A global evaluation of temperature and carbonate ion control on Mg/Ca ratios of ostracoda genus *Krithe*

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[1] Improving estimates of past ocean temperatures is paramount to our understanding of ocean circulation and its role in climate change. Magnesium/calcium (Mg/Ca) ratios of carapaces of the benthic ostracod genus *Krithe* were determined from new, globally distributed core top samples from the Norwegian Sea, Cape Hatteras shelf, Gulf of Mexico, Sulawesi Margin (Indonesia), New Zealand shelf, Ceara Rise, and the North Atlantic. A linear regression of the *Krithe* Mg/Ca ratios and bottom water temperature (BWT) reveals a significant correlation for locations where temperature during carapace calcification was above $\sim$3°C, which can be described by the equation Mg/Ca = (0.972 ± 0.152) * BWT + (7.948 ± 1.103) consistent with previous North Atlantic calibrations. Deviations from the global calibration line below $\sim$3°C follow the same pattern observed for benthic foraminifera, suggesting that the incorporation of magnesium into ostracodal calcite may be secondarily controlled by changes in carbonate ion concentration. Therefore, we propose a linear regression that describes the relationship between magnesium incorporation, temperature, and carbonate saturation for low temperatures (<3°C); Mg/Ca = (0.972 ± 0.152) * BWT + (0.100 ± 0.030) * $\Delta[CO_3^{2-}]$) + (4.440 ± 1.103) (1 SE = ± 0.3°C). While the standard error of the calibration is small, it requires an accurate knowledge of past $\Delta[CO_3^{2-}]$ concentration, which necessitates additional proxy data. Applying the calibration to glacial samples from the deep North Atlantic Ocean we show that estimates of bottom water temperatures generated from the new $\Delta[CO_3^{2-}]$-corrected equations are more consistent with results from oxygen isotopes and pore water studies.

1. Introduction

[2] The determination of oceanic paleotemperatures is integral to understanding past climate changes [*CLIMAP Project Members*, 1984]. Studies have shown a positive correlation between the calcification temperature and the concentration of magnesium in the calcium carbonate lattice of marine biogenic calcite, identifying Mg/Ca as a paleotemperature proxy [e.g., *Chave*, 1954; *Rosenthal et al.*, 1997; *Elderfield and Ganssen*, 2000; *Lear et al.*, 2000]. Foraminifera are the most commonly used microfossil group in paleoceanographic studies; however, different taxa of foraminifera incorporate magnesium differently, requiring species-specific paleotemperature equations [e.g., *Chave*, 1954; *Izuka*, 1988; *Russell et al.*, 1994; *Rosenthal et al.*, 1997; *Lear et al.*, 2002; *Martin et al.*, 2002; *McConnell and Thunell*, 2005; *Marchitto et al.*, 2007]. Some core top calibrations show an exponential relationship between benthic foraminiferal Mg/Ca ratios and BWT [*Chave*, 1954; *Rosenthal et al.*, 1997; *Lear et al.*, 2002], in agreement with thermodynamic calculations [*Lea et al.*, 1999] and inorganic precipitation experiments [*Katz*, 1973]. In addition to temperature, other controls on foraminiferal Mg/Ca ratios have been proposed, including salinity [*Nurnberg et al.*, 1996; *Lea et al.*, 1999; *Arbuszewski et al.*, 2010] and pH [*Lea et al.*, 1999; *Russell et al.*, 2004]. A large degree of scatter and elevated Mg/Ca ratios at low temperatures led to the proposal of a 'Carbonate Ion Effect' [*Elderfield et al.*, 2006; *Rosenthal et al.*, 2006]. Thus, recent foraminiferal studies report a linear Mg/Ca versus BWT relationship after carbonate ion effect correction [*Elderfield et al.*, 2006; *Marchitto et al.*, 2007; *Healey et al.*, 2008].

[3] The mechanism of the carbonate ion effect on the incorporation of trace metals in benthic foraminiferal calcite is unclear, and may result from CO_3^{2-} variations due to post-mortem dissolution processes [*McCorkle et al.*, 1995] or changing saturation during calcification [e.g., *Boyle and Rosenthal*, 1996; *Elderfield et al.*, 2006; *Rosenthal et al.*, 2006]. Similar Mg/Ca ratios of Rose-Bengal stained benthic tests (i.e., recently living) and unstained individuals (i.e., not-recently living) from the same locations indicate that carbonate ion concentration affects the incorporation of magnesium during test formation, rather than post-depositionally [*Marchitto et al.*, 2000; *Elderfield et al.*, 2006; *Rosenthal et al.*, 2006]. Quantification of the carbonate ion effect on benthic foraminiferal Mg/Ca ratios remains uncertain, with arguments for nonlinearity [*Marchitto et al.*, 2005], dependent on threshold values of $\Delta[CO_3^{2-}]$ (the difference between concentration and saturation of CO_3^{2-}, see Methods section [*Marchitto et al.*, 2005; *Rosenthal et al.*, 2006]), and/or dependent on a threshold value of temperature [*Elderfield et al.*, 2006; *Meland et al.*, 2006; *Raitzsch et al.*, 2008]. Carbonate saturation in the modern ocean does not vary significantly above 3°C, and therefore the carbonate ion effect is only substantial at low temperatures [*Elderfield et al.*, 2006].

