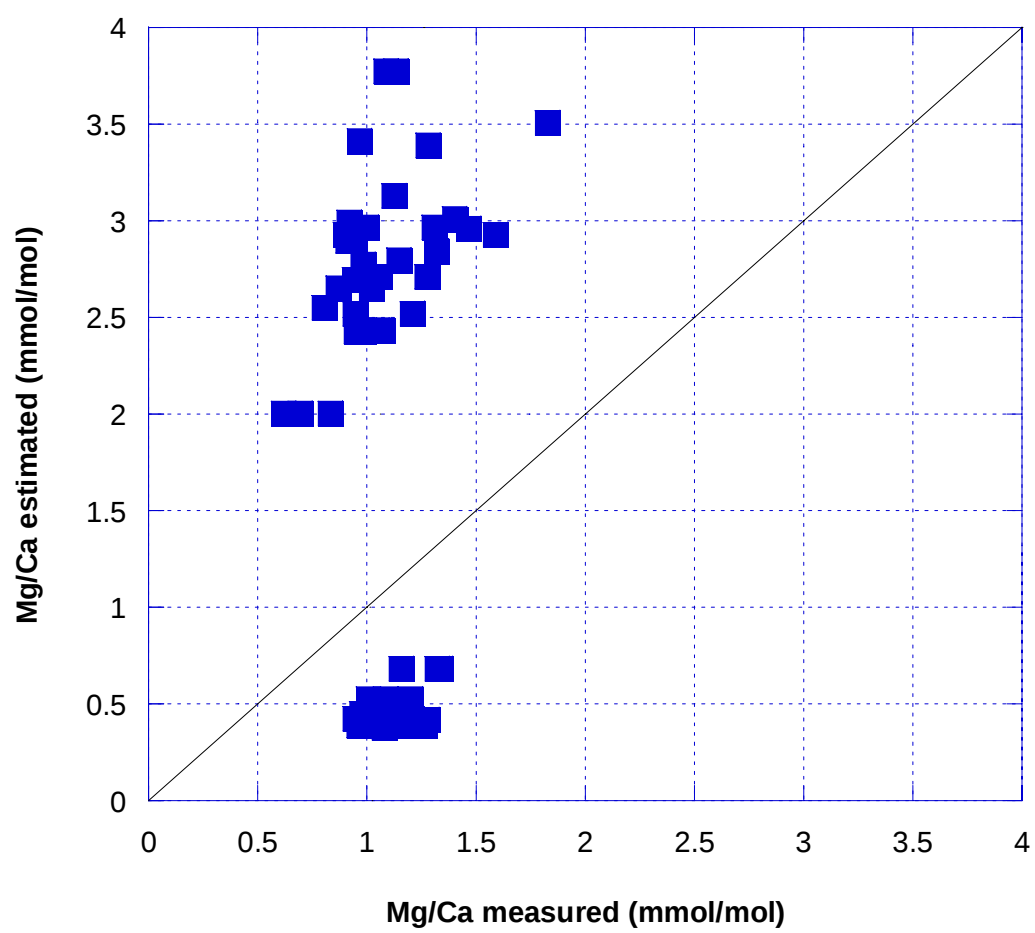


Figure 42: The blue line shows the BWT reconstruction using equation 3 ($\text{Mg/Ca} = 1.04 + 0.077 \cdot \text{BWT} + 0.012 \cdot \Delta[\text{CO}_3^{-2}]$), Mg/Ca data from Martin et al.(2002), and a rough estimate of past $\Delta[\text{CO}_3^{-2}]$ changes (See text). The age to which the test is performed is limited by the assumptions used to estimate $\Delta[\text{CO}_3^{-2}]$ changes. The red line shows the author's original climate reconstruction (Martin et al., 2002).

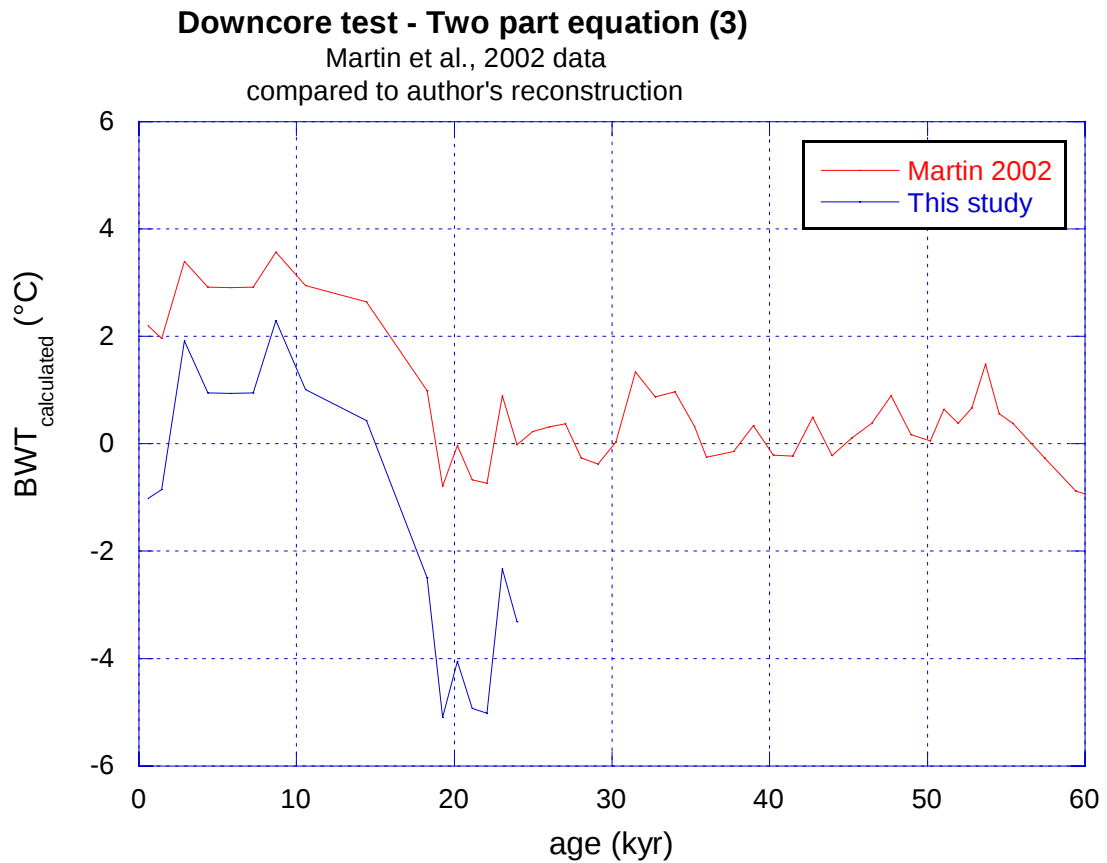


Figure 43: *P. wuellerstorfi* data for this study (Norway, Gulf of Mexico, Cape Hatteras, New Zealand, Indonesia, and Hawaii sites) compared with *P. wuellerstorfi* data from Elderfield et al. (2006).

