CALIBRATION OF TRACE ELEMENT

PALEOCEANOGRAPHIC PROXIES IN

BENTHIC FORAMINIFERA

by

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Calibration of Trace Element Paleoceanographic Proxies in Benthic Foraminifera

Thesis directed by Assistant Professor Thomas M. Marchitto

The concentrations of certain trace elements incorporated into the calcium carbonate shells of foraminifera can provide information about the seawater in which they live. In order to use these trace element concentrations to reconstruct ocean conditions in the past, they must be calibrated by comparing the chemistry of recently living foraminifera to measurements of seawater properties. This thesis utilizes a set of high quality sediment cores from the Florida Straits to calibrate five trace element paleoceanographic proxies (Mg/Ca, Sr/Ca, Li/Ca, Cd/Ca and Zn/Ca) in five species of benthic foraminifera. The Mg/Ca ratio in the shell increases with increasing seawater temperature, and may also be influenced by the seawater carbonate ion concentration. The Mg/Ca – temperature relationship may be improved by dividing Mg/Ca by Li/Ca. Sr/Ca is complicated by several environmental variables. Cd/Ca is proportionate to seawater Cd, which is correlated with the labile nutrient phosphate. Zn/Ca, in at least one species, is proportionate to seawater Zn, which is correlated with the refractory nutrient silica. The trace element geochemistry of benthic foraminifera provides a valuable set of tools to the field of paleoceanography.

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I. Introduction

Beyond the short instrumental record of the past ~100-150 years, there are no direct measurements of key climate parameters such as ocean temperatures, carbon cycling, biological productivity or ocean circulation. Since gaining knowledge of ocean conditions in the past greatly increases our understanding of the Earth's climate system and gives insight into possible future climate changes, it is necessary to develop methods to obtain information about these ocean characteristics through the use of "proxies". A proxy as described here is a variable that can be measured, and is controlled to some degree by a climate variable of interest. The use of proxies is pervasive and vital to the fields of paleoceanography and paleoclimatology. In general, it is advantageous to obtain multiple proxies for each variable, lending increased confidence in paleoclimate reconstructions.

Much of our knowledge of past ocean conditions has come from the isotope and trace element geochemistry of calcium carbonate secreting protozoa called foraminifera. Foraminifera are ubiquitous in the oceans and live throughout the surface ocean as well as along the seafloor. Their shells are preserved in ocean sediments after they die, allowing analysis of foraminifera that lived in the past. It has long been recognized that the geochemistry of foraminiferal shells contain information about the seawater in which they were growing. The most prevalent proxies obtained from foraminiferal shells have been the stable isotopes of oxygen and carbon, which record information about global ice volume, temperature, carbon cycling, and ocean circulation. In addition to the major components of foraminiferal shells (calcium, carbon and oxygen) other elements are incorporated in minor and

trace quantities. The most commonly used of these are divalent cations of similar size to calcium (magnesium, strontium, cadmium, zinc, barium, iron and manganese). However, a few others have also been investigated (copper, sodium, lithium, fluorine, boron, uranium, neodymium and vanadium). For some of these elements, their concentration within the shell is a function of the seawater conditions in which the foraminifera lived. For example, the concentration of magnesium within the shell is a function of water temperature, and the cadmium and zinc concentrations reflect the nutrient concentrations.

In order to properly use these proxies to reconstruct conditions in the past, they must be calibrated against the modern instrumental record to ensure that they accurately record the parameters that we are seeking and to determine if there are other influential variables. This thesis project takes advantage of a set of recent core-top sediments collected from the Florida Straits coupled with measurements of the seawater properties at each core site to calibrate four trace element proxies in the shells of benthic foraminifera. Chapter Two of this thesis presents the calibrations for Mg/Ca and Sr/Ca, proxies for temperature and seawater Sr/Ca respectively. Chapter Three presents calibrations for Cd/Ca and Zn/Ca, proxies for nutrient concentrations.

II. Temperature and Carbonate Ion Proxies: Mg/Ca & Sr/Ca

Abstract

Over the past decade, the ratio of Mg to Ca in foraminiferal tests has emerged as a valuable paleo-temperature proxy. The use of Mg/Ca has allowed the extraction of global ice volume and local salinity from $\delta^{18}O$. Sr/Ca is commonly measured alongside Mg/Ca, but the sources of its variability remain unclear. Benthic foraminiferal Mg/Ca and Sr/Ca were measured from 32 high quality multi-core tops collected in the Florida Straits, spanning a temperature range of 5.8 to 18.6°C. Species specific calibrations are presented for *Cibicidoides pachyderma, Uvigerina peregrina, Planulina ariminensis, Planulina foveolata*, and *Hoeglundina elegans*. The Mg/Ca values and temperature sensitivity vary between species, but all species exhibit a positive near-linear correlation that decreases in slope at higher temperatures. This behavior is in contrast to the exponential relationship seen in planktonic foraminifera and in limited studies of benthic foraminifera. The decrease in sensitivity of Mg/Ca to temperature may be explained by Mg/Ca suppression due to high carbonate ion concentrations. If true, Mg/Ca suppression would complicate paleotemperature reconstructions of thermocline waters. An alternative method that may adjust for the carbonate ion influence on Mg/Ca is dividing Mg/Ca by Li/Ca. The Mg/Li ratio provides better linear relationships to temperature than Mg/Ca alone. Benthic foraminiferal Sr/Ca is complicated by many influential variables, and its use to reconstruct seawater Sr/Ca is subject to large uncertainties.

Introduction

Over the past decade, the magnesium to calcium ratio (Mg/Ca) in foraminifera

has been developed as a proxy for the temperature of the seawater in which the

foraminifer calcified. Foraminiferal Mg/Ca has the potential to provide independent

temperature reconstructions, which combined with shell $\delta^{18}O$ allow the reconstruction

of seawater $\delta^{18}O$ [Mashiotta et al., 1999; Elderfield and Ganssen, 2000]. Planktonic

Mg/Ca has been used to investigate variations in sea surface temperatures [e.g.

Hastings et al., 1998; Mashiotta et al., 1999; Lea et al., 2000; Koutavas et al., 2002;

Stott et al., 2002; Barker et al., 2005], sea surface salinity [e.g. Gussone et al., 2004;

Schmidt et al., 2004; Benway et al., 2006; Newton et al., 2006; Schmidt et al., 2006],

and sea level [Lea et al., 2002]. Benthic Mg/Ca applications have been more limited,

but deep sea temperatures and global ice volume have been investigated over

Quaternary and Cenozoic timescales [Lear et al., 2000; Billups and Schrag, 2002,

2003; Martin et al., 2002; Lear et al., 2003; Marchitto and deMenocal, 2003; Skinner

et al., 2003].

The incorporation of Mg into foraminiferal shells is likely related to

temperature through both thermodynamics and physiological processes [Rosenthal et

al., 1997; Lea et al., 1999; Erez, 2003; Bentov and Erez, 2006]. The

thermodynamics of solid-solution substitution of Mg for Ca in calcite predicts that

Mg/Ca should increase ~3% per °C increase in temperature [Lea et al., 1999]. This

thermodynamic prediction is supported by inorganic precipitation experiments [e.g.

Katz, 1973; Mucci, 1987; Oomori et al., 1987]. On the other hand, the low-Mg

calcite tests of planktonic and deep sea benthic foraminifera contain an order of

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magnitude less Mg, and the response of Mg/Ca to temperature is 2-3 times greater than in inorganic calcite. There is increasing evidence that foraminifera exert strong biological control on the biomineralization process. Foraminifera likely calcify from an internal calcification pool, and the composition of the calcification pool may be altered by the removal of Mg through selective channels and pumps [Erez, 2003; Bentov and Erez, 2006]. Interspecies differences in shell Mg/Ca have been observed in planktonic [Lea et al., 1999; Anand et al., 2003] and benthic foraminifera [Rosenthal et al., 1997; Lear et al., 2002; Elderfield et al., 2006]. Variations in trace metal concentrations within individual shells have been observed in association with organic membranes [Kunioka et al., 2006]. These observations suggest that physiological process and manipulation of the parent solution are important controls on the eventual shell Mg/Ca ratio.

Despite these complications, Mg/Ca does seem to be a reliable recorder of seawater temperature. Since Mg/Ca cannot be predicted by thermodynamic laws, empirical calibration and understanding of influential parameters other than temperature are vital to the application of Mg/Ca as a paleotemperature proxy. Planktonic foraminifera have been calibrated by core-top [Nurnberg et al., 1995; Elderfield and Ganssen, 2000; Lea et al., 2000; Dekens et al., 2002], sediment trap [Anand et al., 2003] and laboratory culture studies [Nurnberg et al., 1996; Lea et al., 1999; Mashiotta et al., 1999]; see Barker et al. [2005] for a review], and these studies have demonstrated a ~9-10% increase in Mg/Ca per degree Celsius in most species. The response of benthic Mg/Ca to temperature is less well constrained. With the exception of recent progress in culturing benthic foraminifera [Hintz et al., 2006a,

2006b], benthic foraminiferal Mg/Ca has been calibrated exclusively by the comparison of core-top samples to bottom water temperatures. A pioneering study by Chave [1955] recognized a positive correlation between the Mg/Ca of mixed species of benthic foraminifera and seawater temperature. Izuka [1988] and Rathburn and De Deckker [1997] found positive correlations between Mg/Ca and temperature for *Cassulina* and *Cibicidoides* respectively. Rosenthal et al. [1997] proposed an exponential temperature response of ~10% per degree Celsius for *Cibicidoides pachyderma* (cf. *C. floridanus*) using core-tops from the Little Bahama Bank. Lear et al. [2002] later adjusted the *C. pachyderma* calibration of Rosenthal et al. [1997] for an apparent analytical bias, and added calibrations for several other species, noting that some species such as *Uvigerina spp*. have lower temperature sensitivities. It now appears likely that the high *Cibicidoides* Mg/Ca values measured in the Little Bahama Bank core-tops were affected by high-Mg overgrowths, and the Mg/Ca in *C. pachyderma* may respond more linearly to temperature [Marchitto et al., 2007]. Recently core-top calibrations have been presented for several other benthic species (Table 1), although questions about the use of exponential relationships and differences in temperature sensitivities between species still remain.

There is also the issue of ancillary influences on benthic Mg/Ca. Recent studies have focused on the possible effect of carbonate ion concentration on Mg incorporation [Elderfield et al., 2006; Rosenthal et al., 2006]; it is thought that Mg/Ca may be reduced at low carbonate ion concentrations, as has been demonstrated for Cd, Ba and Zn [McCorkle et al., 1995; Marchitto et al., 2000, 2005]. The evidence

presented thus far suggests that a carbonate ion effect is limited to waters near or

below saturation, although more analyses are needed from super-saturated waters.

Species	Mg/Ca =	Location	Temperature range °C	Cleaning Method	Reference
C. pachyderma	0.116T + 1.20	Florida Straits	5.8-18.6	R	This Study
Cibicidoides spp.	$1.36e^{0.101T}$	Little Bahama Bank	0.8-18.4	L	Rosenthal et al., 1997
Cibicidoides spp.	$0.87e^{0.109T}$	Little Bahama Bank	0.8-18.4	R	Lear et al., 2002
Cibicidoides spp.	$1.22e^{0.109T}$	Little Bahama Bank	-1.1-18		Martin et al., 2002
Cibicidoides spp.	$0.90e^{0.11T}$	Multiple Regions	-0.6-18.4	O/R	Elderfield et al., 2006
C. kullenbergi	0.11T + 0.88	Off Somalia	2.6-11.8	O	Elderfield et al., 2006
C. wuellerstorfi	$0.85e^{0.11T}$	Atlantic/Pacific	-1-3	R	Martin et al., 2002
U. peregrina	0.079T + 0.77	Florida Straits	5.8-17.2	R	This Study
U. peregrina	0.065T + 0.91	Off Somalia	1.5-11.8	O	Elderfield et al., 2006
Uvigerina spp.	0.075T + 0.87	Arabian Sea	1.7-20	R	Elderfield et a., 2006
Uvigerina spp.	$0.92e^{0.061T}$	Multiple Regions	1.8-18.4	R	Lear et al., 2002
P. ariminensis	0.17T + 0.5	Florida Straits	7.0-12.1	R	This Study
P. ariminensis	$0.91e^{0.062T}$	Multiple Regions	3.0-14.5	R	Lear et al., 2002
P. foveolata	0.04T + 2.1	Florida Straits	11.0-17.8	R	This Study
Planulina spp.	$0.79e^{0.119T}$	Multiple Regions	2.3-12.0	R	Lear et al., 2002
H. elegans	0.030T + 1.01	Florida Straits	5.8-19.0	R	This Study
H. elegans	0.034T + 0.96	Multiple Regions	1.7-18.4	R	Rosenthal et al., 2006
O. umbonatus	$1.01e^{0.11T}$	Multiple Regions	0.8-9.9	R	Lear et al., 2002
O. umbonatus	$1.528e^{0.09T}$	Off Namibia	2.9-10.4	N	Rathmann et al., 2004
M. barleeanus/M. pompilioides	$0.98e^{0.101T}$	Multiple Regions	0.8-18.4	R	Lear et al., 2002
M. barleeanus	$0.658e^{0.137T}$	Near Iceland	0.19-6.99	R	Kristjansdottir et al., 2007
I. norcorossi/I. helenae	$1.051e^{0.060T}$	Near Iceland	0.21-5.25	R	Kristjansdottir et al., 2007
C. neoteretis	$0.864e^{0.082T}$	Near Iceland	0.96-5.47	R	Kristjansdottir et al., 2007
Q. yabei	2.90T + 65.98	Culture	9.7-24.5	O	Toyofuku et al., 2000
P. opercularis	2.22T + 89.69	Culture	9.8-23.1	O	Toyofuku et al., 2000
M. kudakajimaensis	$143.18e^{0.0317T}$	Lakshadweep Islands, India	21.2-28.7	O	Raja et al., 2005

Table 2.1: Benthic foraminiferal Mg/Ca – Temperature calibrations from this study and literature. Cleaning methods are R = full trace metal cleaning method with a reductive step, O = the "Mg – cleaning method" without the reductive step, L = acid leach, and N = no cleaning (laser ablation).

Sr/Ca is commonly measured along with Mg/Ca in foraminifera. However,

the causes of Sr/Ca variability remain unclear. Down-core studies of foraminiferal

Sr/Ca have been conducted in an effort to reconstruct possible glacial/interglacial

seawater Sr/Ca changes [Martin et al., 1999; Stoll et al., 1999; Shen et al., 2001].

Foraminiferal Sr/Ca generally reflects seawater Sr/Ca [Delaney et al., 1985;

Elderfield et al., 2000; Lear et al., 2003]. Although Sr and Ca have long residence times in the ocean, ~5 and ~1 million years respectively [Broecker and Peng, 1982], it has been proposed that significant seawater Sr/Ca changes may occur on glacial/interglacial timescales due to recrystallization of shelf carbonates [Stoll and Schrag, 1998]. Changes in seawater Sr/Ca would significantly affect coralline Sr/Ca temperature reconstructions. Down-core Sr/Ca studies have found that benthic foraminiferal Sr/Ca was elevated by 3-6% during glacial periods, and the changes varied in amplitude between species and locations [Martin et al., 1999; Stoll et al., 1999; Shen et al., 2001]. Since glacial/interglacial seawater Sr/Ca variations are only expected to be 1-3% [Stoll and Schrag, 1998], it seems likely that Sr/Ca is also influenced by environmental parameters. Core-top studies have proposed that benthic foraminiferal Sr/Ca decreases with increasing calcification rate [Elderfield et al., 1996], increasing pressure [Rosenthal et al., 1997], and increasing post-depositional dissolution [McCorkle et al., 1995]. Additionally, culturing studies of planktonic foraminifera showed increasing Sr/Ca with increasing temperature, salinity and pH [Lea et al., 1999; Russell et al., 2004]. If foraminiferal Sr/Ca is to be used to estimate changes in seawater Sr/Ca, the environmental influences and the magnitude of those influences must be understood.

Sr/Ca in the aragonitic benthic foraminifer *Hoeglundina elegans* has been proposed as a temperature proxy [Reichart et al., 2003; Rosenthal et al., 2006], and may be more reliable than Mg/Ca for *H. elegans* [Rosenthal et al., 2006]. However, like Mg/Ca, *H. elegans* Sr/Ca appears to be strongly influenced by carbonate ion concentration at low concentrations [Rosenthal et al., 2006].

This study presents new core-top Mg/Ca and Sr/Ca data for *C. pachyderma*, *U. peregrina*, *P. ariminensis*, *P. foveolata* and *H. elegans* from the Florida Straits. These new data improve the existing Mg/Ca calibrations and add to the understanding of the carbonate ion influence on Mg/Ca. A new method is proposed to improve the Mg/Ca proxy using Li/Ca. This data set also allows the investigation of the causes of Sr/Ca variability.

Materials & Methods

Samples for these calibrations were collected during R/V *Knorr* cruise 166-2, January 2002, in the Florida Straits. Sediments were collected from three regions: the western side of the Florida Current near Dry Tortugas; the eastern side of the Florida Current near Great Bahama Bank and the western side of the Santaren Current near Cay Sal Bank (Figure 2.1; Table 2.2). Thirty-eight successful multi-core casts were recovered with each consisting of eight short cores (30-40cm long, 12cm diameter). The 0-1cm slice of one short core from thirty-two of those multi-core casts was used for this study.
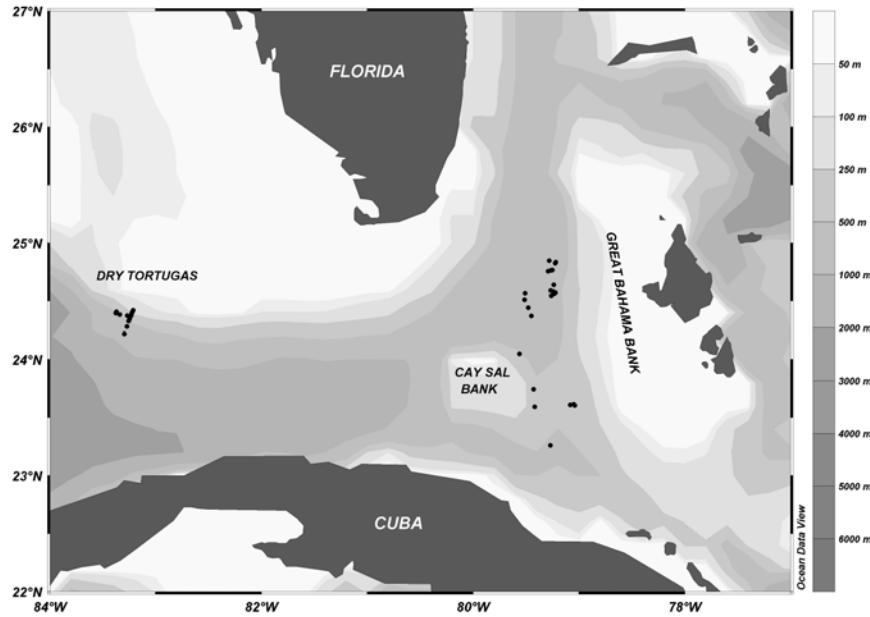
Figure 2.1: Map of the Florida Straits study area. Multi-core sites are indicated by black dots.

Multi-core sites cover depth, temperature, salinity, and CO_3^{2-} ranges of 173-751m, 5.8-18.6 °C, 34.9-36.8 psu, and 86-216 μmol kg^{-1} respectively (Figure 2.2). Sloping of isopycnals associated with the Florida Current causes the eastern side of the Florida Straits to have higher temperature, salinity and CO_3^{2-} at a given depth than the western side of the Straits. Fifty-five CTD casts were made during the course of the cruise. Bottom water samples from the multi-core sites were collected using a Niskin bottle attached to the multi-corer frame, which was rigged to close when the multi-corer hit the seafloor. Aliquots of the Niskin seawater were sampled for salinity, $\delta^{18}O$, alkalinity and ΣCO_2. Due to the sloping of isopycnals, bottom water temperatures could not be determined by simply matching the multi-core depth to a nearby CTD. Instead, bottom water temperatures were determined by matching the Niskin bottle salinities to the corresponding salinities of nearby CTD casts. At twelve of the multi-core sites this method was not possible due to bottle malfunction; at these

sites salinity and temperature were derived from nearby CTDs using the average depth offset in salinity measurements between the multi-core sites and the nearby CTDs. For the Dry Tortugas sites, 15m was added to the depth of the site and the CTD temperature and salinity at that depth was used. Likewise, at the Great Bahama Bank sites, 15m was subtracted from the multi-core depth and the CTD measurements at that depth were used. Carbonate ion concentrations for 12 of the multi-core sites were calculated from alkalinity and ΣCO_2 with the CO2SYS program v. 1.05 [Lewis and Wallace, 1998], using the first and second dissociation constants of carbonic acid from Hansson [1973] and Mehrbach et al. [1973] as refit by Dickson and Millero [1987]. For the other sites, CO_3^{2-} was inferred from a second-order polynomial relationship with salinity ($R^2 = 0.99$).
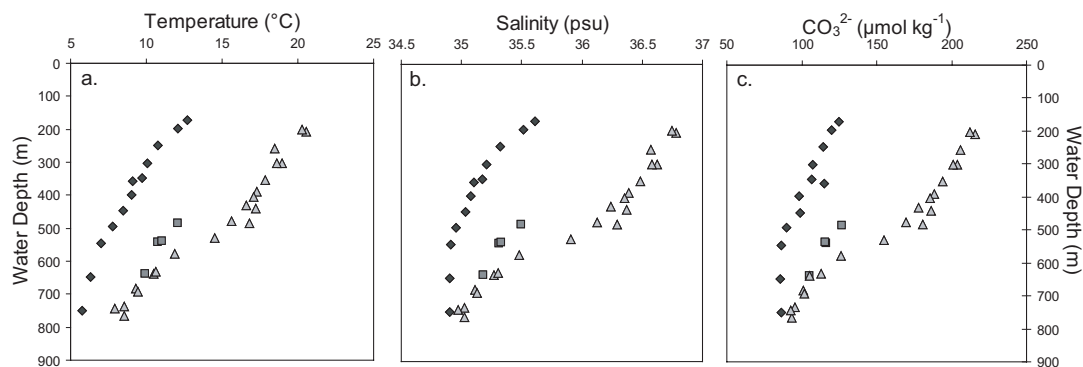
Figure 2.2: Profiles of temperature (a), salinity (b) and carbonate ion concentration (c) at the multi-core sites: Dry Tortugas sites (diamonds), Cay Sal Bank sites (squares) and Great Bahama Bank sites (triangles).