[4] Benthic marine ostracods, microscopic bi-valved crustaceans ~1 mm in length, molt their calcitic carapace and secrete a new carapace every 1 to 3 days [*Turpen and Angell*, 1971]; thus, their carapaces record a 'snapshot' of geochemical conditions [*Okada*, 1982; *Didié and Bauch*, 2002; *Dwyer et al.*, 2002]. Ostracods are ideal for paleoclimate studies because they are widely abundant, have relatively thick carbonate shells, and maintain their chemical composition post-mortem [e.g., *Holmes et al.*, 1995; *Cronin et al.*, 2005]. *Chave* [1954] first showed a positive linear relationship between BWT and Mg/Ca of mixed-species benthic ostracod carapaces from the marine realm. Subsequent studies established that the relationship between Mg/Ca ratios and BWT differed among ostracod superfamily groups [*Cadot et al.*, 1972; *Cadot and Kaesler*, 1977], emphasizing the need for genera-specific paleotemperature equations.

Table 1. Previously Published Paleotemperature Equations for *Krithe* Mg/Ca[a]

BWT (°C)	Location	Equation	Author
1–6	8 Global Sites	Mg/Ca = 1.466 * BWT + 5.189	*Cadot and Kaesler* [1977]
2–6	SCS	Mg/Ca = 1.923 * BWT + 6.430	*Corrège and De Deckker* [1997]
3–14	LBB	Mg/Ca = 1.172 * BWT + 6.729	*Dwyer et al.* [1995]
−2–2	SA	Mg/Ca = 2.667 * BWT + 9.410	*Cronin et al.* [1996]
−2–14	LBB, SA	Mg/Ca = 0.96 * BWT + 8.6113	*Cronin et al.* [1996]
4–9	SCS, LBB, SA, OJP, CF	Mg/Ca = 0.931 * BWT + 8.14; $Mg/Ca = 9.353 * 10^{0.025 * BWT}$	*Dwyer et al.* [2002]
−1.7–16	Arctic, Norwegian, N. Atlantic	Mg/Ca = 1.13 * BWT + 6.42; $Mg/Ca_{K.\ glacialis} = 2.28 * BWT + 11.71$	*Farmer et al.* [2012]
−2–14	Global Calibration	For BWT > 3°C: Mg/Ca = 0.972 * BWT + 7.948 For BWT < 3°C: Mg/Ca = 0.972 * BWT + 0.100 * $\Delta[CO_3^{2-}]$ + 4.440	This study

[a]Location abbreviations are; South Coral Sea (SCS), Little Bahama Bank (LBB), Shallow Arctic less than 900 m (SA), Ontong Java Plateau (OJP), and Chilean Fjords (CF). Units for the equations are mmol/mol for Mg/Ca, °C for BWT, and μmol/kg for $\Delta[CO_3^{2-}]$.