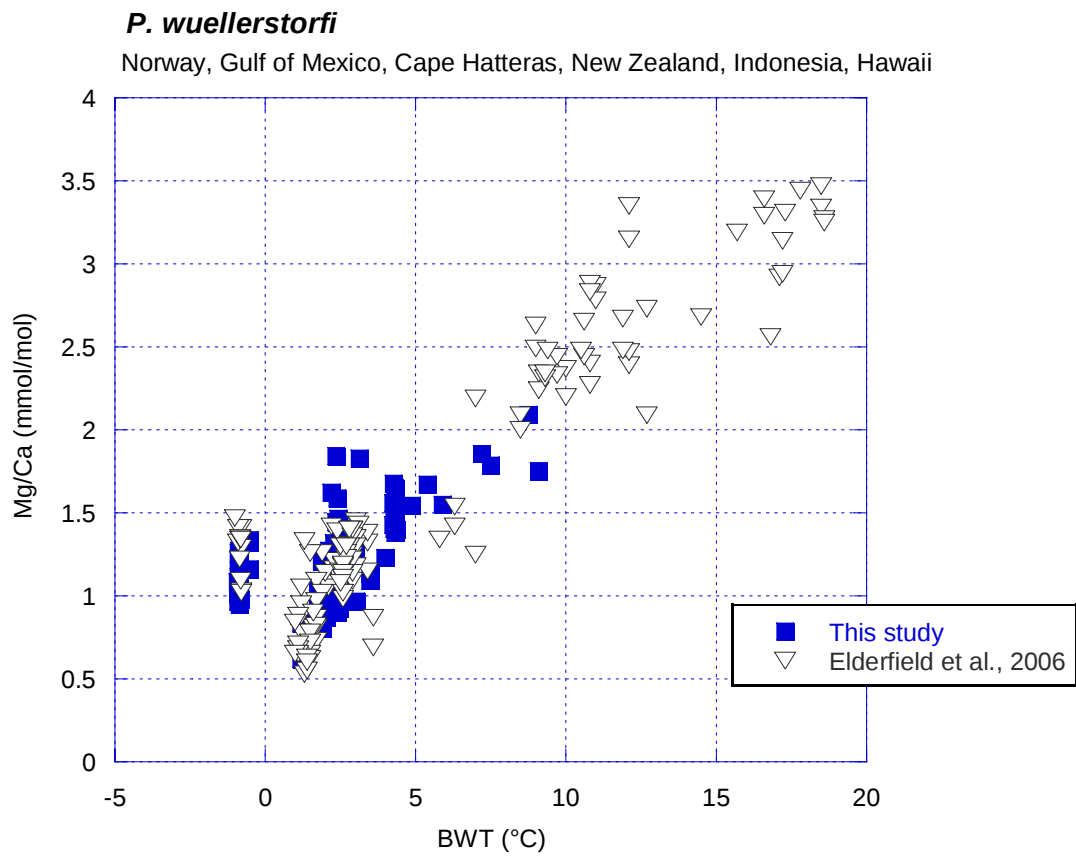


Figure 44: *C. pachyderma* data for this study (Gulf of Mexico and Cape Hatteras sites) compared with *C. pachyderma* data from Marchitto et al. (2007).

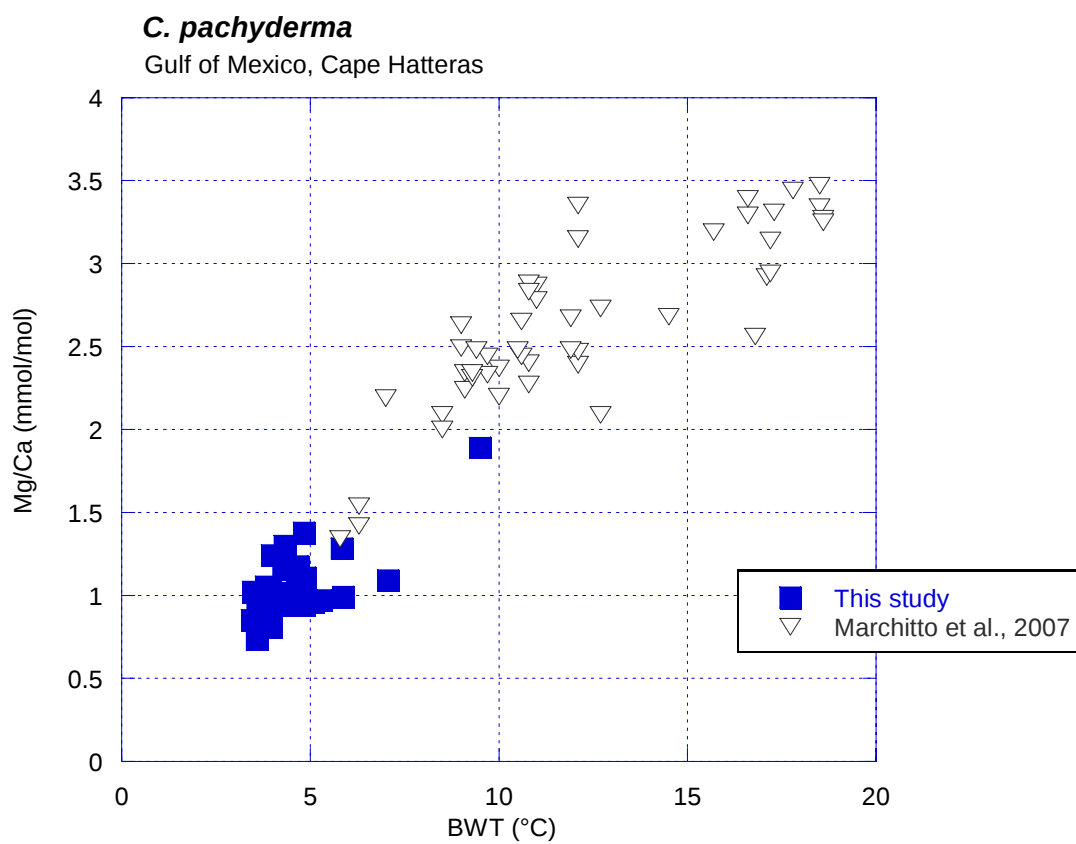


Figure 45: linear and exponential regressions through all *P. wuellerstorfi* and *C. pachyderma* data for all sites (Norway, Gulf of Mexico, Cape Hatteras, New Zealand, Indonesia, and Hawaii).

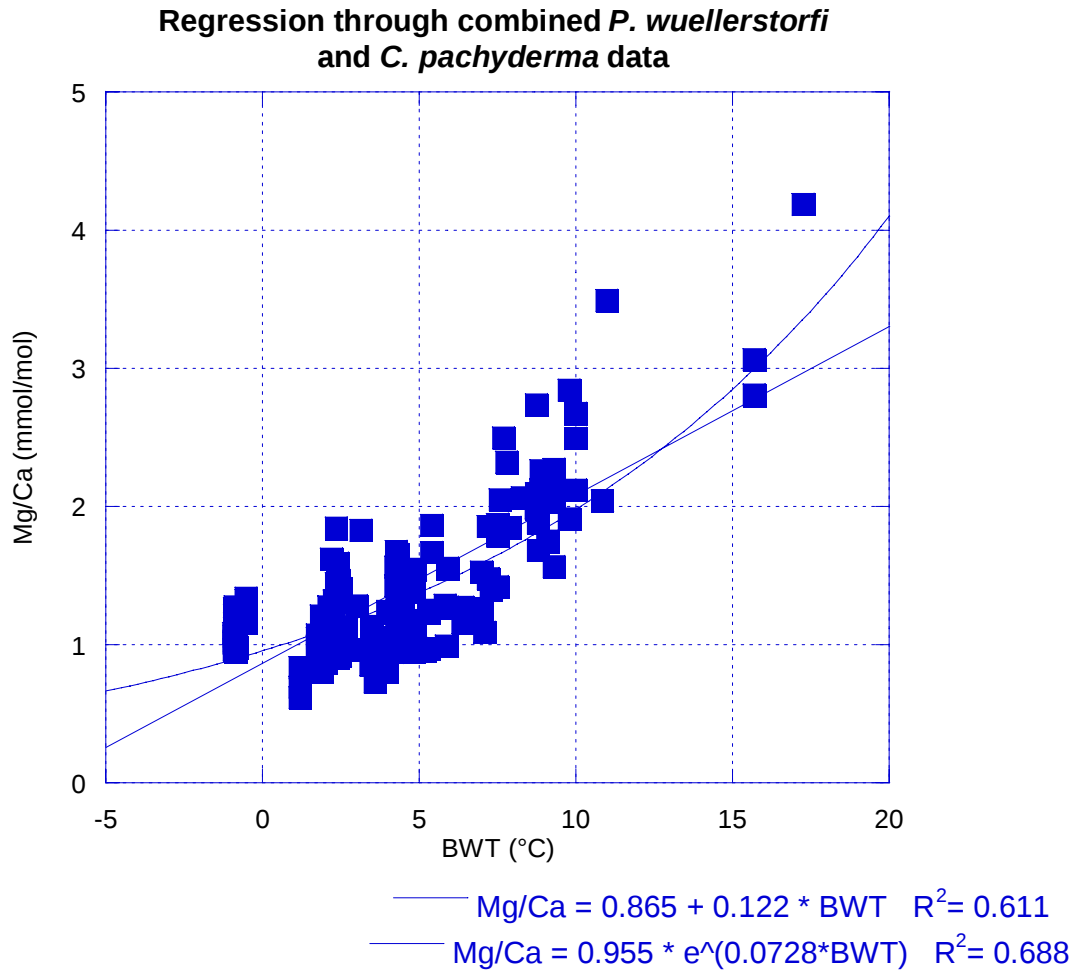


Figure 46: The green line shows the BWT reconstruction using the calibration equation from Elderfield et al. (2006; $\text{Mg/Ca} = 0.82 + 0.056 \cdot \text{BWT} + 0.0087 \cdot \Delta[\text{CO}_3^{-2}]$), Mg/Ca data from Martin et al.(2002), and a rough estimate of past $\Delta[\text{CO}_3^{-2}]$ changes (See text). The age to which the test is performed is limited by the assumptions used to estimate $\Delta[\text{CO}_3^{-2}]$ changes. The red line shows the author's original climate reconstruction (Martin et al., 2002).