AMS radiocarbon ages were measured on *Globigerinoides ruber* (>250 μm) from the 0-1 or 0-2 cm slices from 14 of the KNR166-2 multi-cores [Lund and Curry, 2004, 2006; Lund, 2005]. Five of the core tops contained significant levels of "bomb" radiocarbon (fraction modern >1), three gave ages between 200 and 400 yr, and six ranged from 1000-3000 yr. Sedimentation rates in KNR166-2 cores range between

11 and 66 cm kyr^{-1} near Dry Tortugas and 20 to 350 cm kyr^{-1} on Great Bahamas Bank [Lund et al., 2006].

Benthic foraminifera *Cibicidoides pachyderma, Uvigerina peregrina, Planulina ariminensis, Planulina foveolata* and *Hoeglundina elegans* were picked from the 250-600µm size fraction of each core-top. Samples for trace element analysis contained 4-7 individuals (*C. pachyderma*), 9-10 individuals (*U. peregrina*), 13-15 individuals (*P. ariminensis*), 18-20 individuals (*P. foveolata*), and 9-10 individuals (*H. elegans*). Where abundances allowed, the number of individuals was doubled and samples were crushed, homogenized and split for replicate analysis. Crushed samples were cleaned reductively (using anhydrous hydrazine) and oxidatively (using H_2O_2) in a Class-1000 clean lab, following the methods of Boyle and Keigwin [1985/6] as modified by Boyle and Rosenthal [1996]. Samples were analyzed for Mg/Ca, Sr/Ca, Cd/Ca, Zn/Ca, Li/Ca, U/Ca, Mn/Ca and Fe/Ca by magnetic-sector single-collector ICP-MS, on a Thermo-Finnigan Element2, using methods adapted from Rosenthal et al. [1999] [Marchitto, 2006]. Long-term 1σ precisions are: Mg/Ca = 0.54%, Sr/Ca = 0.57%, Cd/Ca = 1.8%, Zn/Ca = 3.2%, Li/Ca = 0.88%, U/Ca = 1.9%, Mn/Ca = 0.97% and Fe/Ca = 1.4% [Marchitto, 2006]. One *U. peregrina* sample was excluded due to extremely low [Ca] (< 0.001 mM, compared to a target concentration of ~2mM); the sample was presumably lost during cleaning. Mn/Ca and Fe/Ca were measured to screen against contamination from diagenetic coatings or detrital material; values were almost always below 30 µmol mol^{-1} and did not exceed 60 µmol mol^{-1} in any sample, well below thresholds for likely trace metal contamination (>100 µmol mol^{-1}) [Boyle, 1983].

Core	Latitude (°N)	Longitude (°W)	Depth (m)	Temperature (°C)	Salinity (psu)	CO_3^{2-} (µmol kg^{-1})	Conventional ^{14}C Age (yr BP)	NOSAMS Number
5MC[a]	24.4	83.38	447	8.5	35.03	99		
11MC[a]	24.22	83.3	751	5.8	34.90	86	355 ± 35	OS-39958[2]
13MC[a]	24.37	83.24	348	9.7	35.17	106	3040 ± 35	OS-46032[2]
16MC[a]	24.4	83.23	248	10.8	*35.32*	*114*		
19MC[a]	24.42	83.21	173	12.7	35.61	125	1320 ± 50	OS-39967[2]
22MC[a]	24.41	83.37	398	9.0	*35.08*	*98*		
24MC[a]	24.34	83.25	494	7.8	*34.95*	*90*		
28MC[a]	24.28	83.27	648	6.3	34.90	86	2980 ± 40	OS-46037[2]
50MC[a]	24.41	83.22	198	12.1	35.51	120	1080 ± 45	OS-41646[2]
53MC[a]	24.38	83.23	302	10.0	*35.21*	*107*	1800 ± 30	OS-399692
55MC[a]	24.38	83.27	359	9.1	*35.10*	*115*		
62MC[a]	24.33	83.26	547	7.0	*34.91*	*86*	Fm > 1	OS-39971[1]
64MC[c]	23.61	79.04	209	20.6	36.78	*216*		
66MC[c]	23.61	79.05	302	19.0	36.62	*204*		
68MC[c]	23.61	79.08	431	16.6	36.24	*178*		
72MC[b]	23.75	79.43	542	10.8	35.31	116		
76MC[b]	23.59	79.42	539	11.0	35.33	*116*		
79MC[b]	23.26	79.27	486	12.1	*35.50*	*127*		
84MC[c]	24.37	79.45	638	10.5	35.27	105		
89MC[c]	24.56	79.24	353	17.8	*36.48*	*194*	2280 ± 35	OS-40243[2]
92MC[c]	24.55	79.26	478	15.7	36.13	170		
94MC[c]	24.57	79.23	259	18.5	36.57	206	215 ± 35	OS-40244[2]
97MC[c]	24.56	79.23	303	18.6	*36.58*	*201*		
103MC[c]	24.44	79.48	683	9.3	35.11	101		
110MC[c]	24.58	79.24	390	17.3	*36.39*	*188*	Fm > 1	OS-46039[2]
112MC[c]	24.64	79.24	404	17.1	*36.35*	*185*		
118MC[c]	24.59	79.27	531	14.5	35.91	*155*	Fm > 1	OS-39973[3]
121MC[c]	24.77	79.25	578	11.9	35.48	*126*		
123MC[c]	24.76	79.27	632	10.6	35.30	*113*		
125MC[c]	24.76	79.29	694	9.4	35.13	*102*	Fm > 1	OS-39975[3]
134MC[c]	24.84	79.22	441	17.2	36.37	*186*	Fm > 1	OS-46043[2]
138MC[c]	24.83	79.23	484	16.8	36.29	181		

Table 2.2: KNR 166-2 multi-core locations, hydrographic data and radiocarbon ages. Superscripts on Cores indicate (a) Dry Tortugas sites, (b) Cay Sal Bank sites, and (c) Great Bahama Bank sites. Bottom water temperatures were estimated by matching Niskin bottle salinities to nearby CTDs. Italicized salinities and CO_3^{2-} values were estimated as described in text. Sources of radiocarbon ages are indicated by superscripts on the National Ocean Sciences Accelerator Mass Spectrometry Facility (NOSAMS) sample numbers: 1 = Lund and Curry [2004]; 2 = Lund [2005]; 3 = Lund and Curry [2006]. Fm > 1 refers to fraction modern greater than one, indicating the presence of ^{14}C for nuclear weapons testing.

Results

Core-top Mg/Ca and Sr/Ca results are presented in Table 2.3. Mg/Ca values range from 1.34 – 3.47 mmol mol^{-1} for *C. pachyderma*, 1.02 – 2.15 mmol mol^{-1} for *U. peregrina*, 1.74 – 2.73 mmol mol^{-1} for *P. ariminensis*, 2.31 – 2.84 mmol mol^{-1} for *P. foveolata*, and 1.03 – 1.69 mmol mol^{-1} for *H. elegans*. *H. elegans* Mg/Ca measurements from two multi-cores were much higher than measurements from nearby cores and are suspected to be contaminated. These measurements are excluded from the figures and regressions. In all species, Mg/Ca decreases with increasing depth and depth profiles are distinct between regions, with generally lower values on the western (colder) side of the Florida Current (Figure 2.3). The standard deviation of sample splits is larger than the analytical uncertainty, indicating variability within a sample and some inadequate homogenization. Some of the scatter in the data is likely due to individual foraminifera representing a range in ages over the past few thousand years (especially in the Dry Tortugas samples). Since bottom water temperature at the multi-core sites is sensitive to the sloping of isopycnals associated with the Florida Current, if the strength of the current has varied over the past couple thousand years it would introduce some error into our calcification temperature estimates. The Gulf Stream transport through the Florida Straits does appear to have varied by ±10% over the past millennium [Lund et al., 2006].

Sr/Ca measurements range from 1.37 – 1.60 mmol mol^{-1} for *C. pachyderma*, 1.24 – 1.35 mmol mol^{-1} for *U. peregrina*, 1.45 – 1.52 mmol mol^{-1} for *P. ariminensis*, 1.47 – 1.53 mmol mol^{-1} for *P. foveolata*, and 1.76 – 2.71 mmol mol^{-1} for *H. elegans*. Sr/Ca generally decreases with increasing depth, but the profiles are more scattered

than for Mg/Ca, except in *H. elegans* (Figure 2.4). In the calcitic species, Sr/Ca variations are very small over the range of multi-core sites (3-16%), depending on species, with *C. pachyderma* having the largest range. Sr/Ca in *H. elegans* is higher than that of the calcitic species and varies by 40% over the multi-core sites.

Core	C. pachyderma Mg/Ca	Sr/Ca	U. peregrina Mg/Ca	Sr/Ca	P. ariminensis Mg/Ca	Sr/Ca	P. foveolata Mg/Ca	Sr/Ca	H. elegans Mg/Ca	Sr/Ca
5	2.09	1.37	1.48	1.31	2.09	1.49			1.55	1.99
5	2.00	1.45	1.46	1.32	2.04	1.47			1.19	2.01
11	1.34	1.39	1.07	1.24					1.03	1.95
11			1.02	1.25						
13	2.33	1.45	1.52	1.30	2.36	1.47			1.31	2.18
13	2.44	1.43	1.53	1.29	2.25	1.45			1.26	2.07
16	2.40	1.41								
16	2.27	1.41								
19	2.09	1.40					2.58	1.52	1.49	2.46
19	2.73	1.41							1.53	2.49
22	2.63	1.41	1.48	1.29					1.38	2.12
22	2.49	1.44	1.43	1.30						
24			1.69	1.26					1.12	1.93
28	1.42	1.40	1.13	1.24					1.07	1.89
28	1.54	1.39	1.15	1.25					1.03	1.93
50	2.39	1.40			2.73	1.49	2.72	1.52	1.49	2.43
50	2.47	1.41								
53	2.37	1.39	1.46	1.31	2.38	1.46			*2.12*	2.18
53	2.20	1.41	1.41	1.31	2.36	1.48			*2.19*	2.24
55	2.34	1.44	1.64	1.30	2.24	1.49			*5.63*	2.12
55	2.24	1.44	1.69	1.30	2.20	1.49			*4.53*	2.11
62	2.19	1.42	1.36	1.31	1.74	1.48			1.07	1.76
62			1.43	1.30						
66									1.56	2.71
68	3.29	1.52					2.84	1.51	1.64	2.58
68	3.39	1.50							1.49	2.53
72	2.88	1.45	1.63	1.35			2.31	1.51	1.47	2.35
72	2.83	1.46	1.61	1.33						
76	2.87	1.49	1.71	1.32	2.23	1.51	2.43	1.47		
76	2.78	1.47								
79	3.35	1.47	1.89	1.30			2.59	1.49	1.48	2.44
79	3.15	1.45	1.88	1.29						
84	2.48	1.48								
89	3.44	1.60					2.64	1.53		
92	3.19	1.45	2.00	1.35					1.64	2.55
94	3.34	1.55							1.30	2.63
94	3.47	1.55							1.30	2.61
97	3.27	1.55							1.51	2.69
97	3.25	1.56							1.42	2.67
103	2.31	1.41	1.45	1.31	1.84	1.48				
103	2.34	1.41								
110	3.31	1.51	2.15	1.33			2.75	1.51	1.69	2.62
110			2.14	1.32			2.75	1.52	1.46	2.57
112	2.92	1.54							1.48	2.62
112									1.55	2.65
118	2.68	1.44	1.85	1.33			2.41	1.50	1.54	2.37
118			1.84	1.33					1.50	2.39
121	2.48	1.43	1.86	1.33					1.60	2.37
123	2.65	1.46								
125	2.48	1.42			1.84	1.52				
134	2.94	1.48					2.69	1.52	1.61	2.51
134	3.14	1.48							1.52	2.62
138	2.56	1.43	1.88	1.30			2.59	1.52	1.59	2.50
138							2.69	1.51	1.51	2.52

Table 2.3: Benthic foram Mg/Ca and Sr/Ca measurements for each species by core. See Table 2.2 for core locations and seawater properties. All values are mmol mol^{-1}. Four *H. elegans* measurements were excluded due to suspected contamination and are *italicized*.

Figure 2.3: Individual Mg/Ca vs. water depth for a) *C. pachyderma*, b) *U. peregrina*, c) *P. ariminensis*, d) *P. foveolata*, and e) *H. elegans*. Diamonds are multi-cores near Dry Torugas; squares are near Cay Sal Bank, and triangles are near Great Bahama Bank. Note the different Mg/Ca scales.
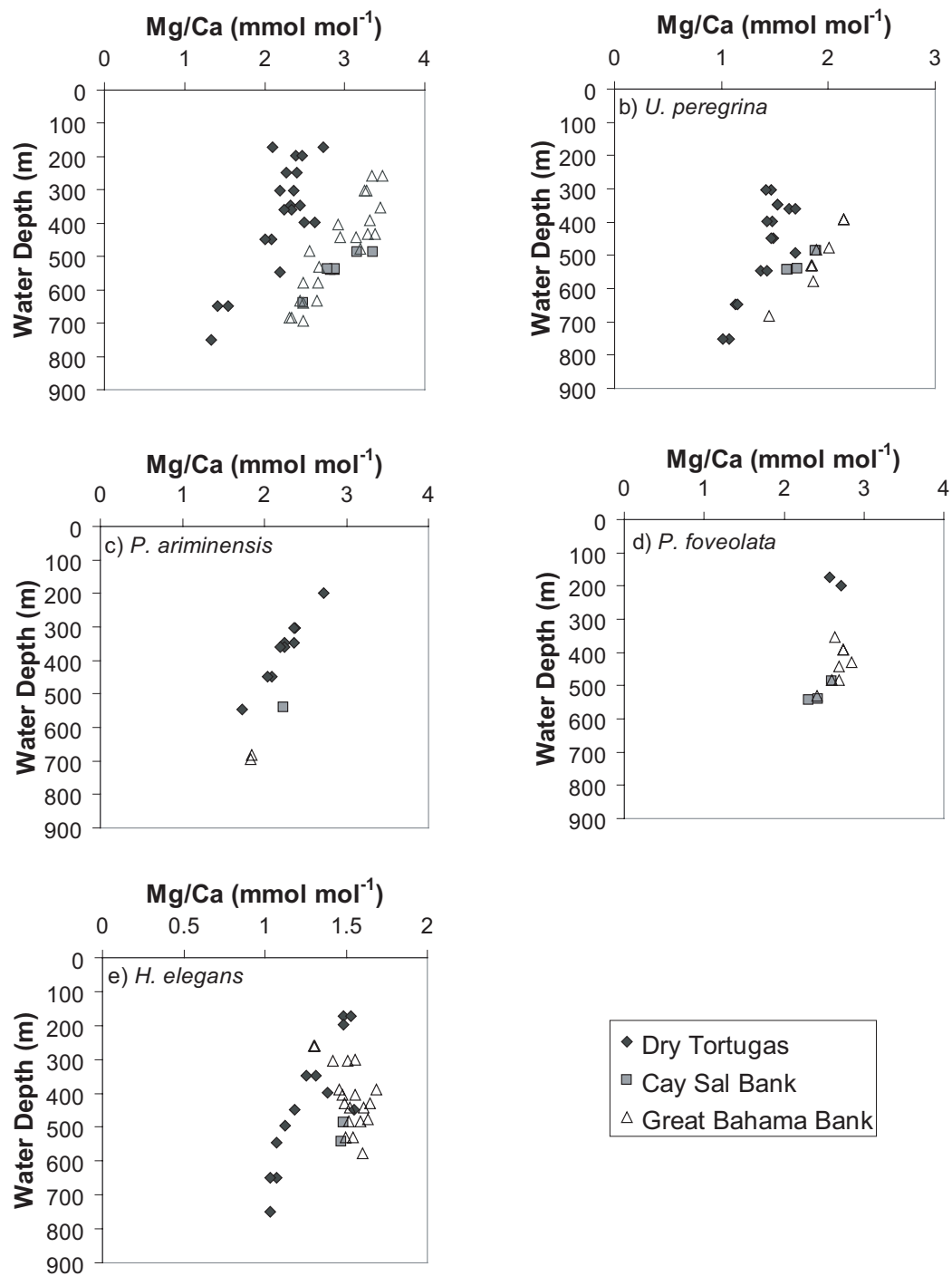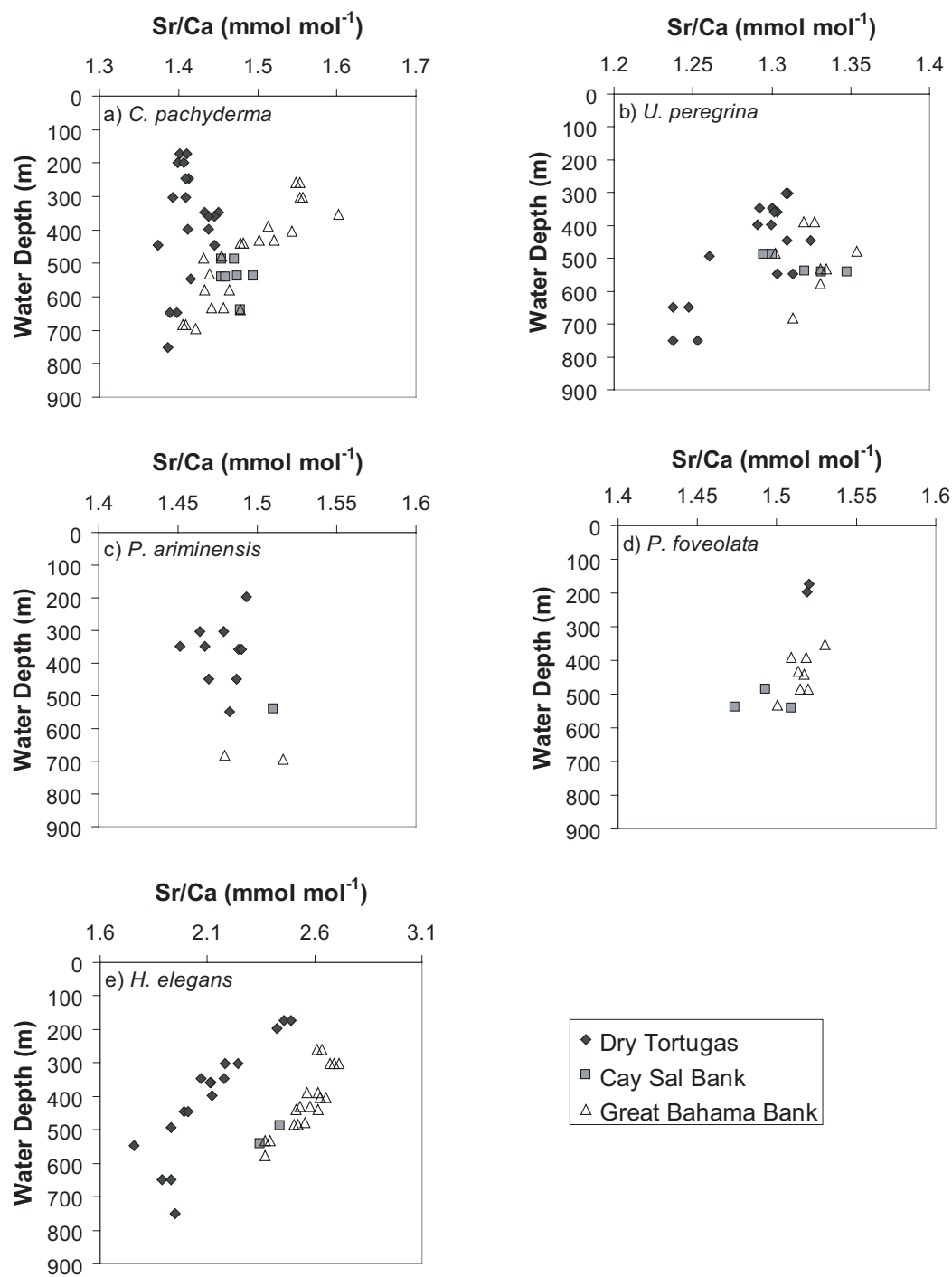
Figure 2.4: Individual Sr/Ca vs. water depth for a) *C. pachyderma*, b) *U. peregrina*, c) *P. ariminensis*, d) *P. foveolata*, and e) *H. elegans*. Diamonds are multi-cores near Dry Torugas; squares are near Cay Sal Bank, and triangles are near Great Bahama Bank. Note the different Sr/Ca scales.

Discussion

Mg/Ca – Temperature Regressions

The Mg/Ca of all the species analyzed in this study is positively correlated with bottom water temperature (Figure 2.5). Below are linear and exponential regressions fitted to the individual data for each species. The errors are the standard errors of the regression coefficients.