[5] *Krithe* [*Brady et al.*, 1874] is a ubiquitous ostracod genus found from 150 m to abyssal water depths [*Whatley and Quanhong*, 1993; *Yasuhara et al.*, 2008]. Carapaces of *Krithe* are smooth with few pores, minimizing the potential for detrital contamination, and making *Krithe* ideal for paleoceanographic reconstructions [e.g., *Bodergat*, 1983; *Corrège*, 1993a, 1993b; *Cronin and Raymo*, 1997; *Zhao and Whatley*, 1997; *Rodriguez-Lazaro and Cronin*, 1999]. *Krithe* incorporates Mg into its carapace homogeneously [*Cadot et al.*, 1972; *Dwyer et al.*, 2002] and is resistant to dissolution [*Swanson and van der Lingen*, 1994]. Previous studies have described a linear relationship between *Krithe* Mg/Ca and BWT [*Cadot and Kaesler*, 1977; *Corrège and De Deckker*, 1997; *Dwyer et al.*, 1995; *Cronin et al.*, 1996; *Dwyer et al.*, 2002], although *Dwyer et al.* [2002] argued that the relationship may be exponential (Table 1). Temperature has been the main factor investigated with respect to magnesium incorporation in *Krithe* carapaces, though salinity has been shown to exert some effect on the Mg/Ca ratios of other ostracod genera from marine [*Bodergat et al.*, 1993], lacustrine [*Guang et al.*, 2008; *Decrouy et al.*, 2012], and estuarine environments [*Cronin et al.*, 2002]. One pilot study suggests that carbonate ion concentration does not affect magnesium incorporation in *Krithe* [*Dwyer et al.*, 2002]. More recently, *Farmer et al.* [2012] show a unique correlation between Mg/Ca and bottom temperatures in the ostracod *Krithe* genus from North Atlantic core tops. Furthermore they found no evidence for a relationship between *Krithe* Mg/Ca and carbonate ion saturation in the North Atlantic Ocean and Nordic Seas although the data from the latter sites were substantially offset from the multispecies North Atlantic calibration, a fact that they attribute to difference in species variations [*Farmer et al.*, 2012]. Here we expand the global Mg/Ca-calibration data set and evaluate the Mg/Ca-temperature calibration in sites from Nordic Seas and Gulf of Mexico (homethermal sites) and new core tops from the Pacific and Atlantic Ocean basins that were not included in previous calibration studies.

[6] The growing understanding of elemental ratios in ostracod calcite has followed foraminiferal studies in generating species-specific paleotemperature equations. Now, similar to the elevated Mg/Ca ratios at low temperatures noted for benthic foraminiferal [e.g., *Martin et al.*, 2002], which led to the proposal of the 'Carbonate Ion Effect' [*Elderfield et al.*, 2006; *Rosenthal et al.*, 2006], *Cronin et al.* [1996] noted elevated *Krithe* Mg/Ca ratios at low temperatures. *Cronin et al.* [1996], and subsequent studies [*Dwyer et al.*, 2000, 2002], excluded samples from the deep Arctic Ocean from calibrations because of the elevated Mg/Ca ratios. *Farmer et al.* [2012] also noted elevated Mg/Ca values from Arctic and Nordic Seas relative to the multispecies Atlantic calibration that the authors explained using a species-specific equation for *Krithe glacialis* with a higher sensitivity to BWT. Given elevated Mg/Ca at low temperatures in both benthic foraminifera and ostracodal trends, and the environmental factors that have been suggested to affect the Mg/Ca ratio in foraminifera, this study aims to reevaluate how temperature and carbonate ion concentration influence magnesium incorporation into the calcite lattice of *Krithe* carapaces. Published paleoceanographic records have shown large changes in oceanic $\Delta[CO_3^{2-}]$ [e.g., *Yu et al.*, 2008], and thus determining the carbonate ion control on paleotemperature proxies is critical.

[7] Herein, we present *Krithe* Mg/Ca ratios from globally dispersed core top locations to elucidate primary and secondary controls on the Mg
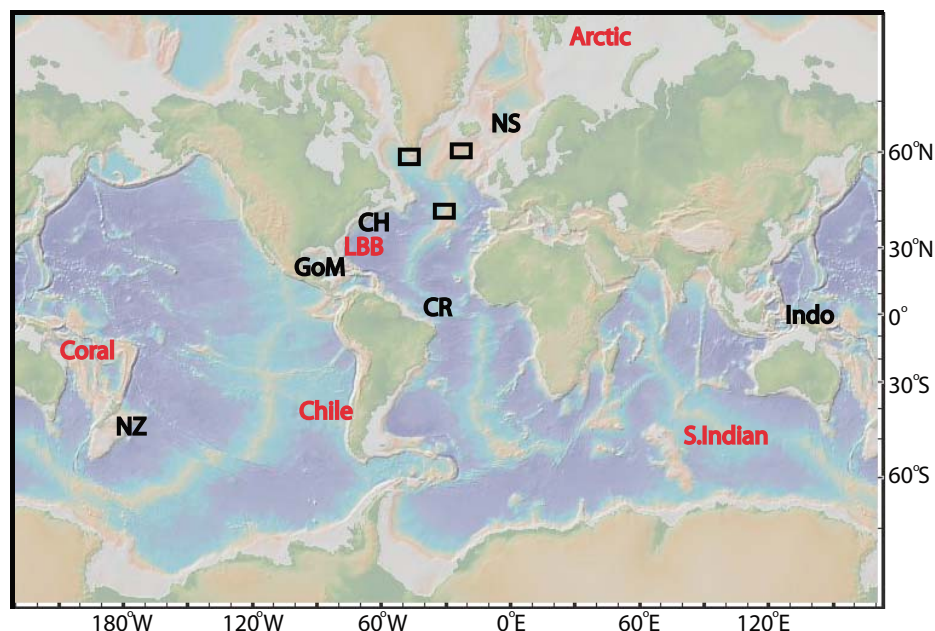
Figure 1. Map showing the global distribution of core tops used in this study. Location abbreviations from this study (black) are; Norwegian Sea (NS), Cape Hatteras shelf (CH), Gulf of Mexico (GoM), Ceara Rise (CR), Sulawesi Margin, Indonesia (Indo), and New Zealand shelf (NZ). Location abbreviations for locations used in previous studies (red) are; Little Bahama Bank (LBB), Coral Sea (Coral), Chilean Fjords (Chile), and Southern Indian Ocean (SI). This study includes data from all previously published studies and our new locations