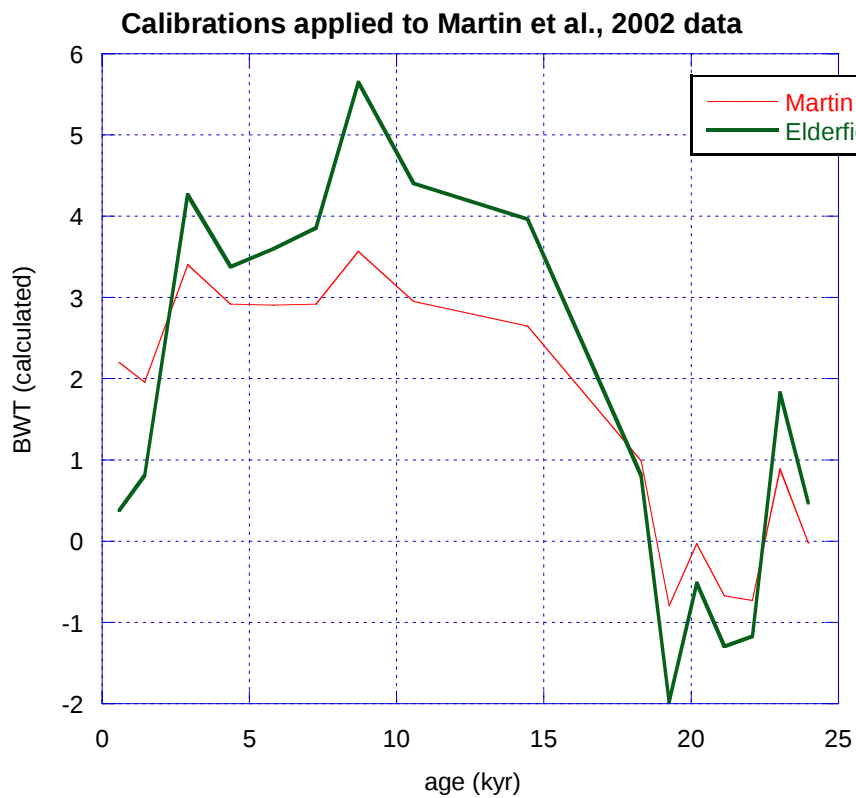
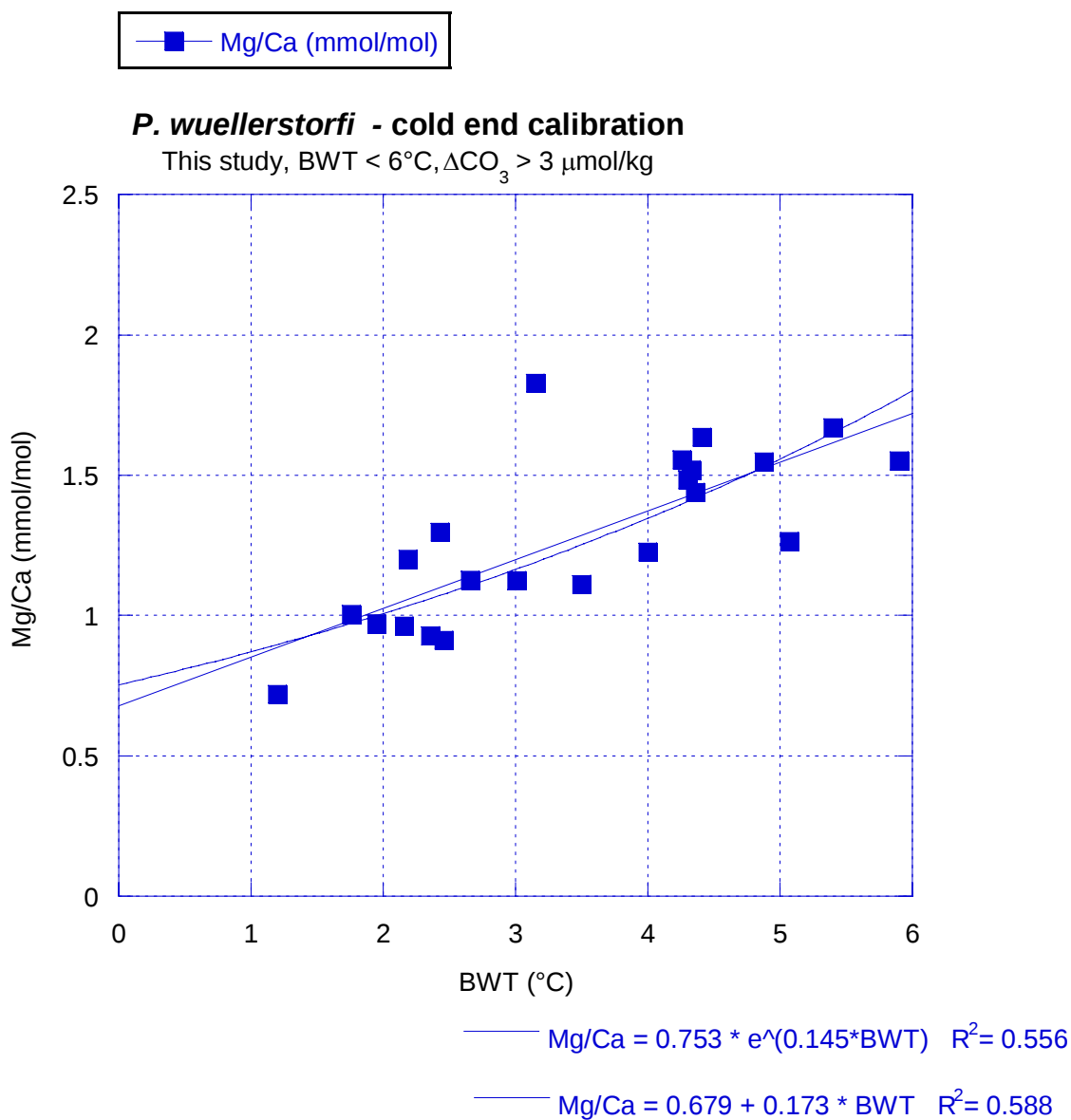


Figure 47: Linear and exponential fit to cold temperature *P. wuellerstorfi* data for the Gulf of Mexico, Cape Hatteras, New Zealand, Indonesia, and Hawaii sites. For purposes of these regressions data are restricted to BWT < 6°C and $\Delta[\text{CO}_3^{2-}] > 0 \text{ } \mu\text{mol/kg}$.



IX. Appendices

Appendix 1: Hydrographic and trace metal data for Norway, Gulf of Mexico, Cape Hatteras, and New Zealand.

Region	Sample	Size	depth (m)	BWT (°C)	CO ₃ μmol/mol	ΔCO ₃ μmol/mol	Mg/Ca mmol/mol	Sr/Ca mmol/mol
<i>P.wueller.</i>								
Norway	MC-14-B	>150μm	965	-0.5	100.0	44.6	1.16	1.46
Norway	MC-14	>150μm	965	-0.5	100.0	44.6	1.34	1.34
Norway	MC-14-B	>150μm	965	-0.5	100.0	44.6	1.32	1.47
Norway	MC-11-B	>150μm	1285	-0.7	100.9	42.5	1.09	1.43
Norway	MC-11-B	>150μm	1285	-0.7	100.9	42.5	1.01	1.45
Norway	MC-11	>150μm	1285	-0.7	100.9	42.5	1.20	1.43
Norway	MC-50-B	>150μm	1906	-0.9	99.4	34.8	1.26	1.38
Norway	MC-50-B	>150μm	1906	-0.9	99.4	34.8	1.15	1.34
Norway	MC-50-B	>150μm	1906	-0.9	99.4	34.8	1.12	1.38
Norway	MC-50	>150μm	1906	-0.9	99.4	34.8	1.21	1.34
Norway	MC-50	>150μm	1906	-0.8	99.5	34.8	1.12	1.36
Norway	MC-48	>150μm	2402	-0.9	99.2	29.0	1.08	1.31
Norway	MC-48	>150μm	2402	-0.9	99.2	29.0	1.27	1.30
Norway	MC-21-B	>150μm	2640	-0.9	98.0	25.9	1.03	1.28
Norway	MC-21-B	>150μm	2640	-0.9	98.0	25.9	1.01	1.27
Norway	MC-21-B	>150μm	2640	-0.9	98.0	25.9	1.06	1.33
Norway	MC-21-B	>150μm	2640	-0.9	98.0	25.9	1.01	1.28
Norway	MC-21	>150μm	2640	-0.9	98.0	25.9	0.96	1.30
Norway	MC-45	>150μm	2799	-0.9	97.6	22.8	1.07	1.28
Norway	MC-45	>150μm	2799	-0.9	97.2	22.8	1.01	1.28
Norway	MC-45	>150μm	2799	-0.9	97.6	22.8	0.95	1.30
Norway	MC-27-C	>150μm	3035	-0.9	95.9	18.3	1.10	1.23
Norway	MC-27-C	>150μm	3035	-0.9	95.9	18.3	1.06	1.25
Norway	MC-24-B	>150μm	3036	-0.9	95.9	18.2	1.01	1.23
Norway	MC-24-B	>150μm	3036	-0.9	95.9	18.2	0.98	1.26
Norway	MC-24	>150μm	3036	-0.9	95.9	18.2	1.10	1.23
Norway	MC-27	>150μm	3341	-0.8	95.6	14.0	1.20	1.22
Norway	MC-27	>150μm	3341	-0.8	95.7	14.0	0.98	1.23
Cape Hatteras	MC 14	>150μm	2602	3.0	111.9	39.9	1.28	1.26