C. pachyderma	$Mg/Ca = 0.116\pm0.014\ T + 1.20\pm0.18$	$R^2 = 0.73$	$p < 0.0001$	$n = 46$	(1)
	$Mg/Ca = 1.55\pm0.12\ e^{0.042\pm0.005\ T}$	$R^2 = 0.70$	$p < 0.0001$	$n = 46$	(2)
U. peregrina	$Mg/Ca = 0.079\pm0.007\ T + 0.77\pm0.08$	$R^2 = 0.82$	$p < 0.0001$	$n = 28$	(3)
	$Mg/Ca = 0.98\pm0.05\ e^{0.045\pm0.004\ T}$	$R^2 = 0.79$	$p < 0.0001$	$n = 28$	(4)
P. ariminensis	$Mg/Ca = 0.17\pm0.04\ T + 0.5\pm0.4$	$R^2 = 0.63$	$p = 0.0012$	$n = 11$	(5)
	$Mg/Ca = 1.0\pm0.2\ e^{0.08\pm0.02\ T}$	$R^2 = 0.63$	$p = 0.0016$	$n = 11$	(6)
P. foveolata	$Mg/Ca = 0.04\pm0.01\ T + 2.1\pm0.2$	$R^2 = 0.44$	$p = 0.014$	$n = 11$	(7)
	$Mg/Ca = 2.1\pm0.2\ e^{0.014\pm0.005\ T}$	$R^2 = 0.44$	$p = 0.013$	$n = 11$	(8)
H. elegans	$Mg/Ca = 0.030\pm0.006\ T + 1.01\pm0.08$	$R^2 = 0.49$	$p < 0.0001$	$n = 32$	(9)
	$Mg/Ca = 1.07\pm0.07\ e^{0.021\pm0.004\ T}$	$R^2 = 0.46$	$p < 0.0001$	$n = 32$	(10)

Exponential fits have traditionally been used to describe the Mg/Ca - temperature relationship due to the expected thermodynamic influence on Mg incorporation (Rosenthal et al., 1997; Lea et al., 1999). As the strong biological control exerted on the biomineralization process by foraminifera has become increasingly evident (eg. Bentov and Erez, 2006), it is not clear that the Mg/Ca response to temperature should be dominated by thermodynamics. Exponential fits to the data presented here are not significantly better or worse than the linear ones. However, there is no hint at an exponential increase of Mg/Ca to temperature, and these data suggest that the sensitivity of Mg/Ca to temperature may actually decrease at higher temperatures, rather than increase. While it is unlikely that the combined influences of temperature dependent physiological processes and thermodynamics on

test Mg/Ca are truly linear, the linear fits are more useful approximations than the

exponential ones given the data presented here.
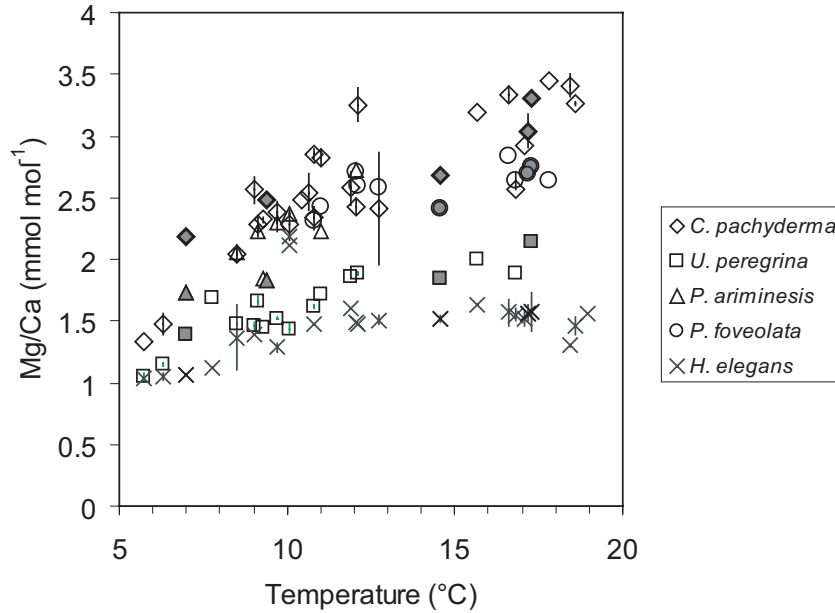
Figure 2.5: Average Mg/Ca plotted against bottom water temperature for each species. Error bars are one standard deviation of sample splits, where applicable. Filled symbols indicate multi-cores determined to be modern by the presence of "bomb" [14]C.

Comparison to Published Data

All existing *Cibicidoides* calibrations rely heavily upon a set of *C.*

pachyderma samples from the Little Bahama Bank [Rosenthal et al., 1997; Lear et al.,

2002; Martin et al., 2002; Elderfield et al., 2006]. Lear et al. [2002] reanalyzed the

samples of Rosenthal et al. [1997], finding a significant (~40%) negative offset from

the original measurements; the offset is assumed to be analytical; however the cause

is unknown. The Lear et al. [2002] data contain significant scatter at higher

temperatures, and the authors attributed some of the scatter to high-Mg overgrowths

and/or downslope transport. The new *C. pachyderma* data overlap with those of Lear

et al. [2002] up to ~12°C (Figure 2.6). At higher temperatures the data presented here

are significantly lower than those of Lear et al. [2002]. It is likely that all of the Little

Bahama Bank *C. pachyderma* measurements >12°C of Lear et al. [2002] are influenced to some degree by high-Mg overgrowths [see Marchitto et al., 2007 for a full discussion].
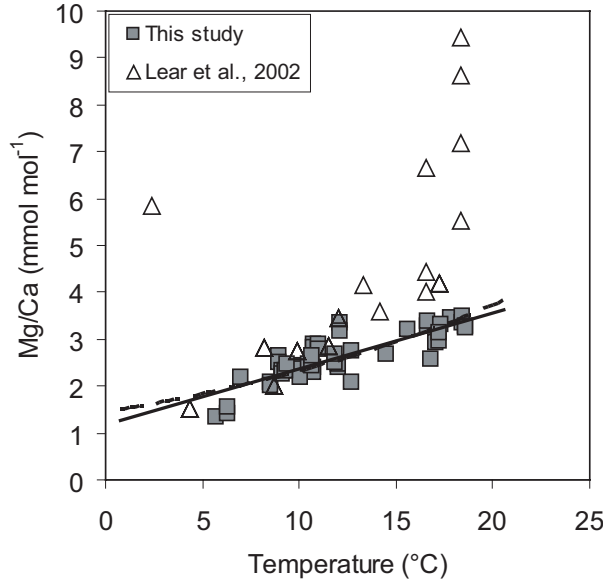
Figure 2.6: Comparison of individual *C. pachyderma* Mg/Ca from this study (gray squares) and from Lear et al. (2002). Equations 1 (solid line) and 2 (dashed line) are shown.

U. peregrina data agree well with the *U. peregrina* measurements from core-tops near Somalia of Elderfield et al. [2006] (Figure 2.7). The addition of the Elderfield et al. [2006] *U. peregrina* data to our linear regression extends the calibration down to 1.49°C and does not significantly change the regression:

$$Mg/Ca = 0.071 \pm 0.005 \; T + 0.86 \pm 0.04 \qquad R^2 = 0.86 \qquad p < 0.0001 \qquad n = 39 \qquad (11)$$

It is important to note that the *U. peregrina* samples of Elderfield et al. [2006] were not cleaned using a reductive step. Several studies have found that measured Mg/Ca in foraminifera cleaned using a reductive step (the "Cd cleaning method") is slightly lower (~0.2 mmol mol^{-1}) than in those cleaned without the reduction step (the "Mg cleaning method") [Martin and Lea, 2002; Barker et al., 2003]; however it is unclear whether this offset in benthic foraminifera is due to dissolution of shell material or

removal of surfacial contaminants. It is encouraging that these data are well described by our linear regression constructed from samples that were reductively cleaned, suggesting that any analytical offset between the two cleaning methods is relatively small. The data also overlap with the *Uvigerina spp.* data of Lear et al. [2002] and Elderfield et al. [2006], indicating that there may not be significant interspecific differences within the genus *Uvigerina,* such as those that have been observed between *Cibicidoides* species [Elderfield et al., 2006]. However, a more thorough examination of other *Uvigerina* species is suggested before this calibration is applied to species other than *U. peregrina*.
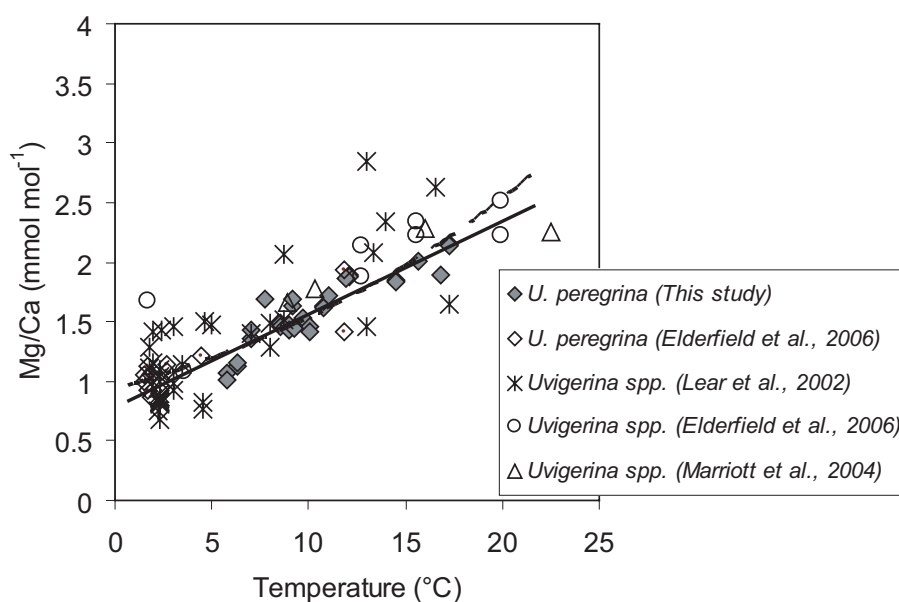
Figure 2.7: Comparison of individual *U. peregrina* Mg/Ca measurements to published *U. peregrina* and *Uvigerina spp.* measurements. Equations 3 (solid line) and 4, (dashed line) are shown.

The *P. ariminensis* data of this study overlap with those of Lear et al. [2002] (Figure 2.8). Addition of the Lear et al. [2002] *P. ariminensis* data to our linear regression extends the calibration down to 3°C. The combined *P. ariminensis* linear regression has a higher R^2 value, although the standard error of the regression is slightly higher (1.47°C vs. 0.98°C).

$$\text{Mg/Ca} = 0.15\pm0.02 \text{ T} + 0.6\pm0.17 \qquad R^2 = 0.80 \qquad p < 0.0001 \qquad n = 18 \qquad (12)$$

To my best knowledge there are no other published core-top Mg/Ca measurements of *P. foveolata*. While the regression presented here has a much lower slope than that of the other calcitic species, it is important to point out that *P. foveolata* was only found in the warmest Florida Straits multi-core sites. *C. pachyderma* and *U. peregrina* also show a decrease in slope at the warm end of the calibration. *P. foveolata* and *P. ariminensis* only overlap in sufficient quantities in two multi-core sites; so direct comparison is difficult. Interestingly though, if all of the *Planulina* data are combined, the linear regression is identical within error to that of *C. pachyderma*:

$$\text{Mg/Ca} = 0.112\pm0.009 \text{ T} + 1.0\pm0.1 \qquad R^2 = 0.80 \qquad p < 0.0001 \qquad n = 39 \qquad (13)$$
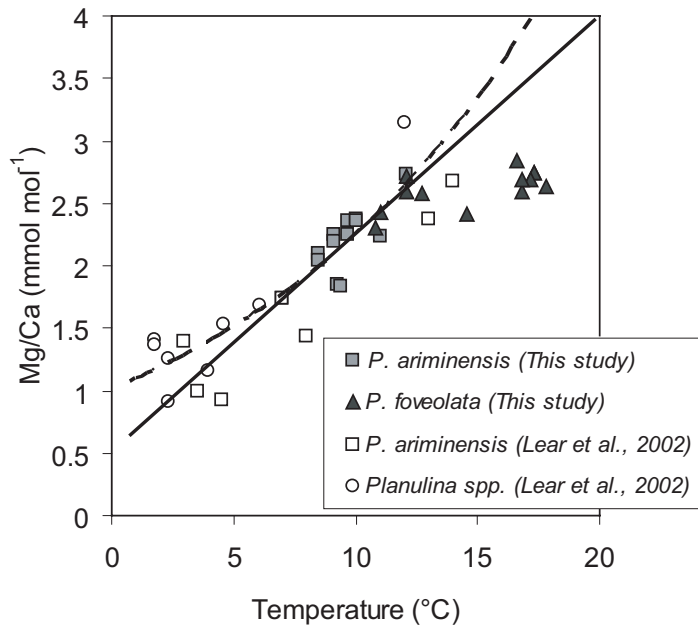
Figure 2.8: Comparison of individual *P. ariminensis* and *P. foveolata* Mg/Ca to published *Planulina* measurements. Equations 5 (solid line) and 6 (dashed line) are shown.

The new *H. elegans* data agree well with Rosenthal et al. [2006] data from the Little Bahama Bank, but their samples from Hawaii and Indonesia have lower Mg/Ca values for the same temperatures (Figure 2.9). Rosenthal et al. [2006] explain the low

Mg/Ca at the Hawaii and Indonesia sites through Mg/Ca reduction due to low ΔCO_3^{2-}. The Florida Straits and Little Bahama Bank have similar carbonate chemistry, which is much higher than the Hawaii and Indonesia sites. While *H. elegans* Mg/Ca does seem to be influenced by temperature, the linear temperature regression (Eq. 9) can only explain about half of the variance in Mg/Ca and the standard error of the regression is quite high (equivalent to 4.5°C). This suggests that *H. elegans* Mg/Ca is a less reliable recorder of seawater temperature, perhaps due to its aragonitic mineralogy or the possibility that the carbonate ion influence is not limited to low concentrations.
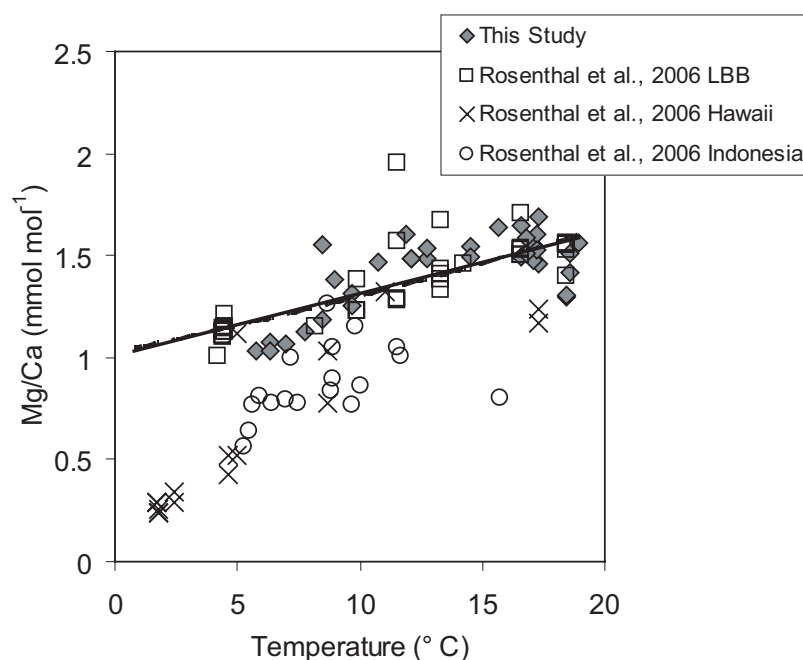
Figure 2.9: Comparison of individual *H. elegans* Mg/Ca measurements to measurements by Rosenthal et al. [2006]. The different regions of Rosenthal et al. core-tops are shown to highlight the influence of carbonate ion concentration. LBB stands for Little Bahama Bank. Equations 9 (solid line) and 10 (dashed line) are shown; the two regressions are overlapping.

Influence of Carbonate Saturation State

It has been proposed that Mg/Ca may be suppressed during calcification due to low ΔCO_3^{2-} [Martin et al., 2002; Elderfield et al., 2006; Rosenthal et al., 2006].

Martin et al. [2002] noticed that abyssal *C. wuellerstorfi* had a steeper Mg/Ca –

temperature slope than that of *C. pachyderma* found at warmer temperatures; the

steeper slope was attributed to decreased saturation at the colder sites. Assuming that

Cibicidoides Mg/Ca is unaffected by ΔCO_3^{2-} at temperatures greater than 2°C,

Elderfield et al. [2006] determined that *C. wuellerstorfi* Mg/Ca decreases by ~0.0086

mmol mol^{-1} per µmol kg^{-1} decrease in ΔCO_3^{2-} over a ΔCO_3^{2-} range of -20 to 80 µmol

kg^{-1}; ΔCO_3^{2-} has a negative influence below ~20 µmol kg^{-1} and a positive influence

above that point. Rosenthal et al. [2006] similarly determined that Mg/Ca of the

aragonitic foraminifer *H. elegans* decreases by ~0.017 per µmol kg^{-1} decrease in

ΔCO_3^{2-} below 15 µmol kg^{-1}.

ΔCO_3^{2-} at the Florida Straits multi-core sites range from 46 to 161 µmol kg^{-1}

with respect to calcite and 22 to 138 µmol kg^{-1} with respect to aragonite. These

values are higher than the deep sea sites where Elderfield et al. [2006] reported a

negative ΔCO_3^{2-} influence on *C. wuellerstorfi*. Rosenthal et al. [2006] concluded that

ΔCO_3^{2-} does not significantly affect *H. elegans* above ~15 µmol kg^{-1}. Therefore,

Mg/Ca at the Florida Straits multi-core sites is not expected to be significantly

affected by ΔCO_3^{2-}. However, we do observe a change in slope of the Mg/Ca –

temperature relationship over the range of the calibration. The Mg/Ca – temperature

slope is steeper at low temperatures and less steep at higher temperatures. The slope

of the *C. pachyderma* Mg/Ca – temperature relationship covering the <11°C interval

is 0.22, whereas the slope covering the >11°C interval is 0.087. The slope for *U.*

peregrina <11°C is 0.096 and >11°C is 0.044. The slope for *H. elegans* <11°C is

0.089, while the slope >11°C is actually negative (-0.0078). As was noted above, *P.*

foveolata found at warm multi-core sites has a lower slope (0.04) than *P. ariminensis* (0.17), which was predominantly found at the cooler sites. Perhaps the ΔCO_3^{2-} effect extends much higher into saturated waters than originally thought, decreasing the Mg/Ca of the samples at the lower end of the calibration. Alternatively, it is possible that Mg/Ca is reduced at the higher end of the calibration due to high carbonate ion concentration. A ΔCO_3^{2-} influence at high concentrations could explain the apparent reduction in temperature sensitivity at higher temperatures. Culturing studies of planktonic [Lea et al., 1999; Russell et al., 2004] and benthic [Hintz et al., 2006c] foraminifera have shown decreases in Mg/Ca with increasing pH or carbonate ion concentration.

It is difficult to separate the effects of ΔCO_3^{2-} and temperature in this data set due to their strong correlation in the Florida Straits ($R^2 = 0.96$), but core-top measurements from the western Mediterranean are consistent with a decrease in Mg/Ca due to high ΔCO_3^{2-}. Cacho et al. [2006] report an average core-top *C. pachyderma* Mg/Ca of 1.96 mmol mol^{-1} at eight sites with modern bottom water temperatures of 12.7°C and ΔCO_3^{2-} of 149 µmol kg^{-1}. This Mg/Ca value plots below the Florida Straits and Little Bahama Bank measurements, and reconstructed temperatures using either the exponential or the linear calibrations are much too cold [Cacho et al., 2006]. Their reported ΔCO_3^{2-} is ~70 µmol kg^{-1} higher than the ΔCO_3^{2-} at similar temperatures in the Florida Straits. If the Mg/Ca value for 12.7°C should be ~2.67 mmol mol^{-1} as determined from Eq. 1, then the sensitivity of Mg/Ca to ΔCO_3^{2-} would be about -0.01 mmol mol^{-1} per 1 µmol kg^{-1}. Interestingly this is the very similar to sensitivity determined by Elderfield et al. [2006], except in the

opposite direction. Since the slope of Equation 1 is likely too low, due reduced Mg/Ca at the warm Florida Straits multi-core sites, the sensitivity of Mg/Ca to ΔCO_3^{2-} may be higher.

A Working Hypothesis

Suppression of Mg incorporation at high carbonate ion saturation is likely related to physiological processes sensitive to changes in saturation state that affect the internal calcification pool. With the data set presented here, it is not possible to determine if Mg/Ca suppression is solely due to ΔCO_3^{2-}, or if other environmental variables are involved. Additional core-top and culturing studies are necessary to sort out the exact causes. However, if these physiological processes also influence other trace elements incorporated in to the foraminiferal calcite, perhaps we can correct for the Mg/Ca suppression at high ΔCO_3^{2-} by using another element.

Lithium is a conservative monovalent cation incorporated into foraminiferal calcium carbonate in trace quantities. It has been proposed that foraminiferal Li/Ca increases with decreasing temperature [Marriott et al., 2004], increasing carbonate ion concentration [Hall and Chan, 2004; Lear and Rosenthal, 2006], and increasing seawater Li/Ca (which may be a proxy for hydrothermal activity and continental weathering on million year timescales) [Delaney and Boyle, 1986; Hathorne and James, 2006]. Benthic foraminiferal Li/Ca (Table 2.4) in the Florida Straits multi-cores increases with increasing depth, and Great Bahama Bank sites have lower Li/Ca than Dry Tortugas sites at similar depths (Figure 2.10), opposite the patterns observed for Mg/Ca. Li/Ca for all species is negatively correlated with temperature (Figure 2.11) and ΔCO_3^{2-} (Figure 2.12). These trends agree with those observed by Hall and

Chan [2004] in Little Bahama Bank core-tops. Hall and Chan [2004] also found that benthic foraminiferal Li/Ca was elevated by 20-50%, depending on species and water depth, during the Last Glacial Maximum. The authors noted that decreased temperature was insufficient to account for the elevated glacial values; they proposed that increased calcification rate due to increased carbonate ion concentration could explain the glacial/interglacial changes. An increase in Li/Ca with increasing CO_3^{2-} is opposite to the trend observed in the Florida Straits and Little Bahama Bank core tops. However, there is evidence that at low CO_3^{2-} Li/Ca decreases with decreasing ΔCO_3^{2-} [Lear and Rosenthal, 2006]. The relationship between Li/Ca and CO_3^{2-} is obviously complex and it seems unlikely that Li/Ca may be used as a direct proxy for CO_3^{2-}, but it still may be useful in correcting Mg/Ca.