incorporation in ostracod carapaces. Previously published *Krithe* paleotemperature equations have been iterative but were mainly comprised of a few locations (Table 1) [*Cadot and Kaesler*, 1977; *Corrège and De Deckker*, 1997; *Dwyer et al.*, 1995; *Cronin et al.*, 1996; *Dwyer et al.*, 2002; *Farmer et al.*, 2012]. Using a new, globally distributed collection of core tops, in conjunction with the previously published core top data, we will examine the Mg/Ca sensitivity to temperature, and examine the effects of carbonate ion concentration during calcification and post-depositional carbonate dissolution. An improved paleotemperature equation for *Krithe* will be a useful paleoceanographic tool, since some deep-sea sediment cores lack commonly studied benthic foraminiferal taxa.

2. Methods

2.1. Core Top Locations

[8] For this study, core top samples were obtained predominantly from multi and box cores from five depth transects, designed to sample a large range of water depths, bottom water temperatures, salinities, and carbonate ion concentrations. In this research, the difference between in situ carbonate ion saturation and concentration, $\Delta[CO_3^{2-}]$ (see below for this calculation) is used instead of $[CO_3^{2-}]$ concentration because benthic foraminiferal Mg/Ca studies have shown that the degree of undersaturation is the key parameter when assessing the control of carbonate ion on Mg/Ca ratios [*Elderfield et al.*, 2006; *Rosenthal et al.*, 2006]. Samples for this study came from the Norwegian Sea, Gulf of Mexico, Cape Hatteras shelf, New Zealand shelf, and Sulawesi Margin, Indonesia (Figure 1 and auxiliary material, Appendices 1 and 2).[1] Core top samples from gravity and piston cores from the North Atlantic and Ceara Rise were also analyzed (Figure 1 and auxiliary material, Appendices 1 and 2).

[9] Norwegian Sea samples were collected from water depths of 418 to 2799 m in the Norway Basin (Figure 1 and auxiliary material, Appendices 1 and 2). These sites are bathed by Norwegian Sea Bottom Water, which forms from winter convection of cold surface water originating from the North Atlantic Drift and Arctic inflow. These samples represent nearly homothermal (−0.8 to 0.8°C) and homohaline (~34.91 PSU) conditions, and are considered to be oversaturated with respect to calcite ($\Delta[CO_3^{2-}]$ = 30.43 to 78.86 μmol/kg; auxiliary

material, Appendices 1 and 2). Norwegian Sea sites provide excellent samples to examine possible carbonate ion effects at low temperatures. The samples were collected by the *R/V Knorr* on Cruise 177–2.

[10] Samples from the northern Gulf of Mexico were collected from water depths of 1026 to 3150 m (auxiliary material, Appendices 1 and 2). These sites are bathed by the Yucatan Current, which becomes the Loop Current that exits the Florida Straight to join the Gulf Stream. The Gulf of Mexico sites also represent nearly homothermal (4.3 to 4.9°C) and homohaline (34.94 to 35.00 PSU), but have a range of $\Delta[CO_3^{2-}]$ values (23.94 to 57.47 μmol/kg). These locations allow for the examination of carbonate ion effects at temperatures >3°C. The Gulf of Mexico samples were sub-sampled from the Deepwater Program: Northern Gulf of Mexico Continental Slope Habitats and Benthic Ecology (DGoMB; Gilbert T. Rowe, TAMU, 2000).

[11] Samples from the Cape Hatteras shelf were collected from water depths of 2214 to 3979 m (auxiliary material, Appendices 1 and 2). Southward flowing North Atlantic Deep Water bathes these sites, which range in bottom water temperature from 2.2 to 3.4°C, salinity from 34.88 to 34.94 PSU, and $\Delta[CO_3^{2-}]$ from 17.39 to 44.12 μmol/kg (auxiliary material, Appendices 1 and 2). These samples were collected by the *R/V Knorr* on Cruise 178, and were chosen to represent a supersaturated environment.