Cape Hatteras	MC-14	>150µm	2602	3.0	111.9	39.9	0.97	1.16
Cape Hatteras	MC 8	>150µm	2997	2.5	110.8	34.1	0.92	1.25
Cape Hatteras	MC-8	>150µm	2997	2.5	110.8	34.1	1.40	0.86
Cape Hatteras	MC 76	>150µm	3065	2.4	108.4	30.9	0.90	1.26
Cape Hatteras	MC-76	>150µm	3065	2.4	108.4	30.9	1.47	0.86
Cape Hatteras	MC 5	>150µm	3382	2.2	108.8	27.3	0.98	1.21
Cape Hatteras	MC 4	>150µm	3865	2.1	106.6	18.5	0.96	1.17
Cape Hatteras	MC-4	>150µm	3865	2.2	106.6	18.5	2.18	1.00
Cape Hatteras	MC 1	>150µm	3979	2.1	107.1	17.4	0.95	1.19
Cape Hatteras	MC-1	>150µm	3979	2.2	107.1	17.4	1.62	0.90
New Zealand	MC-86	>150µm	663	4.9	110.0	57.2	1.55	1.34
New Zealand	MC-76	>150µm	1165	3.2	79.5	22.3	1.83	1.36
New Zealand	MC-133	>150µm	1407	2.7	77.8	18.4	1.13	1.32
New Zealand	MC-82	>150µm	1623	2.5	77.8	16.3	1.00	1.31
New Zealand	MC-82	>150µm	1623	2.5	77.8	16.3	1.31	
New Zealand	MC-22	>150µm	1682	2.4	78.2	16.1	1.59	1.36
New Zealand	MC-92	>150µm	1818	2.3	79.2	15.7	1.32	1.04
New Zealand	MC-92	>150µm	1818	2.2	79.7	15.4	1.15	1.31
New Zealand	MC-102	>150µm	2055	2.1	79.8	13.9	1.28	0.99
New Zealand	MC-102	>150µm	2055	2.1	79.8	13.9	1.06	1.32
New Zealand	MC-118	>150µm	2252	2.0	83.8	15.7	0.87	1.29
New Zealand	MC-118	>150µm	2252	2.0	81.5	15.7	1.02	1.30
New Zealand	MC-26	>150µm	2418	1.9	85.0	15.1	0.81	1.28
New Zealand	MC-106	>150µm	2472	1.9	85.0	14.5	1.21	1.22
New Zealand	MC-106	>150µm	2472	1.9	82.5	14.5	0.95	1.24
New Zealand	MC-38	>150µm	4375	1.2	80.4	-15.2	0.69	1.15
New Zealand	MC-114	>150µm	4375	1.2	80.7	-15.2	0.83	1.21
New Zealand	MC-38	>150µm	4375	1.2	80.7	-15.2	0.62	1.15
Gulf of	S36-3	>150µm	1026	5.1	106.4	50.5	1.26	1.33

Mexico								
Gulf of Mexico	RW3-4	>150µm	1330	4.4	113.6	54.9	1.64	1.35
Gulf of Mexico	MT4-4	>150µm	1402	4.4	116.7	57.3	1.48	1.34
Gulf of Mexico	W4-5	>150µm	1406	4.3	116.9	57.5	1.51	1.36
Gulf of Mexico	C4-5	>150µm	1470	4.3	115.0	55.0	1.54	1.36
Gulf of Mexico	NB2-5	>150µm	1530	4.3	113.2	52.6	1.48	1.36
Gulf of Mexico	RW4-2	>150µm	1580	4.3	111.6	50.5	1.45	1.35
Gulf of Mexico	RW5-3	>150µm	1620	4.3	111.1	49.6	1.41	1.30
Gulf of Mexico	NB3-2a	>150µm	1875	4.3	111.7	47.6	1.56	1.25
Gulf of Mexico	NB4-2	>150µm	2050	4.3	111.6	45.7	1.43	1.28
Gulf of Mexico	MT5-1	>150µm	2275	4.3	111.4	43.1	1.68	1.29
Gulf of Mexico	S38-4	>150µm	2630	4.3	107.5	35.2	1.47	1.30
Gulf of Mexico	MT6-5	>150µm	2743	4.3	106.2	32.6	1.52	1.26
Gulf of Mexico	W5-4	>150µm	2745	4.3	106.2	32.6	1.52	1.26
Gulf of Mexico	S40-3	>150µm	2972	4.3	103.6	27.3	1.65	1.26
Gulf of Mexico	S41-1	>150µm	2974	4.3	103.6	27.2	1.38	1.26
Gulf of Mexico	S39-2	>150µm	3000	4.3	103.3	26.6	1.57	1.25
Gulf of Mexico	RW6-1	>150µm	3015	4.3	103.1	26.2	1.50	1.26
Gulf of Mexico	W6-3	>150µm	3150	4.3	102.5	23.9	1.40	1.21
C. <i>pachyderma</i>								
Cape Hatteras	MC 63	>150µm	830	5.8	90.8	36.6	1.28	1.19
Cape Hatteras	MC-63	>150µm	830	5.9	90.8	36.6	0.99	1.22
Cape Hatteras	MC 30	>150µm	1003	4.8	94.6	38.9	0.94	1.20
Cape Hatteras	MC-30	>150µm	1003	4.9	94.6	38.9	0.98	1.23
Cape Hatteras	MC 31	>150µm	1005	4.8	94.6	38.9	1.38	1.18
Cape Hatteras	MC-31	>150µm	1005	4.9	94.6	38.9	1.11	1.29
Cape Hatteras	MC 31	>150µm	1005	4.8	94.6	38.9	1.05	1.20
Cape Hatteras	MC-41	>150µm	1069	4.7	98.6	42.3	1.18	1.27
Cape Hatteras	MC-39	>150µm	1073	4.7	102.6	46.3	1.03	1.25
Cape	MC-59	>150µm	1308	4.3	106.6	48.1	0.94	1.18