In inorganic calcite, the incorporation of alkali metals has been observed to increase with increasing magnesium concentration of the parent solution (in solutions with less than half the Mg concentration of modern seawater) [Okumura and Kitano, 1986]. The authors explained the correlation through distortions of the calcite structure as more Mg is incorporated in to the calcite. However, since there is not a positive correlation between Mg/Ca and Li/Ca in the benthic foraminifera, it is unlikely that benthic foraminiferal Li/Ca can be explained by structural defects. Perhaps the relationship between Li/Ca and [Mg] is related to ionic interactions within the parent solution, as was proposed for aragonite [Okumura and Kitano, 1986]. While the Mg concentration is relatively constant in seawater, if foraminifera calcify from an internal calcification pool, the internal Mg concentration may vary due to biological alteration [Erez, 2003]. I hypothesize that foraminiferal Mg

incorporation is reduced at high carbonate ion concentrations (or at some combination of parameters occurring at our warmest sites) due to biological removal of Mg from the internal calcification solution. Lower Mg/Ca in the parent solution is expected to lead to lower Mg/Ca values in the shell [Morse and Bender, 1990; Segev and Erez, 2006]. The physiological reason for removal of additional Mg at high ΔCO_3^{2-} or high temperature is unknown, and this hypothesis is based primarily on the observations of Mg/Ca in the Florida Straits samples.   However, if foraminiferal Li/Ca reflects the internal Mg content, then as the internal Mg concentration is reduced, the shell Li/Ca will also be reduced. If we divide Mg/Ca by Li/Ca, then we may be able to correct for the alteration of the internal parent solution, regardless of the mechanism behind the alteration.

Core	C. pachyderma Li/Ca	Mg/Li	U. peregrina Li/Ca	Mg/Li	P. ariminensis Li/Ca	Mg/Li	P. foveolata Li/Ca	Mg/Li	H. elegans Li/Ca	Mg/Li
5	13.04	0.160	17.37	0.085	12.93	0.162			3.90	0.398
5	*8.76*	*0.229*	17.42	0.084	12.87	0.158			3.75	0.317
11	12.38	0.108	16.96	0.063					3.86	0.268
11			17.27	0.059						
13	12.82	0.182	16.50	0.092	12.66	0.186			3.89	0.338
13	13.09	0.187	16.52	0.092	12.39	0.182			3.83	0.328
16	12.20	0.197								
16	12.12	0.188								
19	12.22	0.171					12.48	0.206	3.77	0.394
19	12.61	0.217							3.79	0.405
22	*15.93*	*0.165*	16.97	0.087					4.20	0.329
22	13.43	0.185	16.91	0.085						
24			17.77	0.095					3.62	0.310
28	13.31	0.106	16.90	0.067					3.79	0.283
28	13.36	0.115	16.90	0.068					3.74	0.276
50	12.05	0.198			12.37	0.221	12.33	0.220	3.85	0.386
50	12.02	0.206								
53	12.61	0.188	16.34	0.089	12.44	0.191			*8.48*	*0.250*
53	12.47	0.176	16.27	0.087	12.55	0.188			*9.32*	*0.235*
55	13.07	0.179	16.79	0.098	14.17	0.158			*5.64*	*0.998*
55	13.22	0.170	17.25	0.098	13.82	0.159			*5.12*	*0.884*
62	13.27	0.165	17.24	0.079	13.40	0.129			3.56	0.301
62			17.07	0.084						
66									3.28	0.475
68	11.19	0.294					11.53	0.246	3.65	0.451
68	11.43	0.296							3.36	0.444
72	13.14	0.219	17.14	0.095			16.80	0.137	4.56	0.322
72	13.25	0.214	16.94	0.095						
76	12.94	0.222	16.79	0.102	12.43	0.179	12.55	0.193		
76	12.90	0.216								
79	13.12	0.255	16.07	0.118			11.76	0.220	3.87	0.383
79	12.93	0.244	16.23	0.116						
84	13.73	0.180								
89	11.32	0.304					11.33	0.233		
92	12.86	0.248	16.28	0.123					3.78	0.433
94	10.88	0.307							2.69	0.483
94	11.04	0.315							4.21	0.310
97	11.02	0.297							3.27	0.463
97	11.00	0.295							3.02	0.469
103	13.01	0.177	16.96	0.086	13.20	0.140				
103	13.25	0.177								
110	12.47	0.265	14.98	0.143			11.61	0.237	3.65	0.462
110			15.28	0.140			11.46	0.240	3.24	0.450
112	11.93	0.244							3.23	0.458
112									3.41	0.456
118	13.28	0.202	16.26	0.114			12.26	0.197	4.02	0.384
118			16.24	0.113					3.98	0.376
121	12.66	0.196	16.27	0.114					4.33	0.370
121	12.45	0.214								
123	12.73	0.191								
123	12.77	0.207								
125	13.26	0.187			15.19	0.121				
134	11.51	0.255					12.09	0.223	3.65	0.440
134	11.66	0.269							3.51	0.434
138	11.92	0.215	15.86	0.119			11.91	0.218	3.87	0.410
138							11.87	0.227	3.68	0.411

Table 2.4: Benthic foram Li/Ca and Mg/Li measurements for each species by core. See Table 2.2 for core locations and seawater properties and Table 2.3 for Mg/Ca values. Li/Ca units are μmol mol^{-1}, and Mg/Li units are mol mmol^{-1}. Two *C. pachyderma* and four *H. elegans* measurements were

excluded due to values much higher or much lower than sample splits and nearby cores. The *C. pachyderma* measurements are likely anomalous due to a small sample size. Excluded measurements are *italicized*.
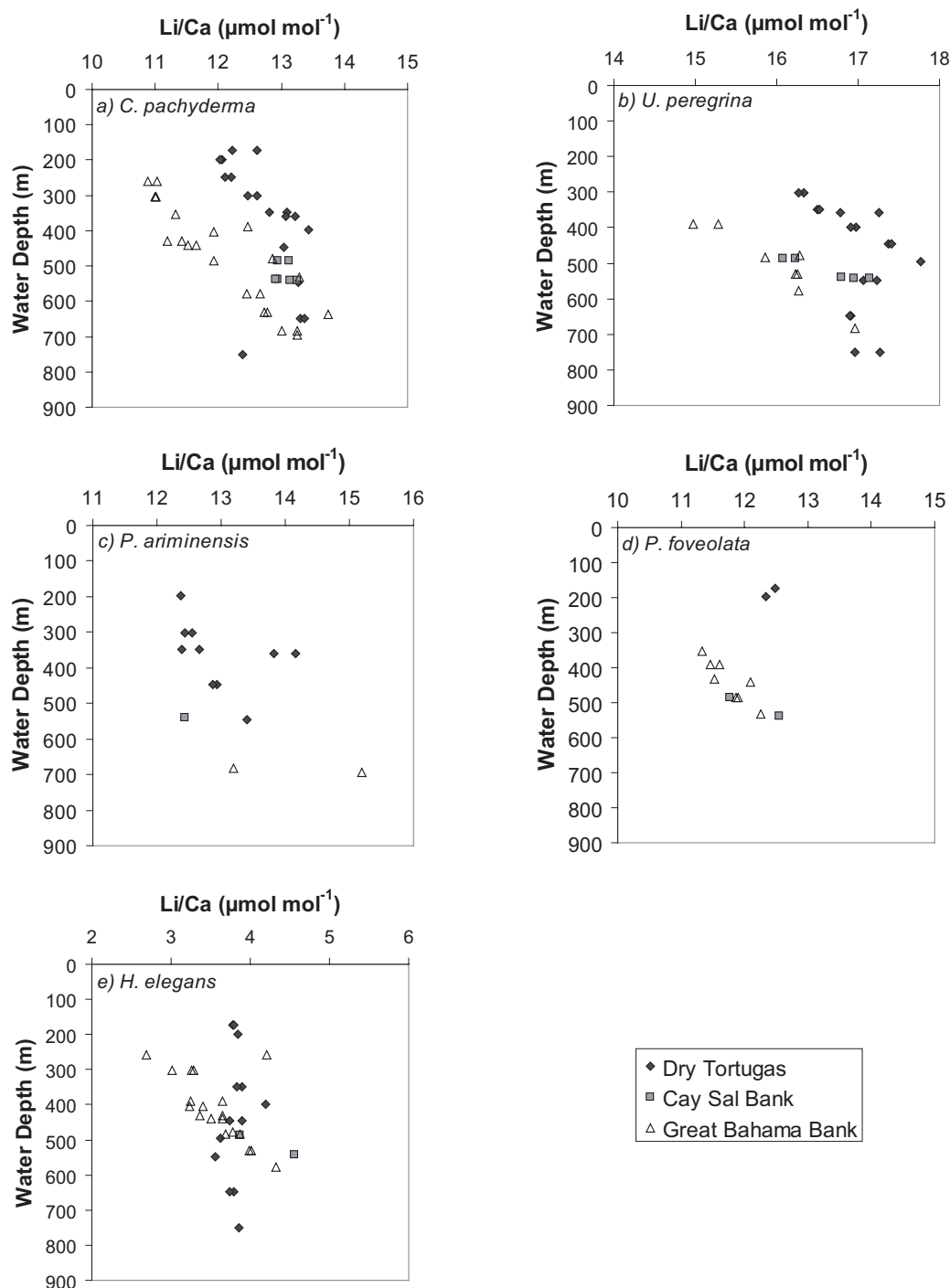
Figure 2.10: Individual Li/Ca vs. water depth for a) *C. pachyderma*, b) *U. peregrina*, c) *P. ariminensis*, d) *P. foveolata*, and e) *H. elegans*. Diamonds are multi-cores near Dry Torugas; squares are near Cay Sal Bank, and triangles are near Great Bahama Bank. Note the different Li/Ca scales.
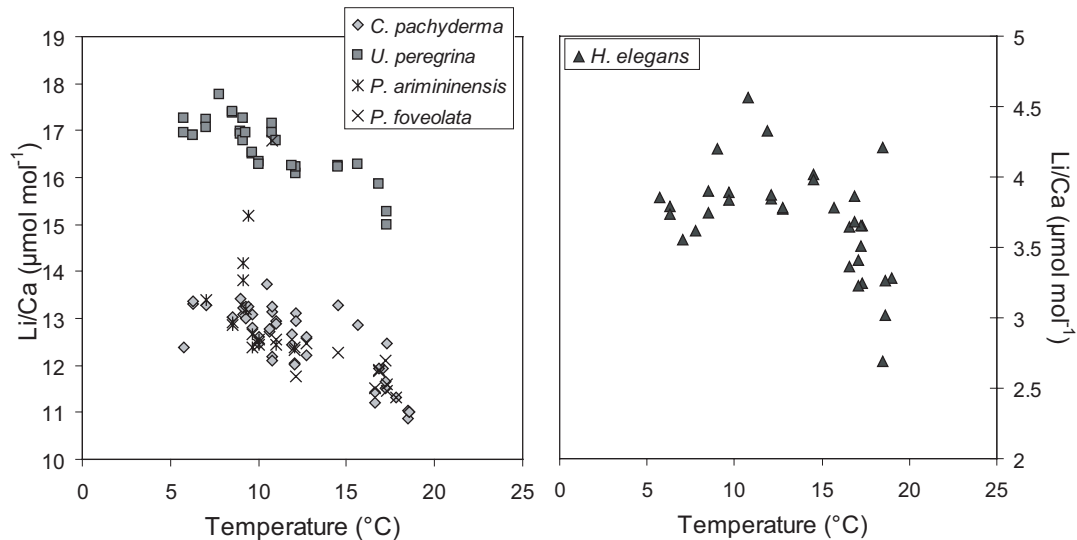
Figure 2.11: Li/Ca vs. bottom water temperature for the Florida Straits multi-cores. Calcitic species are shown in the left graph, and the aragonitic species *H. elegans* is shown in the right graph. Li/Ca for all species decreases with increasing temperature and there are large differences between the species.
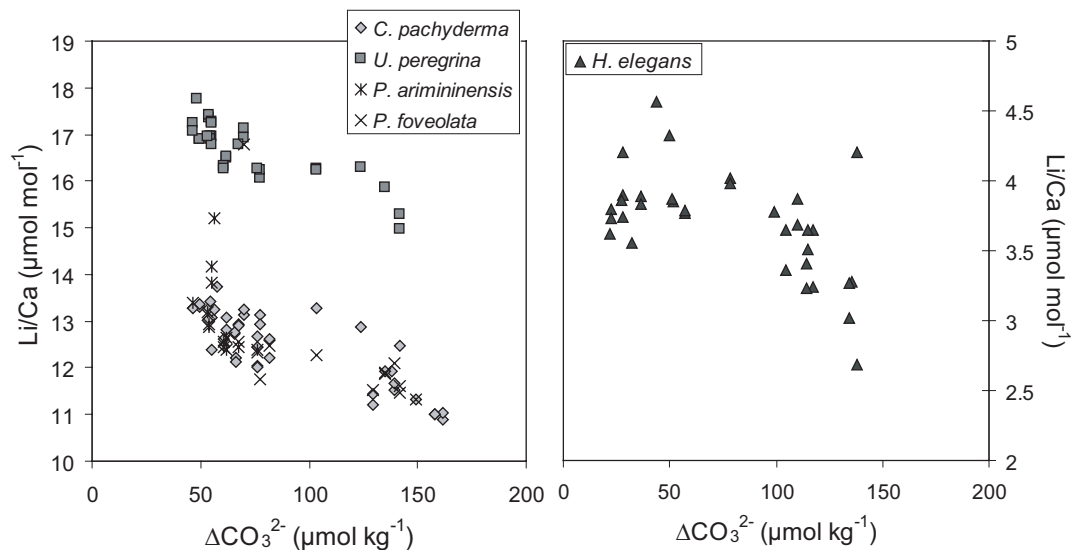
Figure 2.12: Li/Ca vs. ΔCO_3^{2-} for the Florida Straits multi-cores. Calcitic species are shown in the left graph, and the aragonitic species *H. elegans* is shown in the right graph. Li/Ca for all species decreases with increasing ΔCO_3^{2-} and there are large differences between the species.

Dividing Mg/Ca by Li/Ca removes the apparent flattening of the temperature regressions at high temperature (Figure 2.13). For all species except *P. ariminensis* the Mg/Li – temperature linear regression has a higher R^2 value and lower standard

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error than the Mg/Ca – temperature linear regression (Table 2.5). The *P. ariminensis*

values are about the same; since *P. ariminensis* was not found at the warmest multi-

core sites, it does not have a reduced slope to correct for. The improvement is

especially remarkable for *H. elegans*: the R^2 of the Mg/Ca – temperature regression is

0.49, while the R^2 of the Mg/Li – temperature regression is 0.90.

C. pachyderma	Mg/Li = 0.0124±0.0009 T + 0.062±0.01	$R^2 = 0.81$	$p < 0.0001$	$n = 46$ (14)
U. peregrina	Mg/Li = 0.0061±0.0004 T + 0.033±0.004	$R^2 = 0.90$	$p < 0.0001$	$n = 28$ (15)
P. ariminensis	Mg/Li = 0.017±0.004 T + 0.00±0.04	$R^2 = 0.59$	$p = 0.002$	$n = 11$ (16)
P. foveolata	Mg/Li = 0.008±0.002 T + 0.10±0.03	$R^2 = 0.52$	$p = 0.005$	$n = 11$ (17)
Combined *Planulina*	Mg/Li = 0.009±0.001 T + 0.08±0.01	$R^2 = 0.71$	$p < 0.0001$	$n = 24$ (18)
H. elegans	Mg/Li = 0.0143±0.0009 T + 0.20±0.01	$R^2 = 0.90$	$p < 0.0001$	$n = 31$ (19)

|	Mg/Ca		Mg/Li	
Species	R^2	**SE (°C)**	R^2	**SE (°C)**
C. pachyderma	0.73	2.4	0.81	1.8
U. peregrina	0.82	1.6	0.90	1.1
P. ariminensis	0.63	1.0	0.59	1.1
P. foveolata	0.44	3.2	0.52	2.7
Combined *Planulina*	0.67	2.5	0.71	2.2
H. elegans	0.49	4.5	0.90	1.4

Table 2.5: Comparison of Mg/Ca – temperature linear regressions and Mg/Li – temperature linear regressions. The SE is the temperature equivalent of the standard error of the estimate.

It is important to note that Okumura and Kitano [1986] observed differences

in the behavior of Li/Ca in aragonite vs. calcite, with the Li/Ca in aragonite

decreasing slightly with increasing Mg concentration. However, it is unclear whether

this difference was due to the mineralogy or to a change in the sensitivity of Li/Ca to

[Mg] at higher concentrations, since calcite was precipitated at low [Mg] (< ~1/3 of

modern seawater [Mg]) and aragonite at high [Mg] (< ~1/2 of modern seawater

[Mg]). It may be that Li/Ca is only sensitive to [Mg] at low concentrations. It is also

unlikely that foraminiferal Li/Ca will behave exactly the same as Li/Ca in inorganic

CaCO$_3$. While we cannot be certain of the mechanism relating Mg and Li, the Mg/Li - temperature relationships determined from the Florida Straits measurements fit the Little Bahama Bank *H. elegans* measurements of Hall and Chan [2004] and the Arabian Sea *U. peregrina* measurements of Marriott et al. [2004] (Figure 2.13), indicating that the relationship is not coincidental from one data set. This hypothesis should be tested by the addition of paired Mg/Ca and Li/Ca measurements from other regions and further investigation of the effects of carbonate saturation state on the biomineralization process.
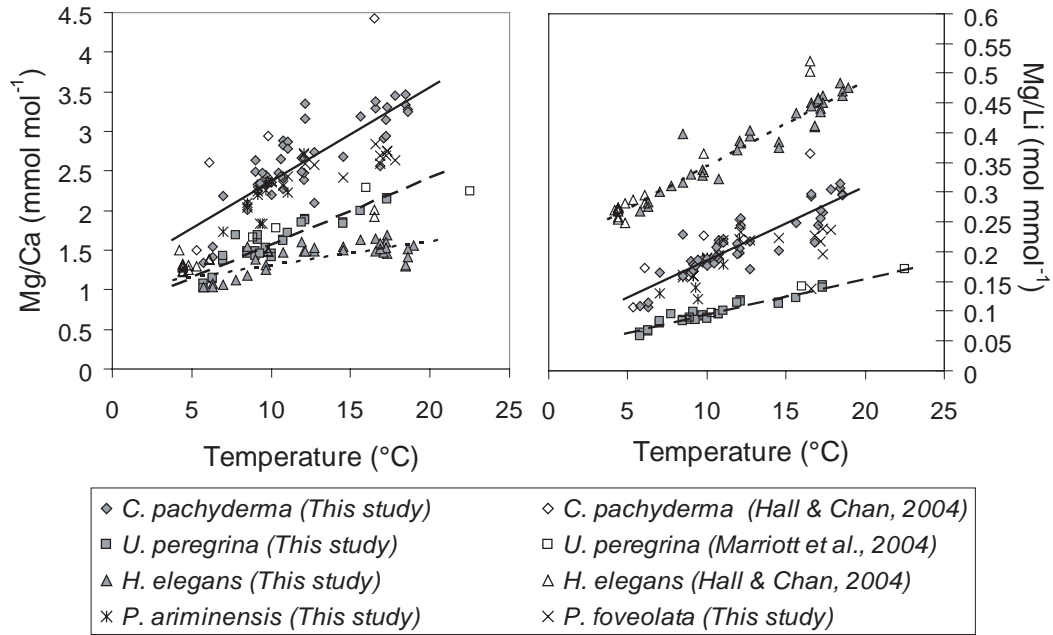
Figure 2.13: Mg/Ca and Mg/Li plotted vs. bottom water temperature for *C. pachyderma* (diamonds), *U. peregrina* (squares), *P. ariminensis* (asterixes), *P. foveolata* (x's) and *H. elegans* (triangles). Several other published Mg/Li measurements are plotted for comparison. The one Hall and Chan [2004] *C. pachyderma* Mg/Ca measurement that is very high may be afflicted by the same Little Bahama Bank overgrowth problem as those of Lear et al. [2002]. Linear regressions through the measurements of this study are shown: *C. pachyderma* (Eqs. 2 & 14, solid lines), *U. peregrina* (Eqs. 4 & 15, dashed lines), *and H. elegans* (Eqs. 9 & 19, dotted lines).

Sr/Ca in Calcitic Species

Sr/Ca in the calcitic species generally decreases with increasing depth and the Great Bahama Bank multi-cores have higher Sr/Ca than Dry Tortugas multi-cores at similar depths (Figure 2.4). *U. peregrina* measurements are lower than those of the other species, and the two *Planulina* species are slightly higher than *C. pachyderma*. Sr/Ca is positively correlated with temperature, salinity and carbonate saturation (Table 2.6; Figure 2.14); there is more scatter than in Mg/Ca and p-values are high for the *Planulina spp*.

	Depth	Temperature	Salinity	ΔCO_3^{2-}
C. pachyderma	$R^2 = 0.03$ p-value = 0.22	$R^2 = 0.62$ p-value < 0.0001	$R^2 = 0.63$ p-value < 0.0001	$R^2 = 0.64$ p-value < 0.0001
U. peregrina	$R^2 = 0.16$ p-value = 0.03	$R^2 = 0.43$ p-value < 0.0001	$R^2 = 0.31$ p-value = 0.0014	$R^2 = 0.23$ p-value = 0.0076
P. ariminensis	$R^2 = 0.19$ p-value = 0.13	$R^2 = 0.04$ p-value = 0.53	$R^2 = 0.04$ p-value = 0.51	$R^2 = 0.01$ p-value = 0.73
P. foveolata	$R^2 = 0.32$ p-value = 0.045	$R^2 = 0.33$ p-value = 0.038	$R^2 = 0.3$ p-value = 0.036	$R^2 = 0.33$ p-value = 0.040

Table 2.6: R^2 and p-values for linear regressions of the Sr/Ca of each species and depth, temperature, salinity and ΔCO_3^{2-}.