[12] New Zealand shelf samples were collected from water depths from 663 to 2472 m in waters bathed by Antarctic Intermediate Water (auxiliary material, Appendices 1 and 2). The sites have bottom water temperatures of 1.9 to 4.9°C, salinities of 34.29 to 34.72 SU, and $\Delta[CO_3^{2-}]$ values of 13.87 to 57.23 μmol/kg (auxiliary material, Appendices 1 and 2). The New Zealand shelf samples were collected by the *R/V Roger Revelle* Cruise 05–03, and represent an undersaturated environment.

[13] Northern North Atlantic, midlatitude North Atlantic, and Ceara Rise samples were collected by *R/V Knorr*, Cruise 166–14, and by the Ocean Drilling Program Legs 94 and 154, respectively (auxiliary material, Appendices 1 and 2). Cores KN166–14 11JPC, 8GGC, and 3GGC were collected from 2707 to 3305 m water depth on Gardar Drift (auxiliary material, Appendices 1 and 2) and are bathed by modern Iceland Scotland Overflow Water [*Worthington*, 1976; *Bianchi and McCave*, 1999]. Cores 11JPC, 8GGC, and 3GGC have Holocene sedimentation rates of ~20 cm/kyr [*Elmore*, 2009], ~8 cm/kyr [*Elmore*, 2009], and ~10 cm/kyr [*Elmore*, 2009], respectively. Core

KN166–14 12JPC was collected from 3078 m water depth near the Charlie Gibbs Fracture Zone (auxiliary material, Appendices 1 and 2); the location is also currently bathed by Iceland Scotland Overflow Water [*Worthington*, 1976]. Core KN166–14 15JPC was collected from 2300 m on Eirik Drift and also has a high sedimentation rate (~15 cm/kyr), though late Holocene sediments have been winnowed from this location [*Neitzke and Wright*, 2007]. The location of 15JPC is bathed by modern Northeast North Atlantic Deep Water, which is comprised of Iceland Scotland Overflow Water and Denmark Straights Overflow Water [*Worthington*, 1976]. Core CHN82–23PC was occupied at a water depth of 3427 m in the central North Atlantic (auxiliary material, Appendices 1 and 2); this site is bathed by modern North Atlantic Deep Water [*Raymo et al.*, 1990].

[14] Ceara Rise cores ODP sites 926, 928, and 989 were collected from a water depth range of 3589 to 4355 m from the western equatorial Atlantic (auxiliary material, Appendices 1 and 2) [*Bickert et al.*, 1997]. Ocean Drilling Program sites 926, 928, and 929 have Holocene sedimentation rates of ~4.5, ~4.8, and ~5 cm/kyr, respectively [*Bickert et al.*, 1997]. The Ceara Rise is bathed by modern North Atlantic Deep Water [*Bickert et al.*, 1997].

[15] Site information for samples from the Sulawesi Margin in Indonesia, which were collected by the *R/V Baruna Jaya* on cruise 08–03, was published in *Rosenthal et al.* [2006] (auxiliary material, Appendices 1 and 2).

2.2. Core Top Hydrography

[16] For each site, hydrographic parameters of bottom water temperature and bottom water salinity were either measured on the cruise from a conductivity-temperature-depth (CTD) cast or found from online databases, including the World Ocean Circulation Experiment (WOCE; http://cdiac.ornl.gov), Transient Tracers in the Oceans (TTO; http://gcmd.nasa.gov/records/GCMD_CDIAC_NDP4.html), or Carina cruise summary data (CARINA; http://cdiac.ornl.gov/oceans/CARINA/Carina_table.html). Total phosphorous, total silicate, total dissolved inorganic carbon, and total alkalinity was measured shipboard for Indonesia [*Rosenthal et al.*, 2006] and found from online databases for other locations. All hydrographic information for the sites discussed is listed in the auxiliary material (Appendix 1). In addition to the core tops discussed herein, hydrographic data have been compiled for as many previously

published core top locations as possible (auxiliary material, Appendix 2). For some of the core top sites discussed in this work, and some previously published core top sites, a correction was required to account for the difference between the presumed late Holocene calcification environment and the measured modern hydrographic conditions caused by the invasion of anthropogenic CO_2 into the subsurface waters in regions of deep water formation [e.g., *Orr et al.*, 1995]. Where applicable, TCO_2 has been corrected to pre-industrial values by subtracting the estimated anthropogenic CO_2 contribution, according to the region and water depth (auxiliary material, Appendices 1 and 2). Estimated anthropogenic CO_2 inputs for northern North Atlantic, Norwegian Sea, and Arctic samples were found in *Sabine et al.* [2004], *Jutterström et al.* [2008], and *Jutterström and Jeansson* [2008], respectively. This correction was only applied for sites where the predicted concentration of anthropogenic CO_2 is greater than 5 μmol/kg, otherwise the anthropogenic effect was considered negligible [*Elderfield et al.*, 2006].