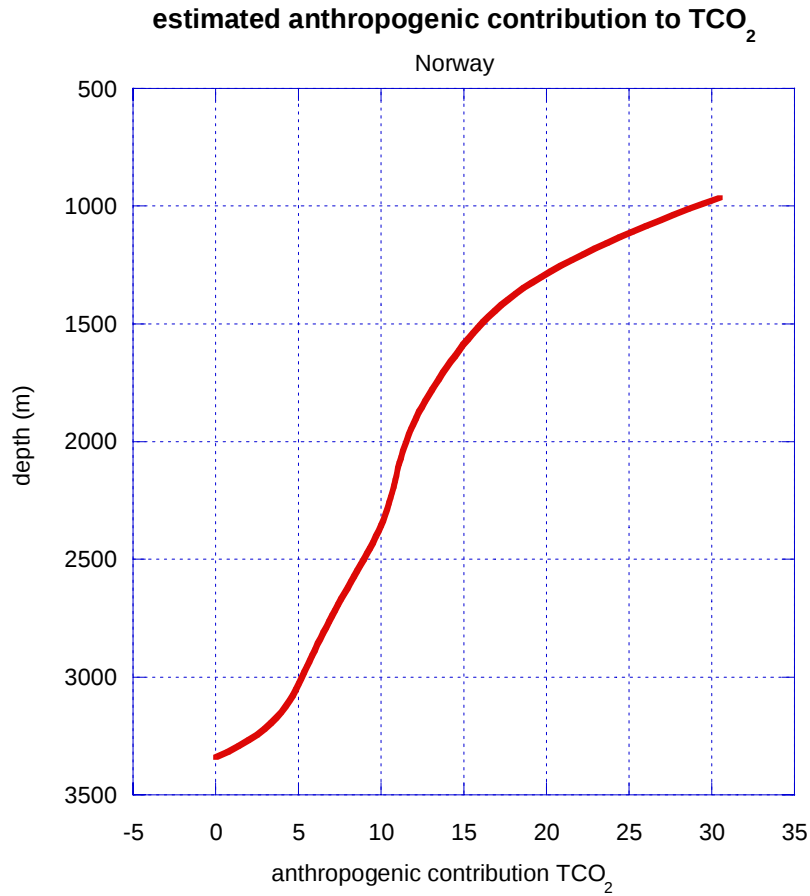
Hatteras								
Cape Hatteras	MC 59	>150µm	1388	4.0	108.2	48.9	0.81	1.20
Cape Hatteras	MC-59	>150µm	1388	4.0	108.2	48.9	1.24	1.17
Cape Hatteras	MC 59	>150µm	1388	4.0	108.2	48.9	0.89	1.20
Cape Hatteras	MC 25	>150µm	1443	3.9	110.6	50.8	0.98	1.18
Cape Hatteras	MC-25	>150µm	1443	3.9	110.6	50.8	1.05	1.18
Cape Hatteras	MC 25	>150µm	1443	3.9	110.6	50.8	0.92	1.14
Cape Hatteras	MC-43	>150µm	1506	3.8	111.6	51.2	1.06	1.16
Cape Hatteras	MC 43	>150µm	1506	3.8	111.6	51.2	0.96	1.17
Cape Hatteras	MC-22	>150µm	1800	3.6	112.1	48.8	0.94	1.18
Cape Hatteras	MC-22	>150µm	1800	3.6	112.1	48.8	0.99	1.14
Cape Hatteras	MC 20	>150µm	1815	3.6	112.1	48.7	0.73	1.15
Cape Hatteras	MC-20	>150µm	1815	3.6	112.1	48.7	0.96	1.20
Cape Hatteras	MC-67	>150µm	1956	3.5	112.0	47.1	1.02	1.17
Cape Hatteras	MC-46	>150µm	2000	3.5	112.0	46.6	0.85	1.16
Gulf of Mexico	MT1-5	>150µm	481	9.5	180.9	129.7	1.89	1.17
Gulf of Mexico	MT2-2	>150µm	677	7.1	141.5	88.6	1.09	1.13
Gulf of Mexico	MT3-5	>150µm	985	5.3	107.7	52.1	0.97	1.24
Gulf of Mexico	S36-3	>150µm	1026	5.1	106.4	50.5	0.96	1.18
Gulf of Mexico	C7-3	>150µm	1066	4.9	105.8	49.5	0.97	1.27
Gulf of Mexico	W4-5	>150µm	1460	4.3	115.3	55.4	1.02	1.20
Gulf of Mexico	C4-5	>150µm	1470	4.3	115.0	55.0	1.30	1.22
Gulf of Mexico	NB2-5	>150µm	1530	4.3	113.2	52.6	0.96	1.22
Gulf of Mexico	RW4-2	>150µm	1580	4.3	111.6	50.5	1.16	1.24
Gulf of Mexico	RW5-3	>150µm	1620	4.3	111.1	49.6	1.18	1.25
O.								
<i>umbonatus</i>								
Cape Hatteras	MC-47	>150µm	2000	3.5	112.0	46.6	0.99	1.17
Cape Hatteras	MC-16	>150µm	2214	3.4	111.9	44.3	1.03	1.18
Cape Hatteras	MC-14	>150µm	2602	3.0	111.9	39.9	1.32	0.84

Cape Hatteras	MC-8	>150µm	2997	2.5	110.8	34.1	1.32	0.85
Cape Hatteras	MC-76	>150µm	3065	2.4	108.4	30.9	1.74	0.88
Cape Hatteras	MC-5	>150µm	3382	2.2	108.8	27.3	1.76	0.91
Cape Hatteras	MC-4	>150µm	3865	2.2	106.6	18.5	2.53	1.08
Cape Hatteras	MC-1	>150µm	3979	2.2	107.1	17.4	0.94	1.20
Cape Hatteras	MC-1	>150µm	3979	2.2	107.1	17.4	0.91	1.17
Norway	MC-50	>150µm	1906	-0.8	99.5	34.8	1.62	0.92
Norway	MC-21	>150µm	2640	-0.9	98.8	25.9	1.27	0.86
Norway	MC-45	>150µm	2799	-0.9	97.6	22.8	1.27	0.86
Norway	MC-24	>150µm	3036	-0.8	96.0	18.2	1.44	0.84
Norway	MC-27	>150µm	3341	-0.8	95.7	14.0	1.36	0.83
Norway	MC-27	>150µm	3341	-0.8	95.7	14.0	1.42	0.84
Norway	MC-31	>150µm	3873	-0.8	95.6	13.7	1.22	0.77
Norway	MC-35	>150µm	3924	-0.8	95.6	13.7	1.21	0.77
New Zealand	MC-76	>150µm	1165	3.2	79.5	22.3	1.88	0.99
New Zealand	MC-82	>150µm	1623	2.5	77.8	16.3	1.57	0.94
New Zealand	MC-22	>150µm	1682	2.4	78.2	16.1	1.66	0.94
New Zealand	MC-92	>150µm	1818	2.3	79.2	15.7	1.56	0.94
New Zealand	MC-102	>150µm	2055	2.1	80.4		1.27	0.91
New Zealand	MC-118	>150µm	2252	2.0	83.8	15.7	1.41	0.89
New Zealand	MC-26	>150µm	2418	1.9	82.3	15.1	1.41	0.93
New Zealand	MC-106	>150µm	2472	1.9	82.5	14.5	1.58	0.91
New Zealand	MC-114	>150µm	3295	1.2	82.9	0.9	1.32	0.85
New Zealand	MC-38	>150µm	4375	1.2	80.7	-15.2	0.85	0.80

Appendix 2: Hydrographic properties for sites from previous studies (Indonesia, Hawaii). See Rosenthal et al., 1997 and Lear et al., 2002.

Site	Core	Water depth (m)	BWT (°C)	Salinity	[CO ₃ ⁻²] (μmol/kg)	ΔCO ₃ (μmol/kg)
Indonesia	81 MC	361	9.1	34.45	87.0	36.7
Indonesia	16 MC	409	8.8	34.47	82.0	31.3
Indonesia	33 MC	505	7.5	34.51	79.0	27.6
Indonesia	88 MC	532	7.2	34.53	78.0	26.3
Indonesia	140 MC	755	5.9	34.55	73.0	19.5
Indonesia	24 MC	832	5.4	34.56	71.0	16.8
Indonesia	22 MC	1189	4	34.58	72.0	14.6
Indonesia	26 MC	1943	3.5	34.60	73.0	8.2
Indonesia	86 MC	2442	3.5	34.60	73.0	2.9
Hawaii	138 MC	1775	2.4	34.62	65.0	2.0
Hawaii	137 MC	2578	1.8	34.62	75.0	3.3
Hawaii	42 MC	2583	1.8	34.62	75.0	3.3
Hawaii	135 MC	2682	1.8	34.60	75.0	2.1

Appendix 3: Anthropogenic CO₂ correction.