The differences between the different regions of the Florida Straits at similar depths indicate that pressure is not the dominant control on Sr/Ca over the small depth range sampled in this study. This does not however negate a depth-related influence on Sr/Ca over large depth ranges [McCorkle et al., 1995; Elderfield et al., 1996; Rosenthal et al., 1997]. Sr/Ca variations in the Florida Straits are small compared to the global data set [Rosenthal et al., 1997] (Figure 2.15). *C. pachyderma* Sr/Ca measurements in the Florida Straits are ~0.3 mmol mol^{-1} higher than *C. wuellerstorfi* measurements from the deep Ontong-Java Plateau (> 4km) [McCorkle et al., 1995]. Florida Straits *U. peregrina* measurements are ~0.4 mmol mol^{-1} higher than *Uvigerina spp*. measurements from the deep eastern equatorial Pacific (3205m)

and ~0.45 mmol mol^{-1} higher than *Uvigerina spp.* measurements from the deep

equatorial Atlantic (3912m) [Martin et al., 1999]. These observations support a

depth-related process as the dominant control on Sr/Ca throughout the oceans;

however, the Florida Straits measurements indicate that other variables may be

important in assessing changes at a single location.
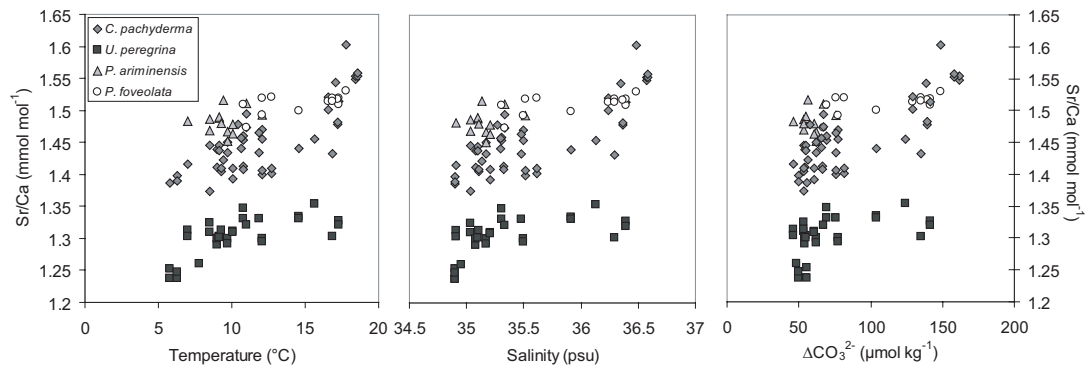
Figure 2.14: Sr/Ca for each of the calcitic species plotted vs. temperature (left), salinity (middle) and ΔCO_3^{2-} (right).
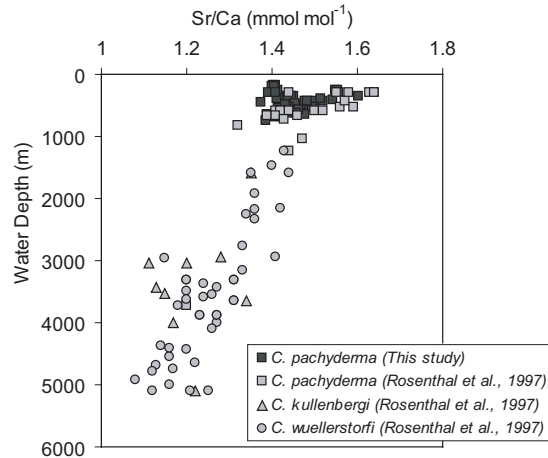
Figure 2.15: Florida Straits *C. pachyderma* Sr/Ca (dark gray symbols) compared to the *Cibicidoides spp.* global data set of Rosenthal et al. [1997] (light gray symbols) plotted vs. water depth. The Rosenthal et al. [1997] data set has been split up by species.

As was stated previously, temperature and carbonate ion concentration as well

as salinity are strongly correlated in the Florida Straits, making the separation of these

influences difficult. If all of the Florida Straits Sr/Ca variation were due to

temperature, *C. pachyderma* Sr/Ca would increase by ~0.011 mmol mol^{-1} or ~0.78%

per °C increase in temperature. If all of the variation was due to salinity, Sr/Ca would increase by ~0.019 mmol mol^{-1} or ~1.3% per 1 psu increase in salinity. Likewise if all of the variation was due to ΔCO_3^{2-}, *C. pachyderma* Sr/Ca would increase by ~0.011 mmol mol^{-1} or ~0.76% per 10 μmol kg^{-1} increase in ΔCO_3^{2-}. These responses are slightly smaller for temperature, slightly larger for salinity and ~2x larger for ΔCO_3^{2-} than those of planktonic foraminifera determined from culturing experiments [Lea et al., 1999; Russell et al., 2004], suggesting that a combination of the three variables may be responsible for the Sr/Ca variance over the multi-core sites.

A portion of the temperature influence on Sr/Ca may be indirect, through an increase in Sr/Ca as Mg/Ca increases [Carpenter and Lohmann, 1992; Shen et al., 2001]. A positive correlation between Sr/Ca and Mg/Ca has been observed in inorganic calcite as well as in various calcitic organisms; this correlation is probably related to increasing lattice strain due to Mg incorporation [Carpenter and Lohmann, 1992]. We observe a positive correlation between Sr/Ca and Mg/Ca within and between species (Figure 2.16), consistent with the conclusions of Carpenter and Lohmann [1992]. An additional potential complication to shallow benthic Sr/Ca is spatial Sr/Ca gradients of 2-3% in the modern ocean due to the production of celestite ($SrSO_4$) skeletons by surface-dwelling acantharia [de Villiers, 1999].
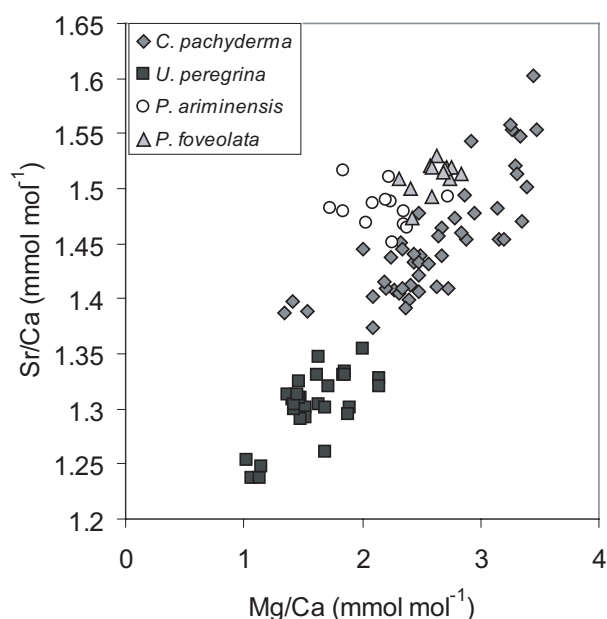
Figure 2.16: Florida Straits Mg/Ca vs. Sr/Ca for each of the calcitic species. There is a strong correlation between Mg/Ca and Sr/Ca for all of the calcitic measurements ($R^2 = 0.68$, p-value < 0.0001).

Given the small amplitude of expected glacial – interglacial seawater Sr/Ca changes (1-3%) [Stoll and Schrag, 1998] and the multitude of environmental variables that may influence Sr/Ca; down-core benthic foraminiferal Sr/Ca records should be interpreted with caution, especially in regions of the ocean that may have been affected by the interplay of different deep water masses [Shen et al., 2001]. The best results for seawater Sr/Ca reconstructions are likely to come from stacking benthic foraminiferal Sr/Ca records from multiple cores [Martin et al., 1999].

Sr/Ca in *H. elegans*

H. elegans Sr/Ca is much higher and variations are much larger than in the calcitic species; this is expected, as $SrCO_3$ is isostructural with aragonite. *H. elegans* Sr/Ca in the Florida Straits is positively correlated with temperature ($R^2 = 0.91$, p-value <0.0001) and carbonate saturation ($R^2 = 0.81$, p-value < 0.0001); these R^2 values are much higher than for *H. elegans* Mg/Ca vs. temperature and ΔCO_3^{2-}. The

Florida Straits measurements agree well with the Little Bahama Bank core-tops of

Rosenthal et al. [2006] (Figure 2.17). Rosenthal et al. [2006] proposed a strong

ΔCO_3^{2-} influence below ~15 µmol kg^{-1} (below the minimum seawater values in the

Florida Straits) while temperature was the major influence at higher saturation.

Rosenthal et al. [2006] separated the temperature and ΔCO_3^{2-} influences by assuming

that Sr/Ca at Little Bahama Bank sites was only influenced by temperature; the

departure of Hawaii and Indonesia Sr/Ca measurements from the Little Bahama Bank

Sr/Ca - temperature relationship was then assumed to be due to ΔCO_3^{2-}. The Florida

Straits measurements are consistent with this theory. The Florida Straits and Little

Bahama Bank have similar carbonate ion concentrations, which are higher than those

at the Hawaii and Indonesia sites. A linear regression fit to the Florida Straits

measurements with temperature is identical within error to that of Rosenthal et al.

[2006]. We cannot, however, rule out a ΔCO_3^{2-} influence above ~15 µmol kg^{-1}; it is

possible that temperature and ΔCO_3^{2-} combine to account for the variance seen over

the Florida Straits multi-core sites. A *H. elegans* Sr/Ca reconstruction of the last

glacial maximum would shed some light on the relative influences of temperature and

ΔCO_3^{2-}.
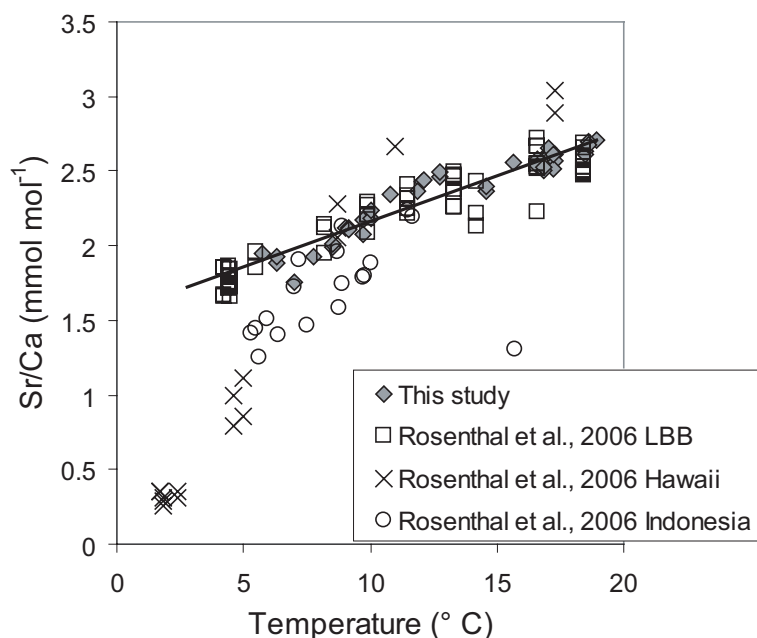
Figure 2.17: Comparison of *H. elegans* Sr/Ca to measurements by Rosenthal et al. [2006]. The different regions of Rosenthal et al. [2006] core-tops are shown to highlight the influence of carbonate ion concentration. The line is a linear regression through the measurements of this study (Sr/Ca = $0.061\pm0.0031T + 1.55\pm0.043$, $R^2 = 0.91$).

Conclusions

Core-top calibrations of Mg/Ca and Sr/Ca in several species of benthic foraminifera were conducted using a suite of multi-cores from the Florida Straits. Benthic foraminiferal Sr/Ca is likely influenced by multiple environmental variables, but a depth-related process seems to be the dominant control on Sr/Ca throughout the ocean. These findings indicate that the use of benthic foraminiferal Sr/Ca to reconstruction seawater Sr/Ca over glacial/interglacial timescales may be subject to large uncertainties, especially in regions of the ocean where large changes in temperature, salinity or ΔCO_3^{2-} have occurred. Benthic foraminiferal Mg/Ca is well correlated with bottom water temperature. The sensitivity of Mg/Ca to temperature decreases at higher temperatures, contrary to the expected increase in sensitivity in an

exponential relationship. The combined thermodynamic and physiological influences on Mg/Ca may result in a more linear relationship to temperature. Alternatively, the decrease in sensitivity at higher temperatures could be explained by Mg/Ca suppression due to high carbonate saturation state. If this is true, it would complicate Mg/Ca paleotemperature reconstructions. The influence of carbonate ion concentration should be tested further though laboratory culturing and additional core-top measurements from regions with differing temperature - CO_3^{2-} relationships. Li/Ca may be useful in correcting for biological removal of Mg from the internal calcification solution. Empirically Mg/Li has a strong linear relationship to temperature. Mg/Li may prove to be a more reliable paleotemperature proxy than Mg/Ca alone; although additional measurements are needed.

III. Paleonutrient Proxies: Cd/Ca & Zn/Ca

Abstract

Understanding the response and contribution of upper ocean processes to atmospheric CO_2 and climate variability in the past is crucial to predicting the role the upper ocean will play under future climate change. Reconstructions of paleonutrient concentrations in thermocline waters provide information of past nutrient cycling and circulation. Two potential upper ocean nutrient proxies are the Cd/Ca and Zn/Ca of benthic foraminifera. However, there are few benthic foraminiferal Cd/Ca measurements from shallow waters, and there are no Zn/Ca measurements from depths <1500m. Cd/Ca and Zn/Ca in several species of benthic foraminifera (*Cibicidoides pachyderma, Uvigerina peregrina, Planulina ariminensis, Planulina foveolata,* and *Hoeglundina elegans*) are calibrated from a set of 32 high quality multi-cores collected in the Florida Straits. Multi-core sites span depths of 173 - 751m, estimated seawater Cd concentrations of 0.002 - 0.47 nmol kg^{-1}, and estimated seawater Zn concentrations of 0.19 – 3.1 nmol kg^{-1}. The Cd/Ca of the benthic foraminifera reliably record seawater Cd concentrations with a partition coefficient of ~1.9 for the calcitic species and ~1.2 for the aragonitic species *H. elegans*. Additionally, Cd incorporation may be slightly influenced by temperature and/or carbonate ion saturation. The measurement of Zn/Ca is plagued by laboratory contamination especially at low concentrations. However, at least one species, *C. pachyderma*, shows great promise for recording seawater Zn concentrations with a high partition coefficient of ~19.

Introduction

Understanding upper ocean nutrient availability and cycling in the past is important to understanding the role of the biological pump in atmospheric CO_2 changes [eg. Broecker, 1982; Sigman and Boyle, 2000]. Paleonutrient reconstructions may also be used to investigate changes in upper ocean circulation [eg. Slowey and Curry, 1995; Marchitto et al., 1998; Willamowski and Zahn, 2000].

Two proxies for seawater nutrient concentrations in the upper ocean are the Cd/Ca and Zn/Ca of benthic foraminifera. Benthic foraminifera from shallow depths intersect the thermocline and avoid uncertainties related to the varying depth habitats of planktonic foraminifera [Slowey and Curry, 1992, 1995]. Cadmium displays a labile nutrient-type distribution in seawater, and is well correlated with phosphate [Boyle et al., 1976; Boyle, 1988; Elderfield and Rickaby, 2000]. Zinc displays a refractory nutrient-type distribution with a deeper regeneration cycle than phosphate; zinc is well correlated with silica in the ocean [Bruland et al., 1978; Bruland and Franks, 1983; Martin et al., 1993]. Cd and Zn are incorporated into the calcium carbonate tests of benthic foraminifera in proportion to the seawater Cd and Zn concentrations respectively [Hester and Boyle, 1982; Marchitto et al., 2000].

Cd/Ca of benthic foraminifera has been used extensively to investigate patterns of past deep ocean circulation [eg. Boyle and Keigwin, 1982, 1985/86; Boyle, 1992; Rosenthal et al., 1997a; Marchitto and Broecker, 2006]. Zn/Ca is a newer paleonutrient proxy, but it has been used to investigate deep ocean circulation and carbonate saturation [Marchitto et al., 2002; Marchitto et al., 2005]. In contrast to the work on deep ocean reconstructions, there have been few measurements of

Cd/Ca in thermocline waters and no measurements of Zn/Ca in waters <1500m. The original calibration of Cd/Ca for the upper ocean (<1150m) by Boyle [1992] was based on eight core-tops and established a partition coefficient (D_{Cd}) of ~1.3 for calcitic benthic foraminifera, where $D_{Cd} = Cd/Ca_{foram} / Cd/Ca_{seawater}$. This partition coefficient less than half of that found in waters deeper than 3000m, and the cause of the depth dependence is unknown. Later core-top calibrations from the Little Bahama Bank confirmed that Cd/Ca reflects seawater Cd concentrations in shallow waters but hinted that D_{Cd} may be slightly higher than 1.3 [Rosenthal et al., 1997; Marchitto, 2004]. The aragonitic *Hoeglundina elegans* appears to have a partition coefficient of ~1, independent of water depth [Boyle et al., 1995]; however this calibration only contains nine measurements from water depths < 1000m.

There are very few published down-core records of benthic Cd/Ca from thermocline waters [van Geen et al., 1996; Marchitto et al., 1998]. These studies revealed important information about ventilation changes in the northeast Pacific [van Geen et al., 1996] and the interplay between North Atlantic Deep Water and Glacial North Atlantic Intermediate Water [Marchitto et al., 1998] Benthic Cd/Ca would likely prove useful in other studies of upper ocean circulation and nutrient cycling if the partition coefficient was better constrained. Additionally, Zn/Ca may add to the understanding of past nutrient cycling due to its deeper regeneration depth and correlation with silica, but its relationship to seawater [Zn] in the upper ocean is unknown.

New core-top Cd/Ca and Zn/Ca measurements are presented for several species of benthic foraminifera from a set of multi-cores collected in the Florida

Straits. Using these core-top measurements I will constrain the partition coefficients of Cd and Zn in the upper ocean and investigate the influence of environmental parameters such as temperature and carbonate saturation on Cd and Zn incorporation.

Materials & Methods

Samples for these calibrations were collected during R/V *Knorr* cruise 166-2, January 2002, in the Florida Straits. Sediments were collected from three regions: the western side of the Florida Current near Dry Tortugas; the eastern side of the Florida Current near Great Bahama Bank and the western side of the Santaren Current near Cay Sal Bank (Figure 2.1; Table 2.2). Thirty-eight successful multi-core casts were recovered each consisting of eight short cores (30-40cm long, 12cm diameter). The 0-1cm slice of one short core from thirty-two of those multi-core casts was used for this study.

Figure 3.1: Map of the Florida Straits study area. Multi-core sites are indicated by black dots.

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Multi-core sites cover depth, temperature, salinity, and CO_3^{2-} ranges of 173-751m, 5.8-18.6 °C, 34.9-36.8 psu, and 86-216 µmol kg^{-1} respectively (Figure 2.2). Sloping of isopycnals associated with the Florida Current causes the eastern side of the Florida Straits to have higher temperature, salinity and CO_3^{2-} at a given depth than the western side of the Straits. Fifty-five CTD casts were made during the course of the cruise. Bottom water samples from the multi-core sites were collected using a Niskin bottle attached to the multi-corer frame, which was rigged to close when the multi-corer hit the seafloor. Aliquots of the Niskin seawater were sampled for salinity, $\delta^{18}O$, alkalinity and ΣCO_2. Due to the sloping of isopycnals, bottom water temperatures could not be determined by simply matching the multi-core depth to a nearby CTD. Instead, bottom water temperatures were determined by matching the Niskin bottle salinities to the corresponding salinities of nearby CTD casts. At twelve of the multi-core sites this method was not possible due to bottle malfunction; at these sites salinity and temperature were derived from nearby CTDs using the average depth offset in salinity measurements between the multi-core sites and the CTDs. For the Dry Tortugas sites, 15m was added to the depth of the site and the CTD temperature and salinity at that depth was used. Likewise, at the Great Bahama Bank sites, 15m was subtracted from the multi-core depth and the CTD measurements at that depth were used. Carbonate ion concentrations for 12 of the multi-core sites were calculated from alkalinity and ΣCO_2 with the CO2SYS program v. 1.05 [Lewis and Wallace, 1998], using the first and second dissociation constants of carbonic acid from Hansson [1973] and Mehrbach et al. [1973] as refit by Dickson

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and Millero [1987]. For the other sites, CO_3^{2-} was inferred from a second-order polynomial relationship with salinity ($R^2 = 0.99$).

Figure 3.2: Profiles of temperature (a), salinity (b) and carbonate ion concentration (c) at the multi-core sites: Dry Tortugas sites (diamonds), Cay Sal Bank sites (squares) and Great Bahama Bank sites (triangles).

Seawater phosphate at the multi-core sites was estimated using bottom water temperatures and a linear relationship between PO_4 and temperature at nearby WOCE stations, AT109LG3 Stations 240 – 250 (~26°N, ~80°W), for T < 20°C ($R^2 = 0.95$). Seawater cadmium was then determined using the Atlantic Ocean Cd:P relationship of Elderfield and Rickaby [2000] (Cd = 1.2/(2.5*(3.3/P -1)+1)). Seawater cadmium was also estimated using the global Cd:P relationships of Boyle [1988] (Cd = 0.21*P, for P < 1.3 µmol kg^{-1}, and Cd = 0.40*P – 0.25, for P > 1.3 µmol kg^{-1}) for comparison. Seawater silica was estimated using bottom water temperature and a third order polynomial relationship between silica and temperature from the nearby WOCE sites ($R^2 = 0.99$). Seawater Zn was estimated using a linear relationship between Si and Zn determined from Si and Zn measurements from water depths less than 1km in the Atlantic Ocean (Zn = 0.145*Si) [Bruland and Franks, 1983; Martin et al., 1993; Ellwood and Van den Berg, 2000; P. Yeats and J. Dalziel, unpublished data, 1997] (Figure 3.3). This upper ocean Zn – Si relationship is forced through the origin and the slope is almost three times higher than the deep water (>1000m) global

relationship of Marchitto et al. [2000]. The slope difference indicates that the Zn – Si

relationship is not entirely linear; however it is unclear at what point and how rapidly

the slope decreases, due to the gap in paired Zn and Si measurements between Zn

concentrations of ~2 and ~5 nmol kg^{-1} [Marchitto et al., 2000]. Estimated bottom

water Cd and Zn concentrations at the multi-core sites are shown in Figure 3.4.