[17] Hydrographic parameters were entered into the CO_2Sys program [*Lewis and Wallace*, 1998] to calculate in situ carbonate ion concentration ($[CO_3^{2-}]_{in\ situ}$; auxiliary material, Appendices 1 and 2). Equilibrium constants K_1 and K_2 were calculated using *Dickson and Millero* [1987] after *Mehrbach et al.* [1973], and K_{SO4} was calculated according to *Dickson* [1990]. Carbonate ion saturation ($[CO_3^{2-}]_{saturation}$) was then determined by

$$[CO_3{}^{2-}]_{saturation} = 90 * e^{[0.16*(z-4)]} \qquad (1)$$

where z is the water depth in kilometers [*Broecker and Peng*, 1982]. Seawater calcite saturation state ($\Delta[CO_3^{2-}]$) was then calculated by

$$\Delta[CO_3{}^{2-}] = [CO_3{}^{2-}]_{in\ situ} - [CO_3{}^{2-}]_{saturation} \qquad (2)$$

2.3. Sample Processing

[18] Following collection, core top samples from Cape Hatteras shelf, New Zealand shelf, and Sulawesi Margin, Indonesia were refrigerated at 4°C, preserved in a 4% buffered formalin-seawater solution, then processed with Rose Bengal stain (1 g/L of 4% formalin-seawater solution [*Walton*, 1952]) for 1 week according to the procedure outlined in *Corliss and Emerson* [1990]. Stained carapaces indicate the occurrence of protoplasm; these carapaces were assumed to be recently living and thus unaltered by any effects of post-mortem dissolution; unstained specimens, with no remaining protoplasm, may have been diagenetically altered

[*Walton*, 1952]. *Elmore* [2009] found no difference in Mg/Ca between stained and unstained carapaces from these three locations, possibly suggesting that diagenetic processes are not a large factor in Mg/Ca ratios. Core tops from other regions could not be stained due to a delay in processing.

2.4. Down Core Samples From KN166–14 11JPC

[19] Jumbo piston core KN166–14 11JPC (11JPC) was collected by the *R/V Knorr* on cruise 166–14 from 2707 m water depth on southern Gardar Drift, in the northern North Atlantic (56°W, 27°W). Following sample collection, the core was refrigerated at 5 °C at the Rift/Drift Core Repository at Rutgers University and sampled at 5 cm intervals, yielding a ~600 year sampling resolution. An age model generated from 15 AMS ^{14}C dates and chronostratigraphic comparison to a stacked benthic record by *Lisiecki and Raymo* [2005] identifies the core top age as ~600 years [*Elmore and Wright*, 2011]. An unconformity exists in this core suggesting that Last Glacial Maximum sediments have been scoured from this location and therefore a comparison between Marine Isotope Stage 3 (MIS 3) and the Holocene (MIS 1) has been used to test the utility of this calibration for paleoceanographic records.

2.5. Analytical Methods

[20] Each sample was washed through a 63 μm sieve to remove silts and clays, and then dried. *Krithe* carapaces were handpicked under a binocular microscope from the >250 μm size fraction from each sample. Previous studies have shown that there is no systematic offset in the Mg/Ca ratio between the left and right valves or between male and female individuals for *Krithe* [*Dwyer et al.*, 2002]. *Krithe reversa* and *K. minima* were excluded from this study because they have been shown to record elevated magnesium concentrations and thus are expected to co-precipitate magnesium differently from other species in the *Krithe* genus [*Corrège*, 1993a, 1993b; *Dwyer et al.*, 2002]. The arctic species, *K. glacialis*, may also differentially co-precipitate magnesium [*Farmer et al.*, 2012]. All adult and A-1 (in their final stage of molting before adulthood) carapaces were collected for analyses to test the hypothesis that they incorporate Mg similarly [*Dwyer et al.*, 2002]. A 'Visual Preservation Index' (VPI) was used to determine the quality of preservation of the carapaces [*Dwyer et al.*, 1995; *Cronin et al.*, 1996]. On a scale of 1,

Table 2. *Krithe* Mg/Ca and *P. wuellerstorfi* $\delta^{18}O$ Data [*Elmore*, 2009] From Holocene and Late MIC 3 Sections of Core 11JPC Used for Paleotemperature Estimates[a]