Estimated anthropogenic contribution to TCO₂, for the Norwegian Sea, after Sabine et al., 2004. Carbonate saturation was corrected as follows:

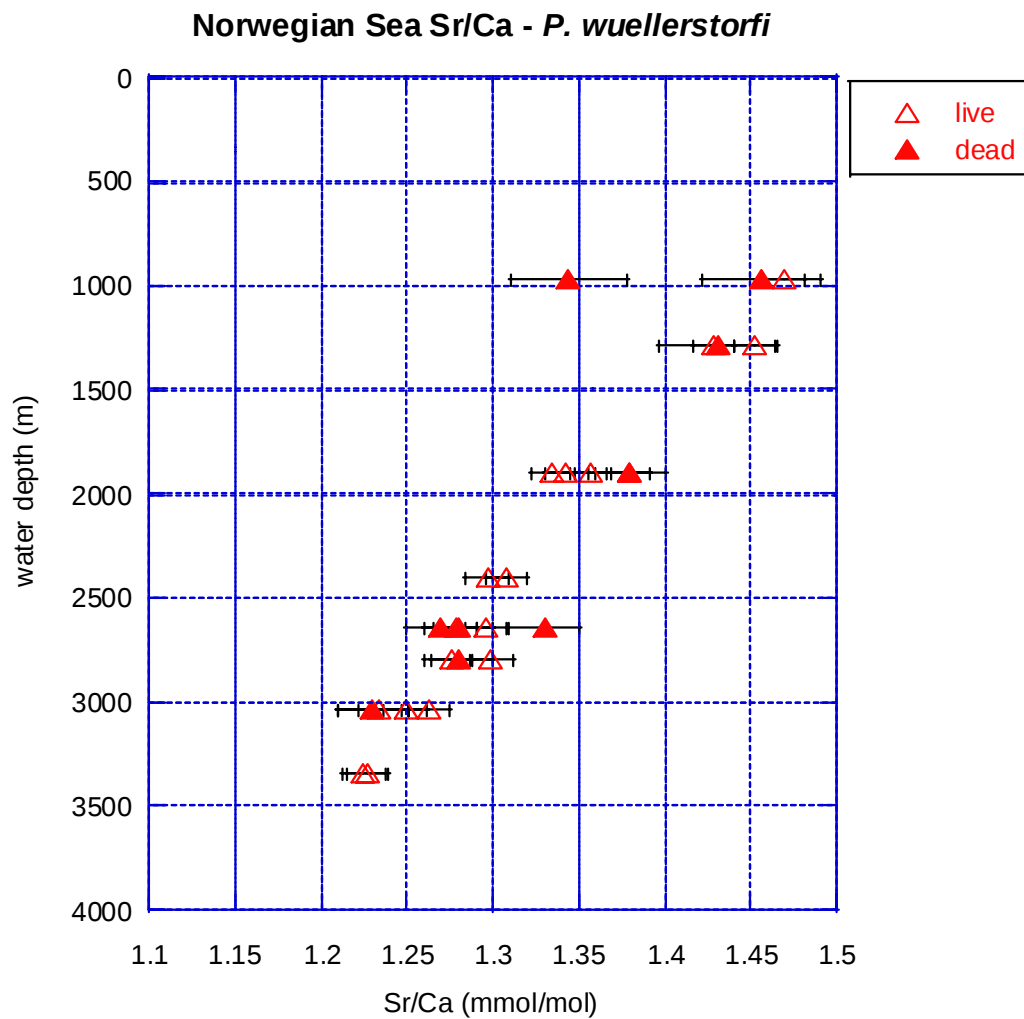
$$\text{TCO}_2 - \text{TCO}_2 \text{ anthropogenic} = \text{TCO}_2 \text{ corrected}$$

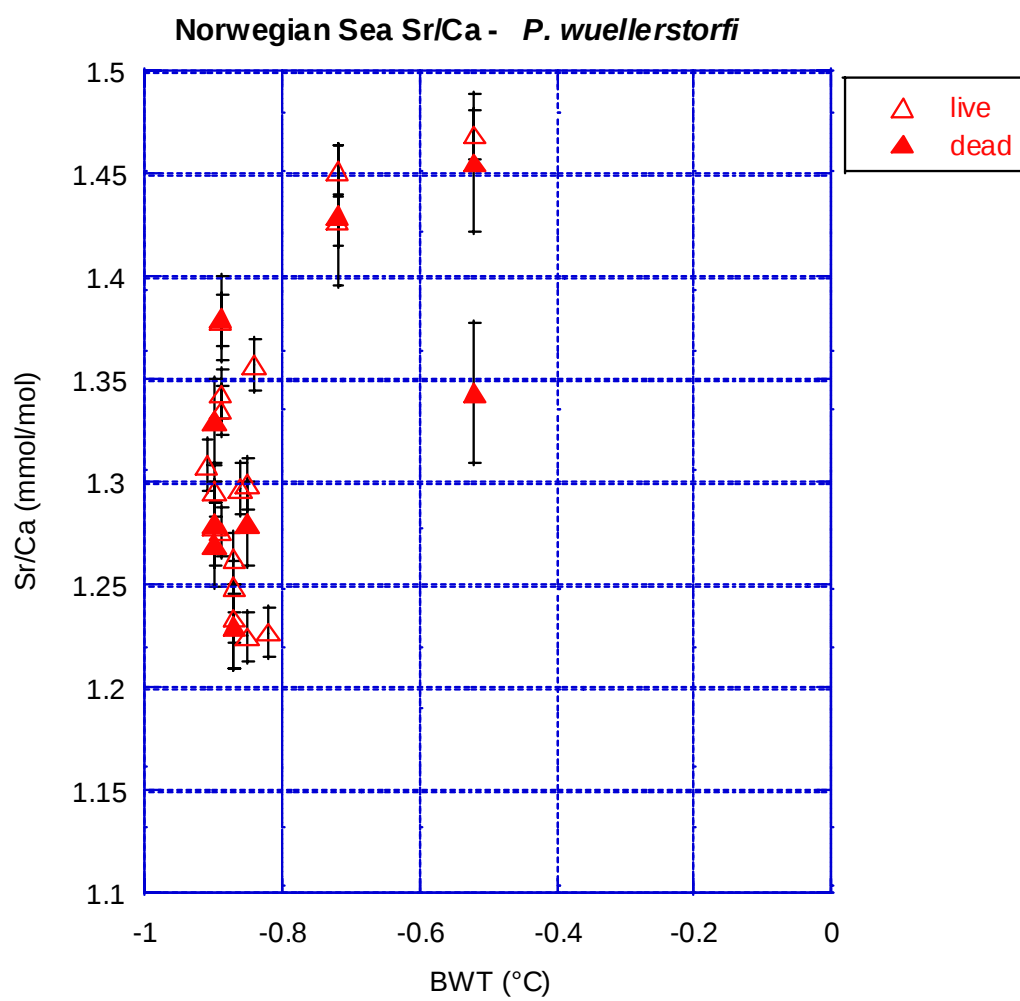
TCO₂ corrected was input into CO2SYS (Lewis and Wallace, 1998) to get corrected [CO₃⁻²].

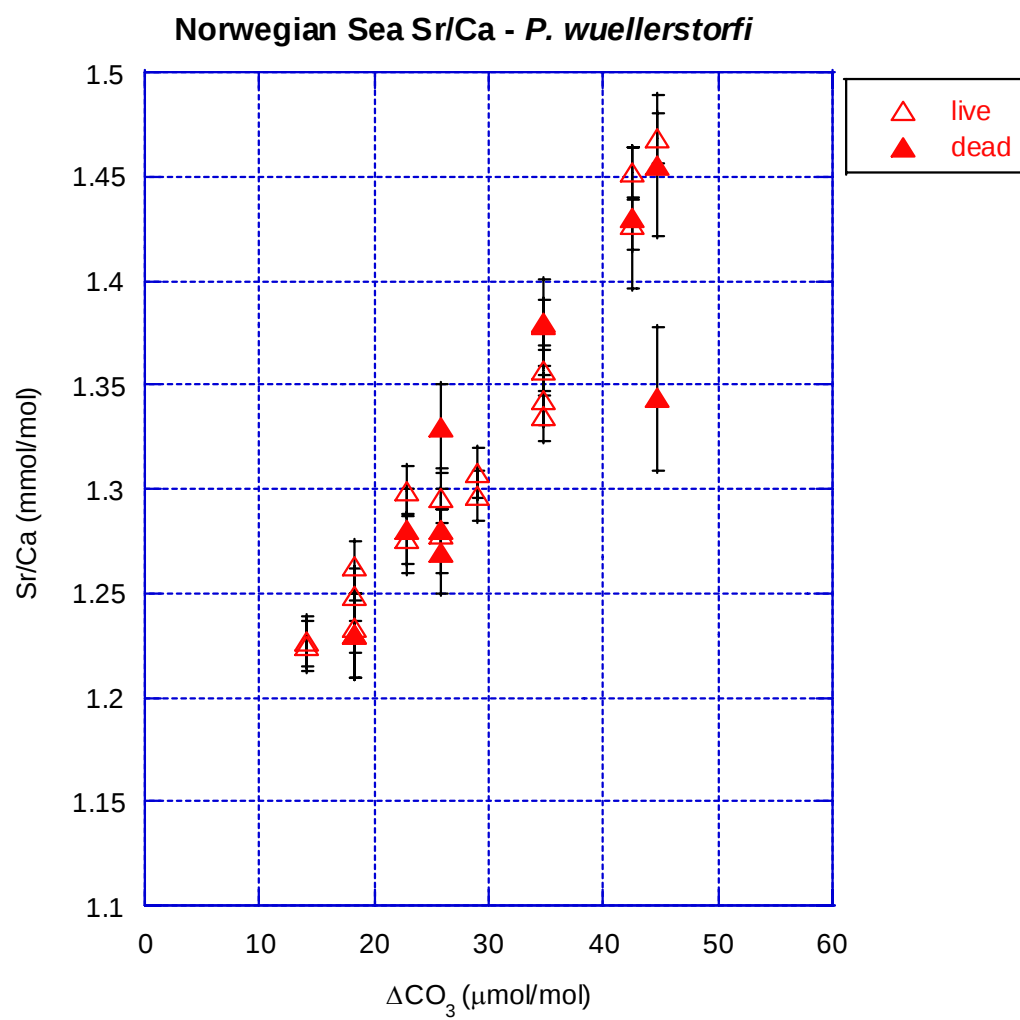
$$\Delta[\text{CO}_3^{-2}] \text{ corrected} = [\text{CO}_3^{-2}]_{\text{corrected}} - [\text{CO}_3^{-2}]_{\text{saturated}}$$

Appendix 4: Additional trace metal data.