Estimated [Zn] at the Florida Straits multi-core sites approaches 4 nmol kg^{-1}; if the

slope decreases rapidly above 2 nmol kg^{-1}, then [Zn] estimates at the deeper Dry

Tortugas sites may be too high.
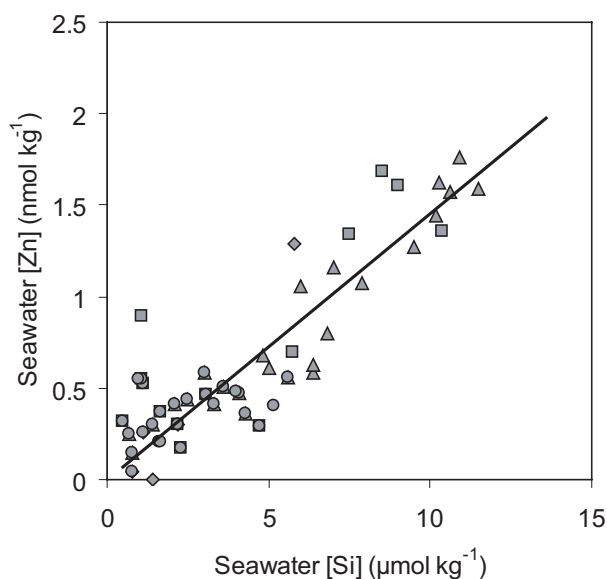
Figure 3.3: Paired seawater [Si] and [Zn] measurements from Bruland and Franks [1983] (diamonds), Ellwood and Van den Berg [2000] (squares), Martin et al. [1993] (triangles) and P. Yeats and J. Dalziel, unpublished data, 1997 (circles). The linear relationship between Si and Zn forced through the origin is [Zn] = 0.145 ±0.005 [Si], (R^2 = 0.91).
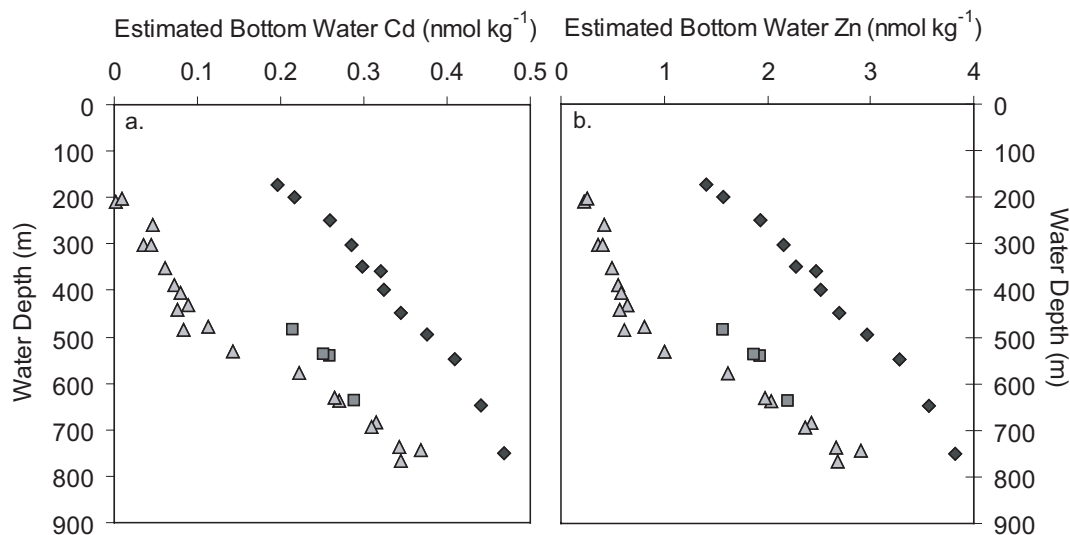
Figure 3.4: Estimated bottom water Cd (a.) (using the Elderfield and Rickaby [2000] relationship) and Zn (b.) concentrations at the multi-core sites. Dry Tortugas sites are indicated by diamonds; Cay Sal Bank sites are squares and Great Bahama Bank sites are triangles.

AMS radiocarbon ages were measured on *Globigerinoides ruber* (>250 μm) from the 0-1 or 0-2 cm slices from 14 of the KNR166-2 multi-cores [Lund and Curry, 2004, 2006; Lund, 2005]. Five of the core tops contained significant levels of "bomb" radiocarbon (fraction modern >1), three gave ages between 200 and 400 yr, and six ranged from 1000-3000 yr. Sedimentation rates in KNR166-2 cores range between 11 and 66 cm kyr^{-1} near Dry Tortugas and 20 to 350 cm kyr^{-1} on Great Bahamas Bank [Lund et al., 2006].

Benthic foraminifera *Cibicidoides pachyderma, Uvigerina peregrina, Planulina ariminensis, Planulina foveolata* and *Hoeglundina elegans* were picked from the 250-600μm size fraction of the 0-1cm slice of each core. Samples for trace element analysis contained 4-7 individuals (*C. pachyderma*), 9-10 individuals (*U. peregrina*), 13-15 individuals (*P. ariminensis*), 18-20 individuals (*P. foveolata*), and 9-10 individuals (*H. elegans*). Where abundances allowed, the number of individuals was doubled and samples were crushed, homogenized and split for replicate analysis.

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Crushed samples were cleaned reductively (using anhydrous hydrazine) and oxidatively (using H_2O_2) in a Class-1000 clean lab, following the methods of Boyle and Keigwin [1985/6] as modified by Boyle and Rosenthal [1996]. Samples were analyzed for Mg/Ca, Sr/Ca, Cd/Ca, Zn/Ca, Li/Ca, U/Ca, Mn/Ca and Fe/Ca by magnetic-sector single-collector ICP-MS, on a Thermo-Finnigan Element2, using methods adapted from Rosenthal et al. [1999] [Marchitto, 2006]. Long-term 1σ precisions are: Mg/Ca = 0.54%, Sr/Ca = 0.57%, Cd/Ca = 1.8%, Zn/Ca = 3.2%, Li/Ca = 0.88%, U/Ca = 1.9%, Mn/Ca = 0.97% and Fe/Ca = 1.4% [Marchitto, 2006]. One *U. peregrina* sample was excluded due to extremely low [Ca] (< 0.001 mM); the sample was presumably lost during cleaning. Mn/Ca and Fe/Ca were measured to screen against contamination from diagenetic coatings or detrital material; values were almost always below 30 μmol mol^{-1} and did not exceed 60 μmol mol^{-1} in any sample, well below thresholds for likely trace metal contamination (>100 μmol mol^{-1}) [Boyle, 1983].

Core	Latitude (°N)	Longitude (°W)	Water Depth (m)	Temperature (°C)	Salinity (psu)	CO_3^{2-} (µmol kg^{-1})	Estimated Seawater Cd (nmol kg^{-1})	Estimated Seawater Zn (nmol kg^{-1})	Conventional ^{14}C Age (yr BP)	NOSAMS Number
5MC[a]	24.4	83.38	447	8.5	35.03	99	0.345	2.693		
11MC[a]	24.22	83.3	751	5.8	34.90	86	0.468	3.820	355 ± 35	OS-39958[2]
13MC[a]	24.37	83.24	348	9.7	35.17	106	0.298	2.279	3040 ± 35	OS-46032[2]
16MC[a]	24.4	83.23	248	10.8	*35.32*	*114*	0.259	1.937		
19MC[a]	24.42	83.21	173	12.7	35.61	125	0.196	1.408	1320 ± 50	OS-39967[2]
22MC[a]	24.41	83.37	398	9.0	*35.08*	98	0.325	2.514		
24MC[a]	24.34	83.25	494	7.8	*34.95*	*90*	0.375	2.971		
28MC[a]	24.28	83.27	648	6.3	34.90	86	0.440	3.566	2980 ± 40	OS-46037[2]
50MC[a]	24.41	83.22	198	12.1	35.51	120	0.216	1.575	1080 ± 45	OS-41646[2]
53MC[a]	24.38	83.23	302	10.0	*35.21*	*107*	0.285	2.163	1800 ± 30	OS-39969[2]
55MC[a]	24.38	83.27	359	9.1	*35.10*	*115*	0.320	2.469		
62MC[a]	24.33	83.26	547	7.0	*34.91*	*86*	0.408	3.275	Fm > 1	OS-39971[1]
64MC[c]	23.61	79.04	209	20.6	36.78	*216*	0.002	0.226		
66MC[c]	23.61	79.05	302	19.0	36.62	*204*	0.036	0.361		
68MC[c]	23.61	79.08	431	16.6	36.24	*178*	0.090	0.652		
72MC[b]	23.75	79.43	542	10.8	35.31	116	0.259	1.937		
76MC[b]	23.59	79.42	539	11.0	35.33	*116*	0.251	1.869		
79MC[b]	23.26	79.27	486	12.1	*35.50*	*127*	0.215	1.567		
84MC[c]	24.37	79.45	638	10.5	35.27	105	0.271	2.035		
89MC[c]	24.56	79.24	353	17.8	*36.48*	*194*	0.061	0.487	2280 ± 35	OS-40243[2]
92MC[c]	24.55	79.26	478	15.7	36.13	170	0.114	0.804		
94MC[c]	24.57	79.23	259	18.5	36.57	206	0.047	0.413	215 ± 35	OS-40244[2]
97MC[c]	24.56	79.23	303	18.6	*36.58*	*201*	0.044	0.399		
103MC[c]	24.44	79.48	683	9.3	35.11	101	0.314	2.420		
110MC[c]	24.58	79.24	390	17.3	*36.39*	*188*	0.073	0.553	Fm > 1	OS-46039[2]
112MC[c]	24.64	79.24	404	17.1	*36.35*	*185*	0.079	0.587		
118MC[c]	24.59	79.27	531	14.5	35.91	*155*	0.143	1.008	Fm > 1	OS-39973[3]
121MC[c]	24.77	79.25	578	11.9	35.48	*126*	0.222	1.625		
123MC[c]	24.76	79.27	632	10.6	35.30	*113*	0.264	1.982		
125MC[c]	24.76	79.29	694	9.4	35.13	*102*	0.309	2.371	Fm > 1	OS-39975[3]
134MC[c]	24.84	79.22	441	17.2	36.37	*186*	0.076	0.567	Fm > 1	OS-46043[2]
138MC[c]	24.83	79.23	484	16.8	36.29	181	0.084	0.619		

Table 3.1: KNR 166-2 multi-core locations, hydrographic data, seawater Cd and Zn concentrations and radiocarbon ages. Superscripts on Cores indicate (a) Dry Tortugas sites, (b) Cay Sal Bank sites and (c) Great Bahama Bank sites. Bottom water temperatures were estimated by matching Niskin bottle salinities to nearby CTDs. Italicized salinities and CO_3^{2-} values were estimated as described in text. Sources of radiocarbon ages are indicated by superscripts on the National Ocean Sciences Accelerator Mass Spectrometry Facility (NOSAMS) sample numbers: 1 = Lund and Curry [2004]; 2 = Lund [2005]; 3 = Lund and Curry [2006]. Fm > 1 refers to fraction modern greater than one, indicating the presence of ^{14}C from nuclear weapons testing.

Results & Discussion

Cd/Ca

Core-top Cd/Ca results are presented in Table 3.2. Cd/Ca values range from $0.016 - 0.097$ µmol mol^{-1} for *C. pachyderma*, $0.020 - 0.095$ µmol mol^{-1} for *U. peregrina*, $0.047 - 0.073$ µmol mol^{-1} for *P. ariminensis*, $0.016 - 0.086$ µmol mol^{-1} for *P. foveolata*, and $0.0061 - 0.057$ µmol mol^{-1} for *H. elegans*. Two Cd/Ca measurements were much higher than the rest of the values and were suspected to be contaminated (one *C. pachyderma* and one *U. peregrina*). These two measurements are excluded from regressions and figures. For all species Cd/Ca increases with increasing depth (Figure 3.5). The three regions display distinct depth profiles; Dry Tortugas multi-core sites have the highest Cd/Ca values and Great Bahama Bank sites have the lowest for similar depths. These profiles are consistent with the expected sloping of isopycnals associated with the Florida Current, with denser waters containing higher nutrient concentrations. Cd/Ca generally reflects the expected Cd/Ca of seawater, and there are no consistent offsets between the calcitic species (Figure 3.6). *H. elegans* Cd/Ca is generally lower than the calcitic species, but displays similar nutrient-type profiles with water depth.

Core	*C. pachyderma* Cd/Ca	Zn/Ca	*U. peregrina* Cd/Ca	Zn/Ca	*P. ariminensis* Cd/Ca	Zn/Ca	*P. foveolata* Cd/Ca	Zn/Ca	*H. elegans* Cd/Ca	Zn/Ca
5	0.059	5.65	0.056	1.00	0.060	1.32			0.035	0.83
5	0.097	*17.24*	0.053	0.95	0.061	*3.06*			0.034	0.43
11	0.068	7.00	*0.162*	*4.95*					0.033	0.40
11			0.062	1.47						
13	0.065	4.79	0.054	0.56	0.058	1.43			0.040	0.35
13	0.065	4.22	0.059	0.58	0.056	1.17			0.043	0.69
16	0.048	3.63								
16	0.048	2.98								
19	0.050	1.99					0.040	0.44	0.038	*2.80*
19	0.075	2.12							0.034	1.50
22	*0.596*	*64.89*	0.053	0.85					0.046	1.60
22	0.059	*7.70*	0.053	0.97						
24			0.057	1.47					0.039	1.07
28	0.058	4.40	0.073	1.21					0.042	0.17
28	0.058	4.74	0.073	1.29					0.049	1.21
50	0.049	2.30			0.047	1.74	0.044	*29.67*	0.039	1.60
50	0.048	2.59								
53	0.053	3.07	0.048	1.21	0.056	1.11			0.053	1.17
53	0.055	*9.89*	0.054	*3.00*	0.064	1.99			0.047	0.44
55	0.063	3.65	0.057	0.80	0.059	2.00			0.057	0.82
55	0.061	3.63	0.095	*12.72*	0.065	*9.73*			0.051	1.63
62	0.056	5.46	0.058	1.07	0.062	1.85			0.035	0.41
62			0.073	*13.48*						
66									0.009	0.90
68	0.028	*6.89*					0.017	0.52	0.010	0.22
68	0.021	0.45							0.014	0.86
72	0.044	5.39	0.086	*8.84*			0.044	1.75	0.032	*3.24*
72	0.045	5.07	0.044	0.74						
76	0.047	4.72	0.045	*3.38*	0.073	*11.46*	0.086	*9.38*		
76	0.049	5.40								
79	0.055	4.88	0.042	1.50			0.041	*15.48*	0.023	0.24
79	0.054	5.64	0.037	0.69						
84	0.082	6.81								
89	0.016	0.19					0.016	*4.58*		
92	0.031	2.18	0.028	*4.36*					0.016	0.61
94	0.016	0.10							0.016	*3.79*
94	0.019	0.13							0.010	*2.33*
97	0.019	0.23							0.012	*7.78*
97	0.018	0.12							0.006	0.21
103	0.084	*8.99*	0.074	2.25	0.061	1.29				
103	0.078	*7.15*								
110	0.020	0.68	0.020	0.61			0.019	*2.65*	0.013	1.61
110			0.026	1.44			0.019	1.57	0.009	1.11
112	0.021	0.82							0.009	0.30
112									0.009	0.51
118	0.038	1.67	0.037	1.65			0.027	0.53	0.018	0.20
118			0.032	0.55					0.021	0.81
121	0.036	2.94	0.039	2.25					0.024	0.39
121	0.038	4.40								
123	0.043	4.14								
123	0.040	4.80								
125	0.055	5.57			0.051	1.70				
134	0.024	2.49					0.016	1.43	0.011	0.77
134	0.020	0.81							0.011	0.33
138	0.026	1.60	0.021	0.66			0.037	1.84	0.018	0.98
138							0.033	*2.77*	0.023	*3.02*

Table 3.2: Benthic foram Cd/Ca and Zn/Ca measurements for each species by core. See Table 3.1 for core locations and seawater properties. All values are µmol mol^{-1}. Measurements that were excluded from figures and regressions because of suspected contamination are *italicized*.
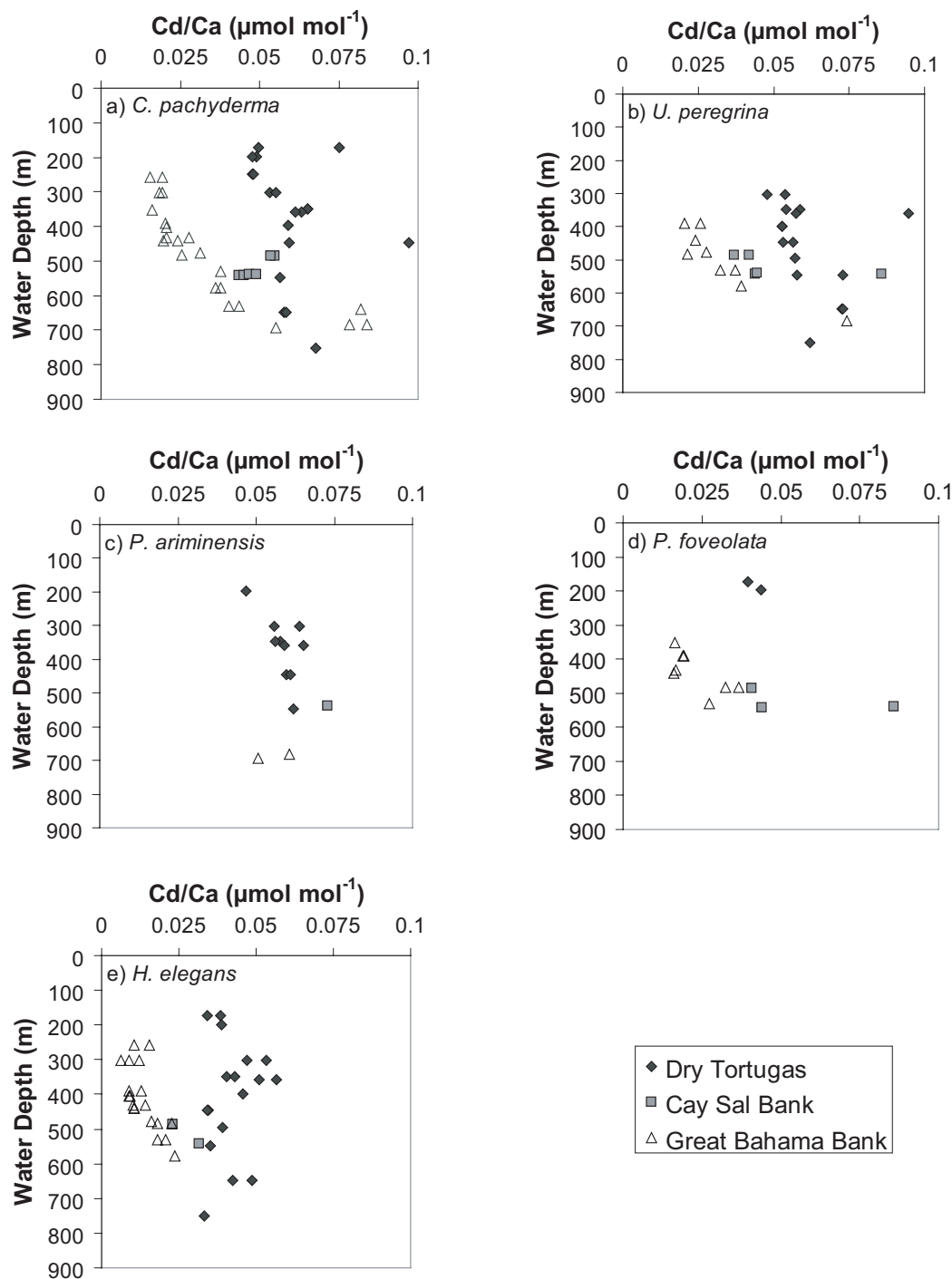
Figure 3.5: Cd/Ca vs. water depth for a) *C. pachyderma*, b) *U. peregrina*, c) *P. ariminensis*, d) *P. foveolata*, and e) *H. elegans*. Diamonds are multi-cores near Dry Torugas; squares are near Cay Sal Bank, and triangles are near Great Bahama Bank.

D$_{Cd}$

A useful measure of how much Cd is incorporated in to the shell relative to the seawater Cd concentration is the empirical partition coefficient (D), where

$$D_{Cd} = Cd/Ca_{foram} / Cd/Ca_{seawater.}$$

This equation can be rearranged so that $Cd/Ca_{foram} = D_{Cd} * Cd/Ca_{seawater}$. The partition coefficient is therefore the slope of the linear regression forced through the origin. Unless otherwise noted the Elderfield and Rickaby [2000] Cd:PO$_4$ relationship was used to estimate Cd$_{seawater}$, and a constant seawater calcium concentration of 10 µmol kg^{-1} was assumed [Boyle, 1992]. For the purpose of determining the partition coefficient, all of the calcitic species were combined. Tachikawa and Elderfield [2002] proposed that infaunal species (such as *U. peregrina*) calcify from porewaters with a constant partition coefficient of ~1, and the similar Cd/Ca measurements of *U. peregrina* and *Cibicidoides sp.* are due to elevated porewater Cd. There are no consistent offsets between *U. peregrina* and the other calcitic species in the Florida Straits samples. The data presented here do not preclude a different partition coefficient for *U. peregrina*; however, porewater Cd measurements would be necessary to investigate this possibility.

The resulting partition coefficient for the calcitic species is ~1.9 (Figure 3.6); the R^2 for the regression not forced through the origin is 0.66. The 95% confidence interval of D$_{Cd}$ is 1.80 - 1.99. The calculated D$_{Cd}$ value is significantly higher than the value determined for the upper ocean (D$_{Cd}$ = ~1.3) by Boyle [1992] using eight core tops. Calculating D$_{Cd}$ using a linear regression is preferred to calculating the D$_{Cd}$ for each measurement and taking the average, as it is less biased towards high values,

which may include slight contamination. For example, the average D_{Cd} of individual measurements is significantly higher (2.25), while the median of individual measurements is comparable (1.96). The standard deviation of individual D_{Cd} measurements is 0.71, indicating considerable variability in the D_{Cd} estimate. Much of the variability is likely due to small errors in the estimation of the Cd/Ca of seawater; at such low Cd concentrations, small errors may become important.