Depth (cm)	Age (ka)	Mg/Ca (mmol/ mol)	BWT (°C) Mg/Ca	$\Delta[CO_3^{2-}]$ (μmol/kg)	BWT (°C) Mg/Ca, $\Delta[CO_3^{2-}]$	Adj. $\delta^{18}O$ *P. wuell.* (‰ V-PDB)	$\delta^{18}O_{SW}$ (‰ V-SMOW)	BWT (°C) $\delta^{18}O$
				Holocene				
10	1.14	10.36				3.56		
35	2.36	8.85				3.48		
55	3.38	10.21				3.40		
100	5.80	10.53				3.52		
105	6.05	9.71				3.59		
120	6.73	11.01				3.55		
165	9.82	9.54				3.40		
175	10.75	9.95				3.50		
Average		10.02	**2.1**	38.8	**1.7**	3.50	0.03	**3.02**
St. deviation		0.67				0.07		
				Late MIC 3				
333	33.81	9.15				4.76		
348	34.60	9.19				5.11		
363	35.44	8.93				4.90		
368	35.72	9.09				4.98		
431	40.09	9.10				4.90		
431	40.09	9.26				4.90		
431	40.09	9.50				4.90		
441	41.01	8.35				4.89		
441	41.01	8.70				4.89		
446	41.48	8.25				5.45		
471	44.17	8.95				4.78		
Average		8.95	**1.8**	63.8	**−1.9**	4.95	0.60	**−1.58**
St. deviation		0.38				0.19		

[a]Average Mg/Ca and estimated $\Delta[CO_3^{2-}]$ values for modern (auxiliary material, Appendices 1 and 2) and glacial [*Yu et al.*, 2008] were used to estimate BWT from Mg/Ca with and without carbonate ion effects using equations (5) and (6), respectively. *Planulina wuellerstorfi* $\delta^{18}O$ data has been corrected by 0.64 ‰ to account for disequilibrium from seawater during calcification (Adj. $\delta^{18}O$ *P. wuell.* [*Shackleton*, 1974]). Temperatures based on *P. wuellerstorfi* $\delta^{18}O$ (BWT $\delta^{18}O$) and $\delta^{18}O_{SW}$ [*Waelbroeck et al.*, 2002] were estimated according to *Shackleton* [1974]: BWT = 16.9 − 4.0 ($\delta^{18}O_{calcite} − (\delta^{18}O_{SW} − 0.27$ ‰)).

signifying clear and unaltered, to 6, crusty and brittle [*Dwyer et al.*, 1995], carapaces used in this study were typically very well preserved (VPI 1–3; Table 2 and auxiliary material, Appendices 1 and 2).

[21] One to three *Krithe* carapaces (∼200 μg each) were selected using a binocular microscope for trace metal geochemical analysis at the Rutgers Inorganic Analytical Laboratory at the Institute of Marine and Coastal Sciences at Rutgers University [*Rosenthal et al.*, 1999]. The carapaces were manually cleaned with a fine-hair brush to remove surficial clays [*Holmes*, 1992; *Jin et al.*, 2006]. Samples were then chemically cleaned to remove any remaining clays, organic matter and metal oxides, according to the procedure outlined in *Rosenthal et al.* [1999], modified from *Boyle and Keigwin* [1985, 1986]. Cleaned samples were titrated with trace-metal clean 0.065 N HNO_3 until complete dissolution was achieved; 100 μl of each primary solution was further diluted to 400 ml with 0.5 N HNO_3. This way most sample solutions have

[Ca] concentration of about 4 mM, thus minimizing the matrix effects on the determination of Mg/Ca. The diluted solutions were analyzed by Thermo Element Sector Field Inductively Coupled Plasma Mass Spectrometer (SF-ICP-MS). The long-term precision of Mg/Ca analysis was ±1.24%, ±1.16% and ±0.57% (1 S.D.), as determined by repeated measurements of three consistency standards with Mg/Ca ratios of 1.25, 3.32 and 7.51 mmol/mol, respectively. Elemental ratios of Mn/Ca, Fe/Ca, Al/Ca, and Ti/Ca were used to screen samples for contamination due to diagenetic coatings or lingering detrital material.