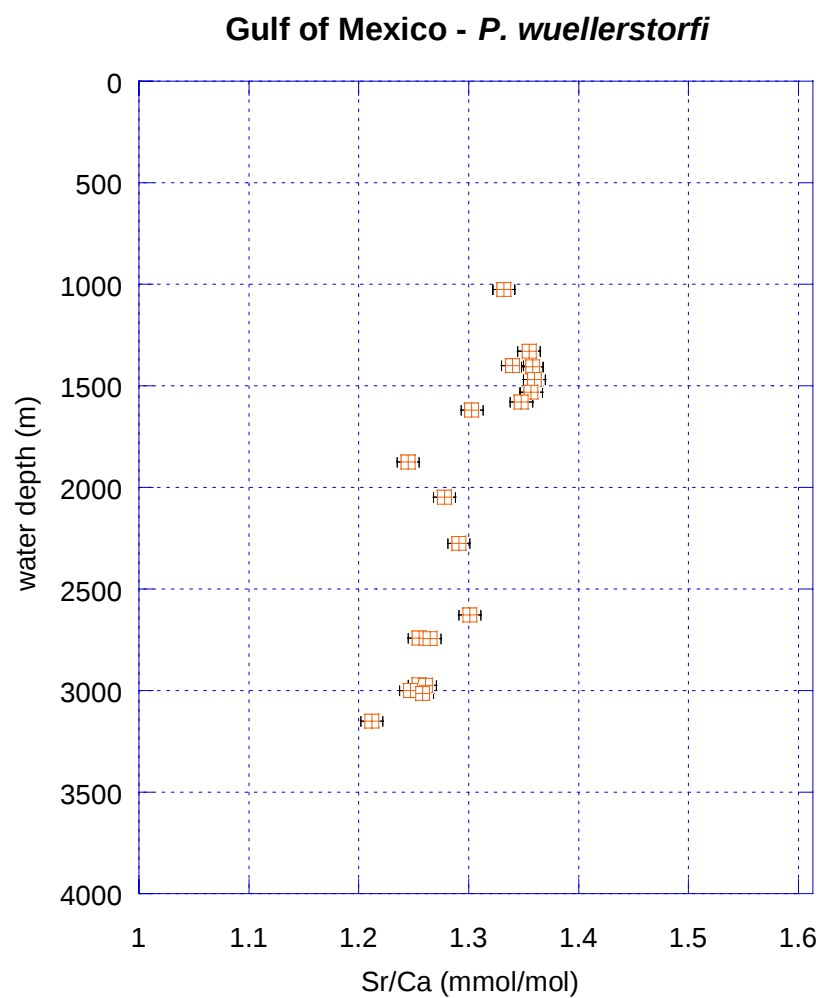
Norwegian Sea Sr/Ca data for live (stained) and dead (unstained) *P. wuellerstorfi*. Error bars show standard error.