If the $Cd:PO_4$ relationship of Boyle [1988] is used to determine Cd/Ca of seawater, the resulting partition coefficient is significantly lower, 1.61 with a 95% confidence interval of 1.52 to 1.69, than the one calculated using the Elderfield and Rickaby [2000] relationship. This indicates that the source of approximately half of the difference between the DCd estimate determined here and that of Boyle [1992] is the method of seawater [Cd] estimation. This difference illustrates the importance of understanding the systematics of the Cd:P relationship. The continuous curved relationship of Elderfield and Rickaby [2000] is likely a better estimate than the two segment linear relationship of Boyle [1988], but measurements of seawater [Cd] at the multi-core sites would greatly increase the confidence in the D_{Cd} estimates. The Florida Straits Cd/Ca measurements agree well with the Little Bahama Bank measurements of Rosenthal et al. [1997b] and Marchitto [2004] (Figure 3.7); however, the partition coefficients calculated from the two other data sets are slightly higher than for the Florida Straits data.
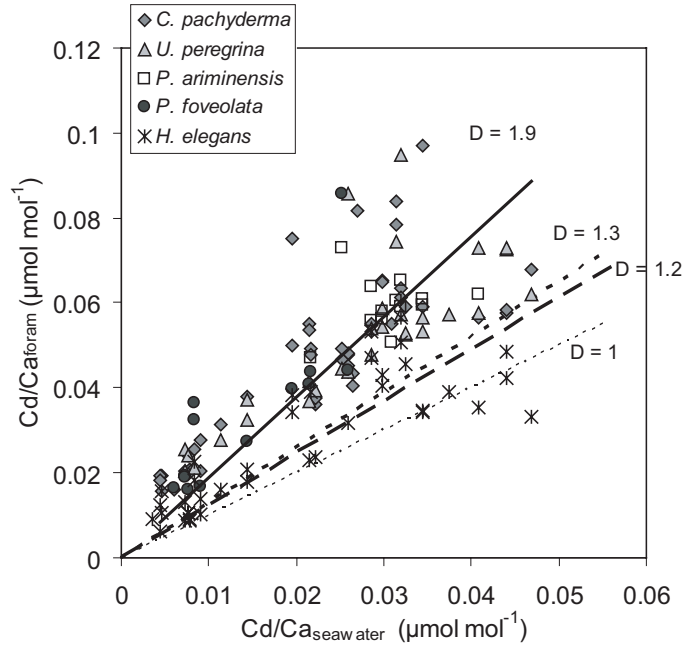
Figure 3.6: Plot of estimated seawater Cd/Ca using the Elderfield and Rickaby [2000] Cd:P relationship vs. measured foraminiferal Cd/Ca. The slope of a linear regression forced through the origin is measure of the partition coefficient (D_{Cd}). The solid line is a linear regression through all of the calcitic species measurements. The dashed line is through *H. elegans* measurements. The dotted lines indicate partition coefficients of 1.3 and 1.0 for comparison.

Figure 3.7: Comparison of calcitic Cd/Ca measurements plotted against estimated seawater Cd/Ca from this study (triangles), Rosenthal et al. [1997] (squares), and Marchitto [2004] (circles). All of the Cd/Ca of seawater values used in this plot were calculated using the Cd:PO_4 relationship of Boyle [1988]. There are three linear regressions plotted, one for each study. This study (solid line): Cd/Ca$_{foram}$ = 1.61($\pm$0.04)Cd/Ca$_{seawater}$. Rosenthal et al. [1997b] (dotted line): Cd/Ca$_{foram}$ = 1.84($\pm$0.10)Cd/Ca$_{seawater}$. Marchitto et al. [2004] (dashed line): Cd/Ca$_{foram}$ = 1.77($\pm$0.07)Cd/Ca$_{seawater}$.

A partition coefficient was determined for *H. elegans* in the same manner as the calcitic species. *H. elegans* is expected to have a depth independent partition coefficient of ~1 [Boyle, 1995]. The D_{Cd} determined here is ~1.2 with a 95% confidence interval of 1.10 - 1.35. The R^2 for the regression not forced through the origin is 0.72. This value is therefore significantly higher than 1. If D_{Cd} is calculated for each individual measurement the mean is 1.54, and the median is 1.40. The standard deviation of individual D_{Cd} measurements is 0.55. If the Boyle [1988] Cd:P relationship is used, the calculated D_{Cd} is ~1, with a 95% confidence interval of 0.92 to 1.13, again indicating that the higher D_{Cd} for *H. elegans* estimated in the Florida Straits is likely a result of the seawater Cd estimates. The Florida Straits Cd/Ca measurements agree well with the Little Bahama Bank measurements of Marchitto [2004] and the upper ocean Atlantic measurements of Boyle et al. [1995] (Figure 3.8). It should be noted that Marchitto [2004] found a systematic positive offset from measurements of Boyle et al. [1995] on the same cores, although the offset was less than the average reproducibility of replicate picks (±0.023 µmol mol^{-1}). A linear regression (forced through the origin) of the combined data from this study, Boyle et al. [1995], and Marchitto [2004] gives a partition coefficient of ~1. D_{Cd} for *H. elegans* may be slightly higher than one, and the seawater Cd estimates used for calibration should be readdressed.

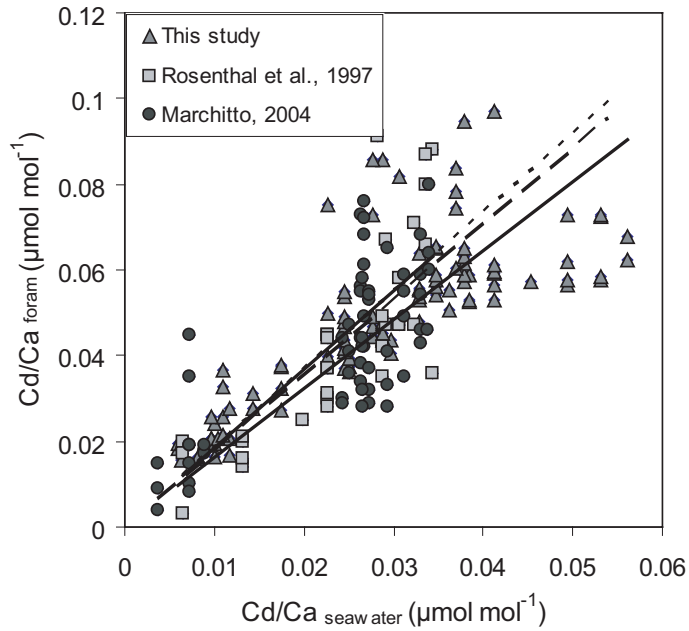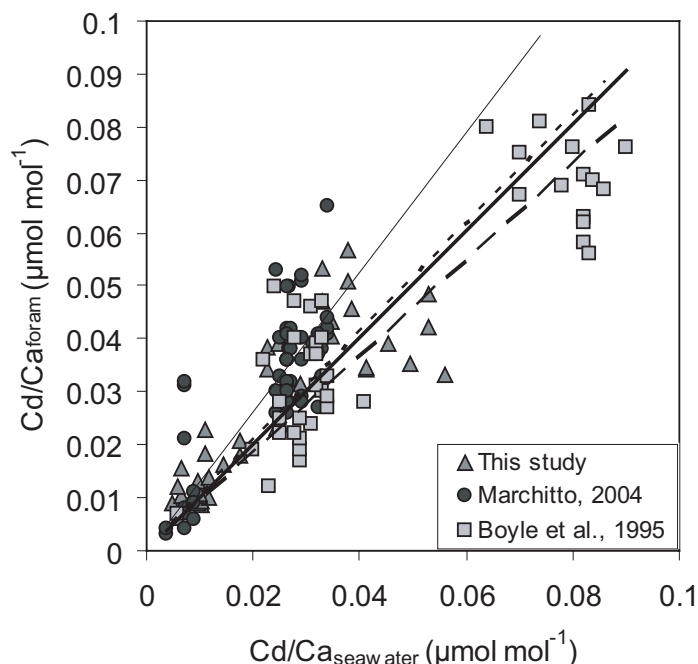**Figure 3.8:** Comparison of *H. elegans* Cd/Ca measurements plotted against estimated seawater Cd/Ca from this study (triangles), Boyle et al. [1995] (squares), and Marchitto [2004] (circles). All of the Cd/Ca of seawater values used in this plot were calculated using the Cd:PO$_4$ relationship of Boyle [1988]. There are four linear regressions plotted, one for each study and one for all of the data combined. This study (dotted line): Cd/Ca$_{foram}$ = 1.03($\pm$0.05)Cd/Ca$_{seawater}$. Boyle et al. [1995] (dashed line): Cd/Ca$_{foram}$ = 0.91($\pm$0.03)Cd/Ca$_{seawater}$. Marchitto et al. [2004] (thin solid line): Cd/Ca$_{foram}$ = 1.32($\pm$0.05)Cd/Ca$_{seawater}$. Combined (thick solid line): Cd/Ca$_{foram}$ = 1.01($\pm$0.03)Cd/Ca$_{seawater}$.

Environmental Influences on D$_{Cd}$

Before these partition coefficients can be used to reconstruct paleo-nutrient

concentrations, we must determine if other environmental parameters, such as

temperature or carbonate saturation, influence Cd incorporation. Plotting the partition

coefficients (D$_{Cd}$) for each measurement against water depth reveals a consistent

positive offset between the Great Bahama Bank samples and the Dry Tortugas

samples, and D$_{Cd}$ decreases slightly with increasing depth (Figure 3.9). This pattern

is also seen if the Boyle [1988] Cd:P relationship is used to estimate seawater [Cd].

As seawater PO$_4$ or Cd were not measured at the Florida Straits multi-core sites, it is

possible that there are errors in the seawater Cd estimates. I am confident that the

phosphate measurements from nearby WOCE stations used here are reasonably

representative of the hydrography and nutrient concentrations of the Florida Straits

multi-core sites, but at such low seawater Cd concentrations, a small divergence from

the estimated seawater Cd will result in a large change in the partition coefficient.

These errors would be larger at the Great Bahama Bank multi-core sites, due to the

lower seawater Cd concentrations. If not due to some systematic error in seawater

[Cd] estimation, the depth and regional variation of D_{Cd} suggests that Cd

incorporation may be influenced by some environmental parameter that decreases

with increasing depth (e.g. temperature, salinity, carbonate ion concentration).

Marchitto [2004] found no significant temperature influence on Cd incorporation.

D_{Cd} is known to decrease as carbonate ion saturation with respect to calcite (ΔCO_3^{2-})

decreases; however this effect is thought to be limited to undersaturated waters

[McCorkle et al., 1995; Marchitto et al., 2005].   Florida Straits D_{Cd} is positively

correlated with temperature and ΔCO_3^{2-}, with D_{Cd} increasing by ~0.14 per °C ($R^2 =$

0.50, p-value < 0.0001) or ~0.14 per 10 µmol kg^{-1} ($R^2 = 0.49$, p-value < 0.0001)

(Figure 3.10). *H. elegans* D_{Cd} increases by ~0.075 per °C ($R^2 = 0.30$, p-value =

0.0004) or ~0.077 per 10 µmol kg^{-1} of ΔCO_3^{2-} ($R^2 = 0.30$, p-value = 0.0004). It is

difficult to determine whether temperature, ΔCO_3^{2-} or some combination of the two

parameters may be influencing D_{Cd}, due to the strong correlation between the two

environmental parameters in the Florida Straits ($R^2 = 0.96$). It is also unclear why a

temperature or ΔCO_3^{2-} influence would be apparent in the Florida Straits and not in

the Little Bahama Bank [Marchitto, 2004], since the ranges of temperature and

ΔCO_3^{2-} are similar in these two regions. Seawater Cd measurements from the Florida

Straits multi-core sites or additional Cd/Ca measurements from other regions should

help to clarify the influence of environmental parameters on D_{Cd}.
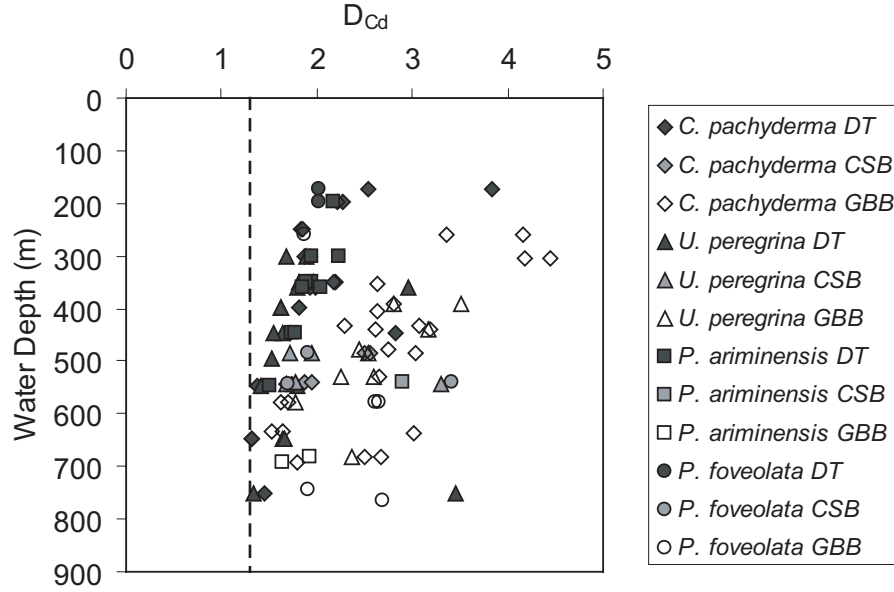
Figure 3.9: D_{Cd} for individual measurements of the calcitic species plotted against water depth. DT stands for multi-core sites near Dry Tortugas, CSB are sites near Cay Sal Bank and GBB are sites near Great Bahama Bank. D_{Cd} values are elevated in the Great Bahama Bank sites. D_{Cd} also decreases slightly with increasing depth. The dashed line indicates a D_{Cd} of 1.3 for comparison.
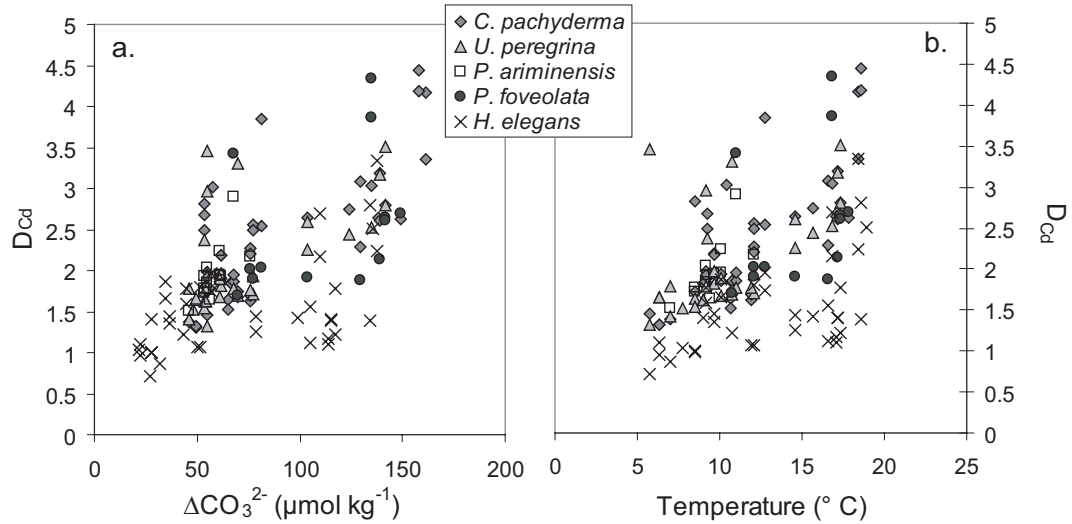
Figure 3.10: D_{Cd} plotted vs. (a.) ΔCO_3^{2-} and (b.) temperature. Linear regressions for DCd of the calcitic species and ΔCO_3^{2-} ($R^2 = 0.45$) or temperature ($R^2 = 0.44$) are weak but significant ($p < 0.01$); as are linear regressions for *H. elegans*: ΔCO_3^{2-} ($R^2 = 0.30$), temperature ($R^2 = 0.30$)

Zn/Ca

Core-top Zn/Ca results are presented in Table 3.2. Laboratory contamination was a major problem for Zn/Ca analysis. Even working in a Class-1000 clean lab, at least 30 out of the 141 measurements are suspected of some Zn contamination. In some cases measurements were obviously contaminated with very high values or measurements much higher than sample splits. In other cases the context of the measurements was necessary; examination of depth profiles (Figure 3.11) gave an indication of where measurements should fall. Zn/Ca measurements that were at least one $\mu mol\ mol^{-1}$ greater than replicates or nearby cores with similar seawater [Zn] were excluded. Zn/Ca values (excluding measurements determined to be contaminated) range from $0.10 - 7.00\ \mu mol\ mol^{-1}$ for *C. pachyderma*, $0.55 - 2.25$ $\mu mol\ mol^{-1}$ for *U. peregrina*, $1.11 - 2.00\ \mu mol\ mol^{-1}$ for *P. ariminensis*, $0.44 - 1.84$ $\mu mol\ mol^{-1}$ for *P. foveolata*, and $0.17 - 1.63\ \mu mol\ mol^{-1}$ for *H. elegans*. *C. pachyderma* Zn/Ca increases with increasing depth in distinct profiles for each region, with Dry Tortugas cores having higher Zn/Ca values than Great Bahama Bank cores for similar depths (Figure 3.11). Profiles for the other species are less clear; although *U. peregrina* Zn/Ca does increase with depth. The scatter in the Zn/Ca measurements is likely due to additional slight Zn contamination in the laboratory as well as uncertainties in the estimation of Zn/Ca of seawater.
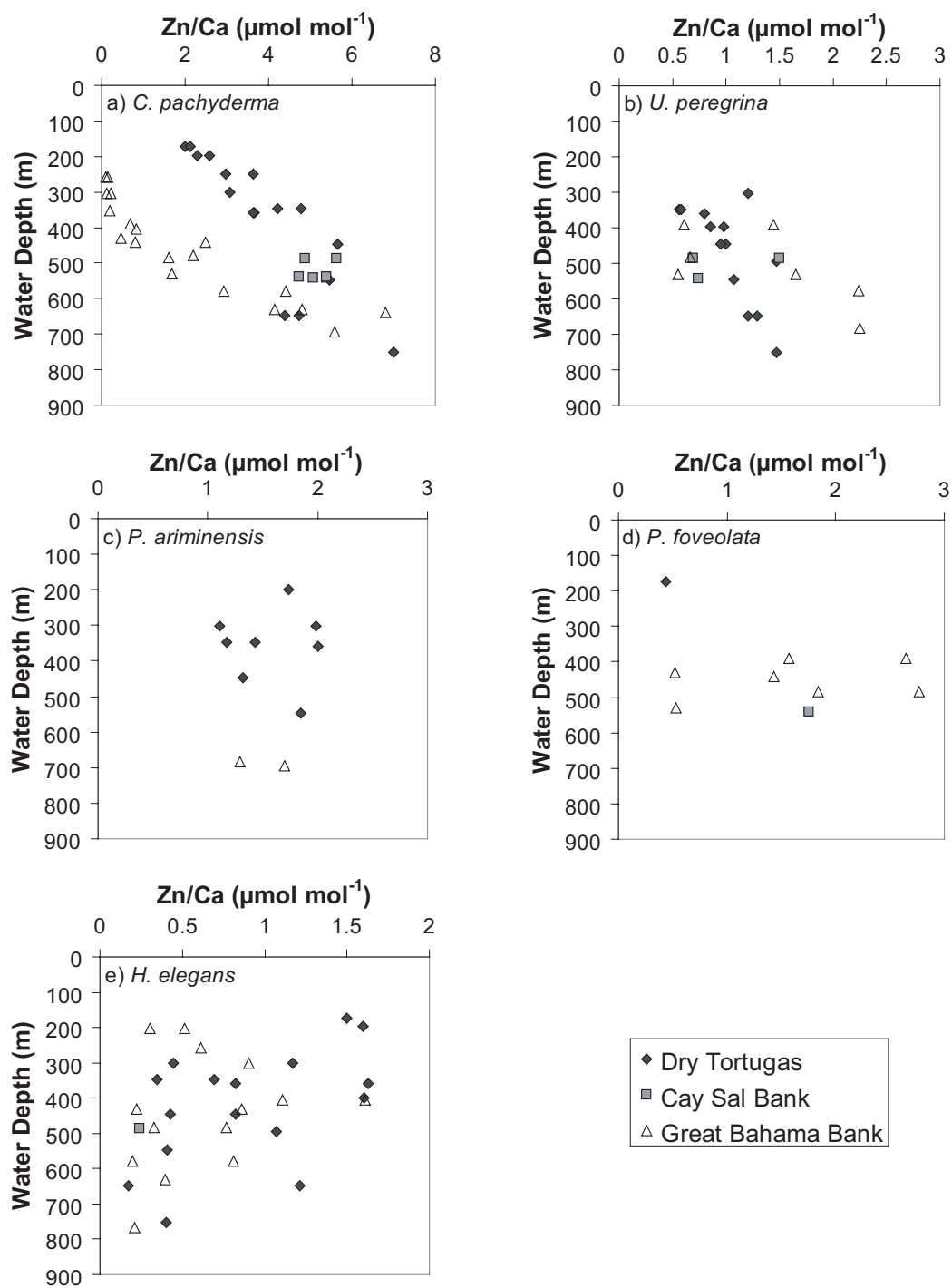
Figure 3.11: Zn/Ca vs. water depth for a) *C. pachyderma*, b) *U. peregrina*, c) *P. ariminensis*, d) *P. foveolata*, and e) *H. elegans*. Diamonds are multi-cores near Dry Torugas; squares are near Cay Sal Bank, and triangle are near Great Bahama Bank. Note the differing Zn/Ca scales.

D$_{Zn}$

The partition coefficient for Zn/Ca (D$_{Zn}$), where

$$D_{Zn} = Zn/Ca_{foram} / Zn/Ca_{seawater}$$

can be determined in the same way as D$_{Cd}$ by determining the slope of a linear regression, forced though the origin, fit to the Zn/Ca of seawater and the measured Zn/Ca of the foraminifera (Figure 3.12). Due to the obvious differences in Zn/Ca values between the species seen in the depth plots, partition coefficients are determined for each individual species. D$_{Zn}$ for *C. pachyderma* is ~19 with a 95% confidence interval of 17.2 to 21.0. The R^2 for the regression not forced through the origin is 0.67. The mean of individual D$_{Zn}$ measurements is 18.6 and the median is 16.7. This is much higher than the partition coefficient calculated for *C. wuellerstorfi* (~9) by Marchitto et al. [2000].

The partition coefficient determined for *U. peregrina* is ~4.5 with a 95% confidence interval of 3.3 to 5.6. However, the R^2 of the regression not forced through the origin is 0.02 and the slope is not significantly different from zero. The mean of the individual D$_{Zn}$ measurements is 6.9 and the median is 3.9. This partition coefficient is lower than the one determined by Marchitto et al. [2000] for deepwater *U. peregrina* samples (D$_{Zn}$ = ~9). Perhaps like Cd, Zn incorporation is reduced in shallow water. However, if seawater [Zn] estimates are too high, then the calculated D$_{Zn}$ would be too low. Seawater [Zn] would need to be approximately half of what has been estimated to account for the discrepancy. If this were true, the partition coefficient for *C. pachyderma* would be ~38.