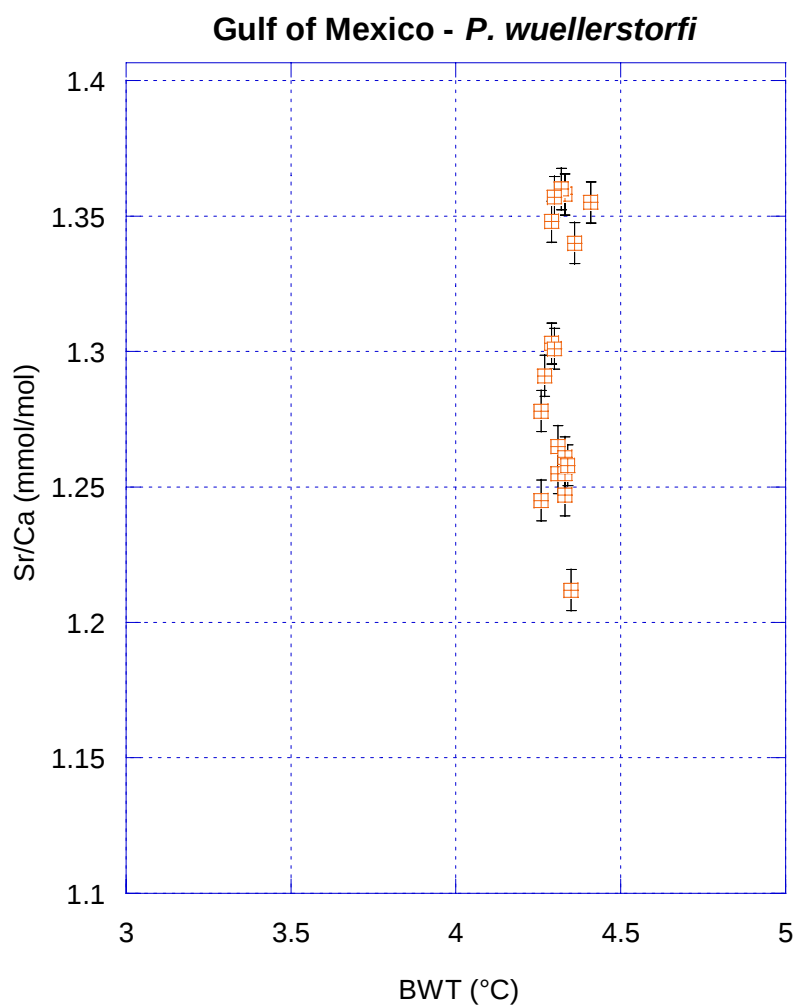


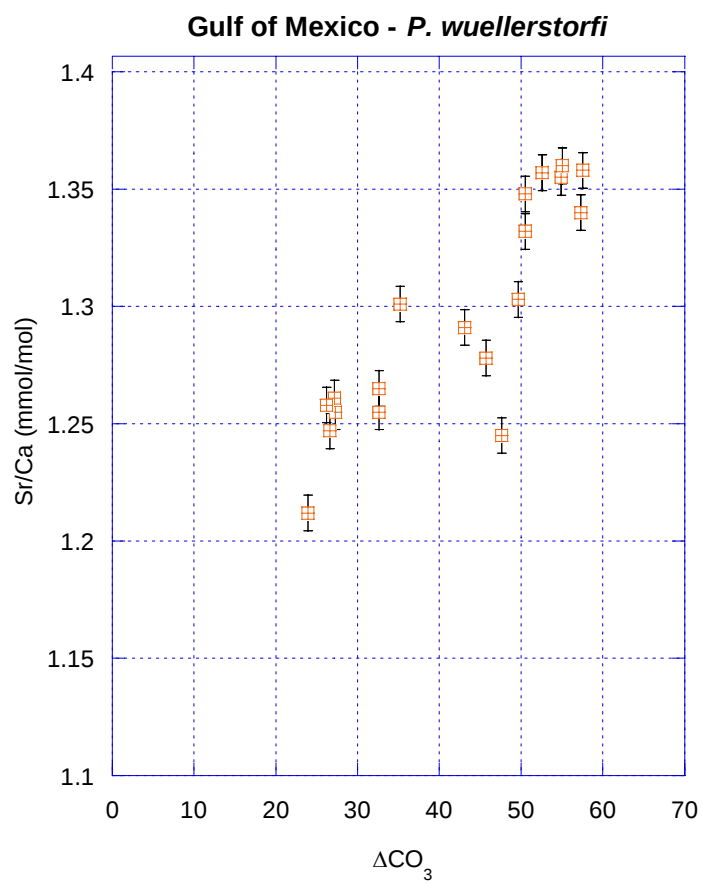




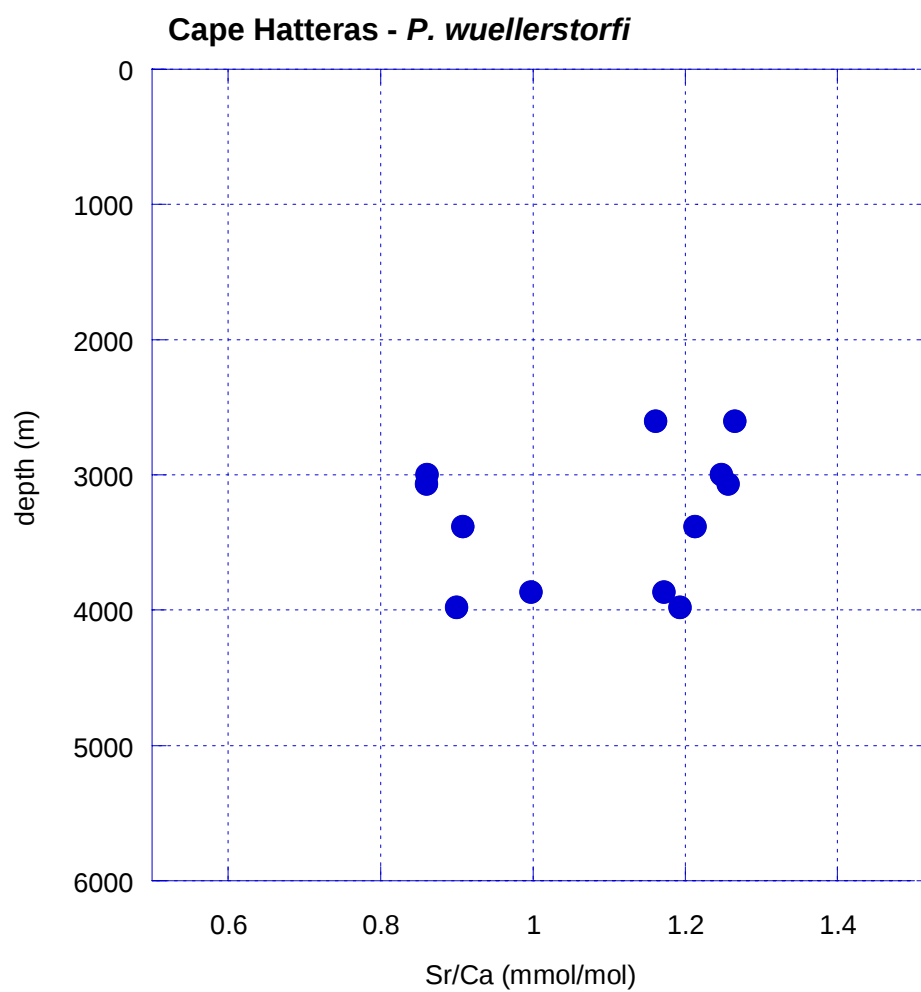
Gulf of Mexico Sr/Ca data for *P. wuellerstorfi*. Error bars show standard error. No live (stained) data is shown; samples were not stained due to long storage time before processing.

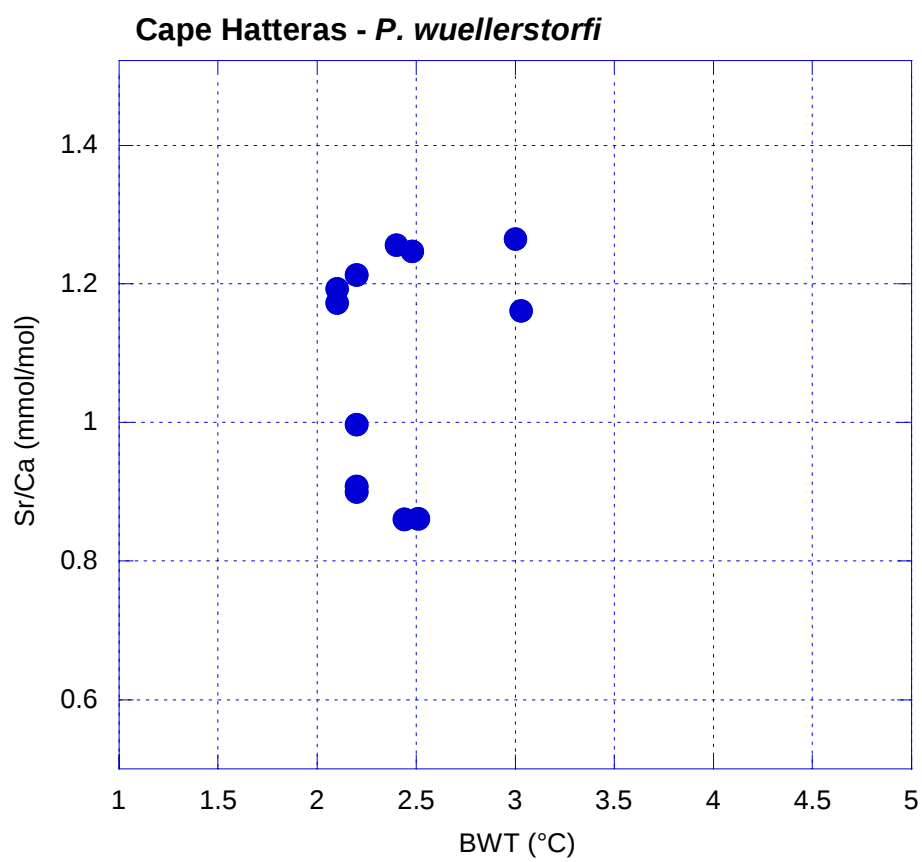


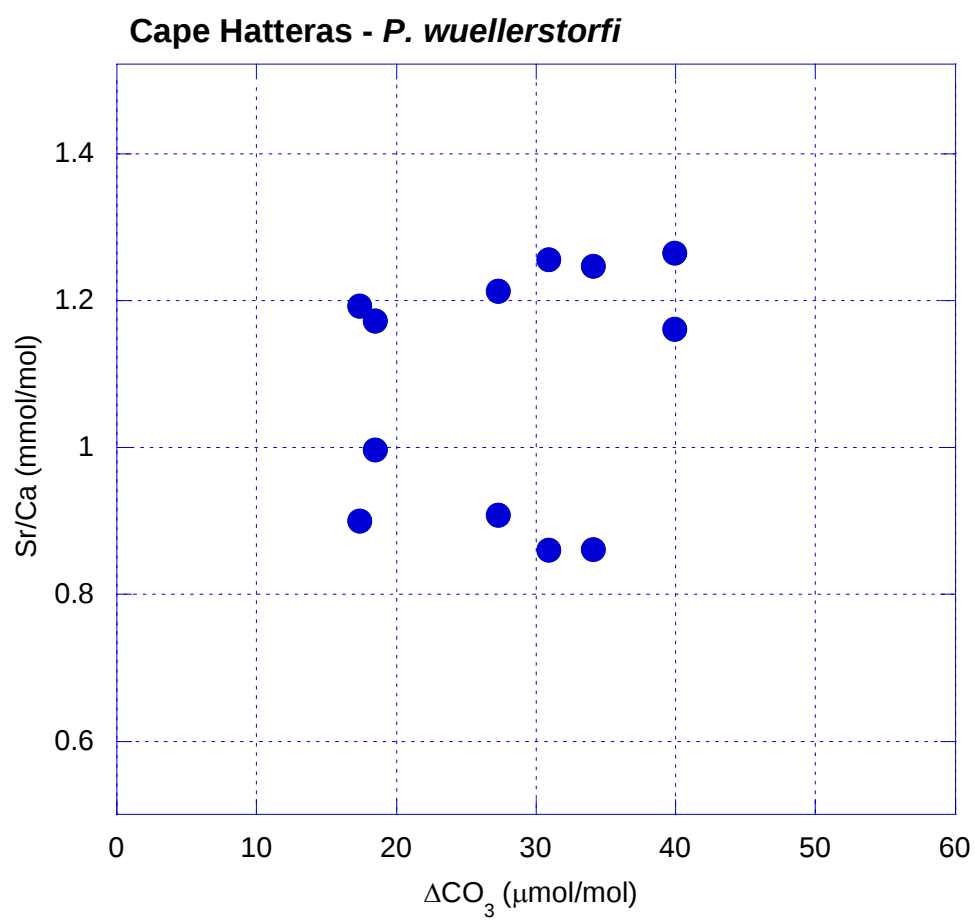




Cape Hatteras Sr/Ca ratios is *P. wuellerstorfi*







New Zealand Sr/Ca ratios in *P. wuellerstorfi*.