With the small sample size of uncontaminated measurements of the two *Planulina* species it is difficult to confidently ascribe a partition coefficient. A linear regression through the ten *P. ariminensis* measurements yields a D_{Zn} of ~6.4 with a 95% confidence interval of 5.2 to 7.7. If the regression is not forced through the origin, the R^2 is 0.01 and the slope is not significantly different from zero. The mean of the individual D_{Zn} measurements is 6.8 and the median is 6.0. A linear regression through the nine *P. foveolata* measurements is also not significant. The mean D_{Zn} of the individual *P. foveolata* measurements is 22.4 and the median is 25.3. Because of the very low seawater Zn/Ca values at the sites where *P. foveolata* are found, a small amount of contamination will be significant. It is likely that most of the *P. foveolata* Zn/Ca measurements are contaminated to some degree. The calculated D_{Zn} for *H. elegans* is ~3 with a 95% confidence interval of 2.2 to 4.4. However, this value is likely unreliable due the large scatter in *H. elegans* Zn/Ca and the lack of coherent depth profiles.

The large range in temperature and other environmental parameters between the multi-core sites allow the investigation of the possible influences of these parameters on Zn incorporation. Given its high partition coefficient, any significant environmental influences on D_{Zn} should be most apparent in *C. pachyderma*. There are no consistent offsets in *C. pachyderma* D_{Zn} between the regions (Figure 3.13), and D_{Zn} is very weakly correlated with temperature ($R^2 = 0.09$, p-value = 0.06) or carbonate saturation ($R^2 = 0.15$, p-value = 0.01). Due to the scatter in the D_{Zn} of the other species it is difficult to determine if they are affected by environmental parameters, but there are no obvious trends with environmental parameters. I

conclude that there do not appear to be any significant environmental influences on

Zn incorporation.
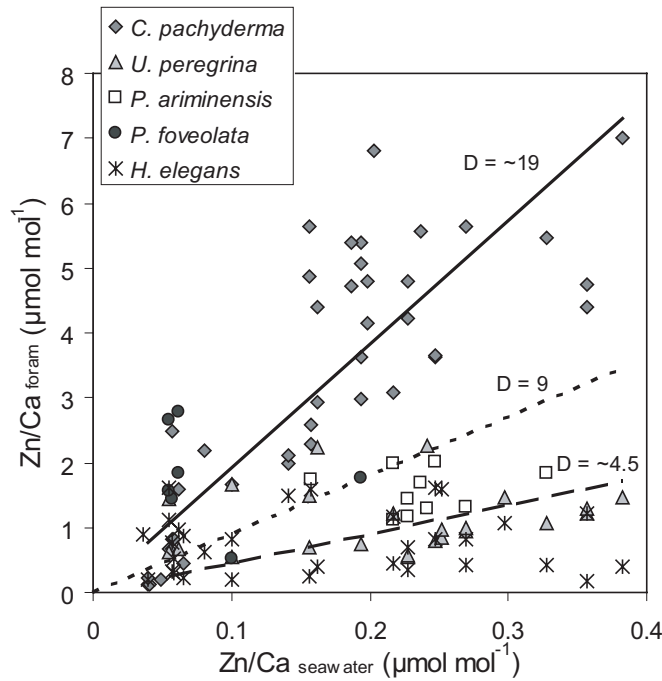
Figure 3.12: Zn/Ca measurements for each species plotted against the estimated Zn/Ca of seawater. The solid line is a linear regression forced through the origin for the *C. pachyderma* measurements indicating a D_{Zn} of ~19. The dashed line is a linear regression forced through the origin for the *U. peregrina* measurements indicating a D_{Zn} of ~4.5. A D_{Zn} of 9 is shown for comparison (dotted line).
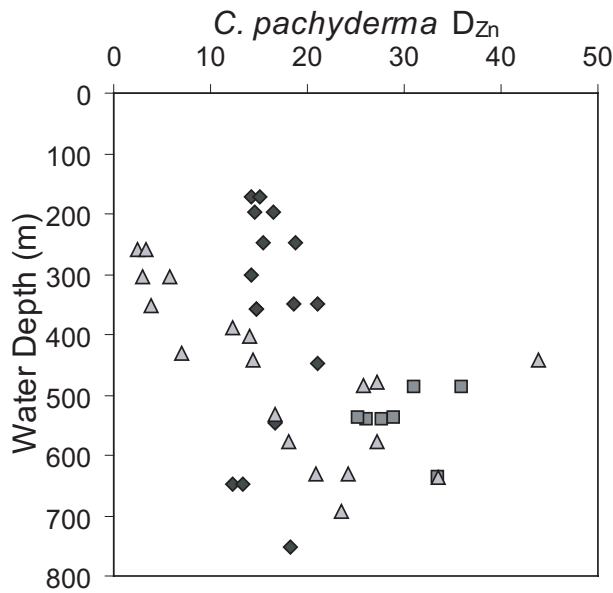
Figure 3.13*: C. pachyderma* D_{Zn} plotted vs. water depth. Multi-core sites near Dry Tortugas are plotted as diamonds, Cay Sal Bank sites are squares and Great Bahama Bank sites are triangles. There is no consistent offset between the three regions.

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Conclusions

The Cd/Ca of calcitic benthic foraminifera reflects the Cd/Ca of seawater in thermocline waters with a partition coefficient of ~1.9, and there are no consistent differences between calcitic species. This partition coefficient is significantly higher than that of Boyle [1992] for sites <1150 m. The method used to estimate seawater Cd concentrations significantly affects the D_{Cd} estimate and should be examined carefully. D_{Cd} may be slightly influenced by temperature and/or carbonate ion. Cd/Ca in *H. elegans* reflects seawater Cd/Ca with a partition coefficient of ~1.2, also slightly higher than the previously determined value of Boyle [1995], although the difference disappears if the Cd:P relationship of Boyle [1988] is used to estimate seawater Cd. *H. elegans* D_{Cd} also may be slightly influenced by temperature and/or carbonate ion. Potential temperature/carbonate ion influences on D_{Cd} could significantly affect reconstructions of thermocline circulation on glacial/interglacial timescales and should be investigated further with core-tops from other regions.

Zn/Ca measurement is complicated by laboratory contamination, especially in samples from sites with very low seawater Zn concentrations. The contamination problem is minimized in *C. pachyderma* because this species reflects seawater Zn/Ca with a high partition coefficient of ~19. The high D_{Zn} of *C. pachyderma* will allow relatively precise reconstructions of seawater Zn. D_{Zn} of *U. peregrina* appears to be lower in thermocline waters (~5) than previously determined from deep ocean samples (~9). Finally, there do not appear to be any significant environmental influences on D_{Zn}.

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Appendix I.

Compilation of trace element measurements sorted by species. [Ca] units are mM; Mg/Ca and Sr/Ca units are mmol mol^{-1}. Units for all others are μmol mol^{-1}. Italicized values were excluded from figures and regressions due to low [Ca] or suspected contamination.

Core	[Ca]	Li/Ca	Mg/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Cd/Ca	U/Ca	Fe/Ca
C. pachyderma									
5	2.591	13.04	2.09	9.22	5.65	1.37	0.0593	0.0110	10.63
5	0.012	*8.76*	2.00	-7.02	*17.24*	1.45	0.0971	0.0135	13.54
11	1.790	12.38	1.34	15.90	7.00	1.39	0.0678	0.0107	9.02
13	1.605	12.82	2.33	6.80	4.79	1.45	0.0653	0.0142	15.18
13	2.375	13.09	2.44	9.05	4.22	1.43	0.0650	0.0163	17.21
16	2.620	12.20	2.40	9.35	3.63	1.41	0.0477	0.0178	5.75
16	2.995	12.12	2.27	9.06	2.98	1.41	0.0480	0.0188	5.97
19	0.804	12.22	2.09	5.22	1.99	1.40	0.0498	0.0123	5.55
19	1.431	12.61	2.73	6.79	2.12	1.41	0.0752	0.0154	6.93
22	0.035	*15.93*	2.63	6.77	*64.89*	1.41	*0.5962*	0.0108	19.90
22	0.324	13.43	2.49	6.71	*7.70*	1.44	0.0589	0.0134	4.60
28	2.593	13.31	1.42	10.90	4.40	1.40	0.0578	0.0090	14.24
28	2.724	13.36	1.54	11.53	4.74	1.39	0.0583	0.0107	15.98
50	1.712	12.05	2.39	7.88	2.30	1.40	0.0491	0.0179	7.26
50	3.084	12.02	2.47	9.75	2.59	1.41	0.0478	0.0216	7.82
53	3.171	12.61	2.37	10.31	3.07	1.39	0.0532	0.0137	17.81
53	1.631	12.47	2.20	8.89	*9.89*	1.41	0.0552	0.0124	12.50
55	1.268	13.07	2.34	8.94	3.65	1.44	0.0633	0.0150	19.93
55	1.465	13.22	2.24	9.53	3.63	1.44	0.0614	0.0147	21.38
62	1.270	13.27	2.19	8.82	5.46	1.42	0.0564	0.0172	7.57
68	0.867	11.19	3.29	59.69	*6.89*	1.52	0.0276	0.0082	4.98
68	1.451	11.43	3.39	50.62	0.45	1.50	0.0205	0.0084	5.43
72	0.864	13.14	2.88	10.97	5.39	1.45	0.0437	0.0063	3.54
72	1.310	13.25	2.83	9.98	5.07	1.46	0.0451	0.0066	43.53
76	0.485	12.94	2.87	9.79	4.72	1.49	0.0468	0.0062	4.62
76	0.511	12.90	2.78	7.29	5.40	1.47	0.0491	0.0054	3.97
79	0.670	13.12	3.35	15.83	4.88	1.47	0.0550	0.0065	17.47
79	0.438	12.93	3.15	17.94	5.64	1.45	0.0537	0.0067	20.43
84	0.976	13.73	2.48	9.81	6.81	1.48	0.0818	0.0137	54.17
89	0.824	11.32	3.44	31.15	0.19	1.60	0.0161	0.0241	2.20
92	0.310	12.86	3.19	15.74	2.18	1.45	0.0312	0.0084	1.45
94	1.084	10.88	3.34	19.65	0.10	1.55	0.0156	0.0133	2.15
94	1.355	11.04	3.47	27.48	0.13	1.55	0.0194	0.0129	6.21
97	0.743	11.02	3.27	28.44	0.23	1.55	0.0194	0.0116	2.09
97	0.975	11.00	3.25	28.03	0.12	1.56	0.0183	0.0115	1.84
103	1.868	13.01	2.31	10.14	*8.99*	1.41	0.0839	0.0093	14.21

Core	[Ca]	Li/Ca	Mg/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Cd/Ca	U/Ca	Fe/Ca
103	1.585	13.25	2.34	11.50	*7.15*	1.41	0.0783	0.0096	16.80
110	0.544	12.47	3.31	9.66	0.68	1.51	0.0205	0.0075	2.29
112	1.265	11.93	2.92	19.40	0.82	1.54	0.0208	0.0096	3.38
118	1.251	13.28	2.68	6.92	1.67	1.44	0.0379	0.0079	11.30
121	1.753	12.66	2.48	8.29	2.94	1.43	0.0361	0.0075	5.48
121	0.906	12.45	2.67	10.85	4.40	1.46	0.0376	0.0077	5.86
123	1.738	12.73	2.44	5.16	4.14	1.44	0.0435	0.0077	6.30
123	2.885	12.77	2.65	6.28	4.80	1.46	0.0405	0.0083	5.72
125	1.006	13.26	2.48	6.29	5.57	1.42	0.0552	0.0079	7.77
134	1.959	11.51	2.94	26.50	2.49	1.48	0.0241	0.0078	4.34
134	2.054	11.66	3.14	16.84	0.81	1.48	0.0197	0.0081	3.57
138	1.517	11.92	2.56	4.04	1.60	1.43	0.0256	0.0062	4.18

U. peregrina

Core	[Ca]	Li/Ca	Mg/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Cd/Ca	U/Ca	Fe/Ca
5	1.618	17.37	1.48	3.62	1.00	1.31	0.0564	0.0031	6.07
5	2.030	17.42	1.46	4.06	0.95	1.32	0.0531	0.0030	6.52
11	0.663	16.96	1.07	2.47	*4.95*	1.24	*0.1620*	0.0032	6.64
11	0.969	17.27	1.02	1.56	1.47	1.25	0.0622	0.0036	4.10
13	3.302	16.50	1.52	3.24	0.56	1.30	0.0543	0.0022	3.62
13	1.607	16.52	1.53	3.00	0.58	1.29	0.0589	0.0027	6.12
22	2.159	16.97	1.48	3.27	0.85	1.29	0.0527	0.0031	3.30
22	2.029	16.91	1.43	3.70	0.97	1.30	0.0528	0.0033	5.55
24	1.916	17.77	1.69	0.84	1.47	1.26	0.0572	0.0050	4.19
28	2.604	16.90	1.13	2.44	1.21	1.24	0.0726	0.0029	2.56
28	2.576	16.90	1.15	2.41	1.29	1.25	0.0730	0.0031	2.83
53	2.533	16.34	1.46	1.15	1.21	1.31	0.0479	0.0026	4.06
53	2.363	16.27	1.41	1.43	*3.00*	1.31	0.0539	0.0026	4.84
55	2.026	16.79	1.64	4.15	0.80	1.30	0.0574	0.0028	9.80
55	2.371	17.25	1.69	5.07	*12.72*	1.30	0.0947	0.0033	12.31
62	1.302	17.24	1.36	1.64	1.07	1.31	0.0577	0.0031	3.87
62	1.489	17.07	1.43	1.92	*13.48*	1.30	0.0729	0.0029	5.91
72	0.957	17.14	1.63	1.55	*8.84*	1.35	0.0857	0.0030	9.65
72	3.107	16.94	1.61	1.76	0.74	1.33	0.0438	0.0036	3.33
76	1.961	16.79	1.71	0.57	*3.38*	1.32	0.0446	0.0043	2.66
79	1.670	16.07	1.89	2.67	1.50	1.30	0.0418	0.0024	3.27
79	1.845	16.23	1.88	3.86	0.69	1.29	0.0368	0.0027	5.19
92	0.888	16.28	2.00	-0.18	*4.36*	1.35	0.0277	0.0020	1.64
103	1.481	16.96	1.45	7.76	2.25	1.31	0.0744	0.0036	12.61
110	1.764	14.98	2.15	-0.34	0.61	1.33	0.0205	0.0025	0.75
110	1.650	15.28	2.14	-0.29	1.44	1.32	0.0256	0.0027	1.17
118	1.348	16.26	1.85	0.94	1.65	1.33	0.0372	0.0025	1.34
118	1.589	16.24	1.84	0.84	0.55	1.33	0.0323	0.0023	1.14
121	0.719	16.27	1.86	-0.09	2.25	1.33	0.0393	0.0017	1.38
134	0.000	*-11.47*	6.67	-1470.34	*4.75*	*0.36*	*0.0240*	0.0037	-4338.65
138	1.115	15.86	1.88	0.01	0.66	1.30	0.0213	0.0018	1.58

P. ariminensis

Core	[Ca]	Li/Ca	Mg/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Cd/Ca	U/Ca	Fe/Ca
5	2.903	12.93	2.09	21.49	1.32	1.49	0.0596	0.0192	12.04
5	2.372	12.87	2.04	19.28	*3.06*	1.47	0.0611	0.0145	14.69
13	2.539	12.66	2.36	16.85	1.43	1.47	0.0578	0.0166	12.16

Core	[Ca]	Li/Ca	Mg/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Cd/Ca	U/Ca	Fe/Ca
13	3.864	12.39	2.25	14.08	1.17	1.45	0.0561	0.0144	10.85
50	0.752	12.37	2.73	13.86	1.74	1.49	0.0469	0.0177	17.14
53	3.795	12.44	2.38	17.37	2.00	1.46	0.0557	0.0158	11.82
53	2.960	12.55	2.36	16.98	*9.73*	1.48	0.0637	0.0177	47.81
55	1.918	14.17	2.24	13.29	1.11	1.49	0.0590	0.0146	13.27
55	0.533	13.82	2.20	15.31	1.99	1.49	0.0652	0.0128	16.16
62	0.480	13.40	1.74	18.04	1.85	1.48	0.0619	0.0107	14.68
76	3.161	12.43	2.23	25.65	*11.46*	1.51	0.0730	0.0061	5.31
103	0.855	13.20	1.84	16.40	1.29	1.48	0.0605	0.0082	2.90
125	3.112	15.19	1.84	15.37	1.70	1.52	0.0507	0.0106	4.23

P. foveolata

Core	[Ca]	Li/Ca	Mg/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Cd/Ca	U/Ca	Fe/Ca
19	0.863	12.48	2.58	11.51	0.44	1.52	0.0397	0.0175	7.37
50	0.554	12.33	2.72	11.00	*29.67*	1.52	0.0437	0.0189	8.67
68	2.830	11.53	2.84	10.24	0.52	1.51	0.0168	0.0130	3.88
72	2.452	16.80	2.31	23.36	1.75	1.51	0.0441	0.0077	3.42
76	3.954	12.55	2.43	24.44	*9.38*	1.47	0.0858	0.0074	3.20
79	4.562	11.76	2.59	29.40	*15.48*	1.49	0.0409	0.0171	17.97
89	2.615	11.33	2.64	6.51	*4.58*	1.53	0.0165	0.0124	3.61
110	3.025	11.61	2.75	6.24	*2.65*	1.51	0.0194	0.0100	4.47
110	2.955	11.46	2.75	6.43	1.57	1.52	0.0191	0.0118	4.51
118	4.889	12.26	2.41	12.86	0.53	1.50	0.0273	0.0077	1.98
134	0.428	12.09	2.69	5.98	1.43	1.52	0.0162	0.0089	6.85
138	1.240	11.91	2.59	8.09	1.84	1.52	0.0366	0.0100	7.03
138	2.965	11.87	2.69	9.98	*2.77*	1.51	0.0326	0.0134	8.42

H. elegans

Core	[Ca]	Li/Ca	Mg/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Cd/Ca	U/Ca	Fe/Ca
5	2.429	3.90	1.55	-2.11	0.83	1.99	0.0346	0.0570	-0.30
5	4.011	3.75	1.19	-1.98	0.43	2.01	0.0342	0.0611	-0.45
11	5.089	3.86	1.03	-1.96	0.40	1.95	0.0333	0.0608	-0.91
13	5.043	3.89	1.31	-1.62	0.35	2.18	0.0405	0.0613	1.07
13	5.088	3.83	1.26	-1.40	0.69	2.07	0.0432	0.0483	0.76
19	0.833	3.77	1.49	-1.06	*2.80*	2.46	0.0384	0.0450	2.92
19	1.503	3.79	1.53	-0.94	1.50	2.49	0.0342	0.0397	0.11
22	0.558	4.20	1.38	-0.80	1.60	2.12	0.0457	0.0534	0.57
24	3.943	3.62	1.12	-0.67	1.07	1.93	0.0390	0.0423	0.17
28	3.896	3.79	1.07	-0.64	0.17	1.89	0.0423	0.0581	-0.21
28	0.391	3.74	1.03	-0.59	1.21	1.93	0.0485	0.0541	0.54
50	2.263	3.85	1.49	2.50	1.60	2.43	0.0389	0.0457	1.24
53	0.713	*8.48*	*2.12*	-0.12	1.17	2.18	0.0534	0.0403	1.05
53	3.273	*9.32*	*2.19*	-0.03	0.44	2.24	0.0471	0.0447	0.47
55	3.659	*5.64*	*5.63*	6.38	0.82	2.12	0.0567	0.1015	22.51
55	5.180	*5.12*	*4.53*	3.58	1.63	2.11	0.0509	0.0862	8.73
62	6.987	3.56	1.07	-0.31	0.41	1.76	0.0354	0.0494	-0.24
66	2.103	3.28	1.56	-0.36	0.90	2.71	0.0090	0.0189	-0.20
68	2.238	3.65	1.64	-0.58	0.22	2.58	0.0101	0.0291	0.13
68	1.743	3.36	1.49	-0.54	0.86	2.53	0.0140	0.0238	0.28
72	0.847	4.56	1.47	-0.15	*3.24*	2.35	0.0316	0.0477	0.50
79	1.511	3.87	1.48	-0.51	0.24	2.44	0.0231	0.0542	-0.17
92	1.409	3.78	1.64	-0.62	0.61	2.55	0.0161	0.0285	-0.42

Core	[Ca]	Li/Ca	Mg/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Cd/Ca	U/Ca	Fe/Ca
94	0.913	2.69	1.30	-0.54	*3.79*	2.63	0.0156	0.0198	1.11
94	1.465	4.21	1.30	0.39	*2.33*	2.61	0.0105	0.0177	1.92
97	1.449	3.27	1.51	-0.43	*7.78*	2.69	0.0123	0.0205	1.44
97	2.296	3.02	1.42	-0.56	0.21	2.67	0.0061	0.0170	-0.19
110	1.402	3.65	1.69	-0.54	1.61	2.62	0.0130	0.0186	0.34
110	2.136	3.24	1.46	-0.62	1.11	2.57	0.0089	0.0164	1.39
112	1.071	3.23	1.48	-0.45	0.30	2.62	0.0093	0.0173	4.44
112	1.392	3.41	1.55	-0.68	0.51	2.65	0.0087	0.0207	-0.24
118	1.704	4.02	1.54	-0.66	0.20	2.37	0.0180	0.0298	-0.31
118	2.459	3.98	1.50	-0.65	0.81	2.39	0.0206	0.0297	1.29
121	2.119	4.33	1.60	-0.67	0.39	2.37	0.0238	0.0453	-0.24
134	0.795	3.65	1.61	-0.59	0.77	2.51	0.0105	0.0218	0.47
134	1.117	3.51	1.52	-0.57	0.33	2.62	0.0106	0.0227	-0.21
138	1.387	3.87	1.59	-0.50	0.98	2.50	0.0182	0.0324	-0.08
138	1.152	3.68	1.51	-0.47	*3.02*	2.52	0.0227	0.0279	0.04