3. Results and Discussion

3.1. Inter- and Intraregional Variability

[22] Core top Mg/Ca ratios from this study range from ∼3 to 17 mmol/mol over a BWT range of −1 to 12°C (Figure 2 and auxiliary material, Appendix 3). A linear regression of these data
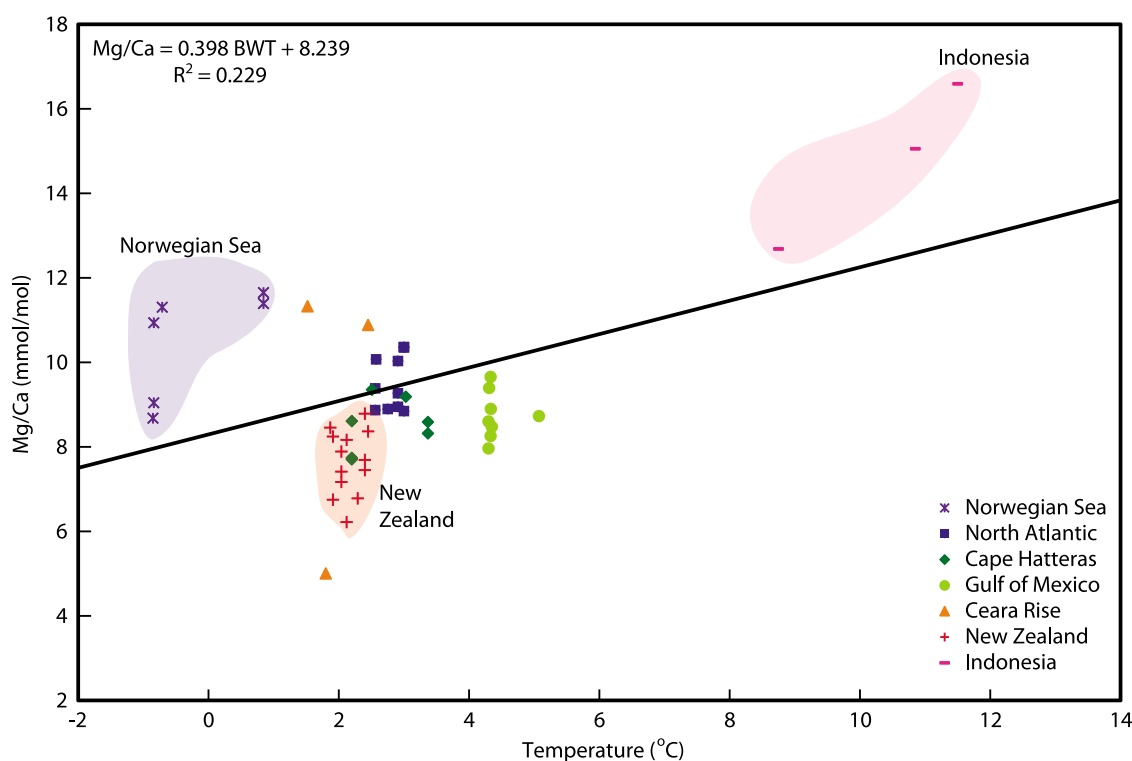
Figure 2. Comparison of *Krithe* Mg/Ca ratios and bottom water temperature for new core tops from the Norwegian Sea (purple), North Atlantic Ocean (blue), Cape Hatteras shelf (dark green), Gulf of Mexico (light green), Ceara Rise (orange), New Zealand shelf (red), and Sulawesi Margin, Indonesia (pink). Shaded regions represent a non-statistical grouping of data of data from Norwegian Sea (purple), Norwegian Sea (red), and Indonesia (pink). A linear regression of the data (black line) has an R^2 value of 0.23, indicating low correlation.

reveals that Mg/Ca and BWT does not show very significant correlation (R^2 = 0.229; P- value = 0.0014; slope = 0.398 mmol/mol/°C; intercept = 8.239 mmol/mol; Figure 2). However, when examined by region, distinct Mg/Ca versus BWT relationships emerge (Figure 2). Samples from the cold, carbonate saturated Norwegian Sea and warm Sulawesi Margin, Indonesia sites have elevated Mg/Ca ratios with respect to the general trend (Figure 2). Mg/Ca ratios from New Zealand shelf sites, particularly the shallowest New Zealand shelf sites, are lower than the general Mg/Ca trend (Figure 2). Some of the range in Mg/Ca values (for instance within the Gulf of Mexico; Figure 2) can be explained by individual variability as analyses were completed on 1–2 carapaces and when averaged fall close to the general regression line. Additionally, the scatter around this regression, particularly at low temperatures, suggests that there may be secondary, non-temperature related controls on the incorporation of magnesium into the calcitic carapace of *Krithe*.

[23] A positive linear relationship is also observed between core top *Krithe* Mg/Ca ratios from this study and $\Delta[CO_3^{2-}]$ (R^2 = 0.326; P- value = 0.000025; Figure 3). It is difficult to determine, however, whether these relationships are due to direct dependence on $\Delta[CO_3^{2-}]$ or temperature because both parameters co-vary in the deep ocean. We use the two homo-thermal, homo-haline transects, from the Norwegian Sea and Gulf of Mexico, to examine the effect of $\Delta[CO_3^{2-}]$, independent of temperature and salinity changes (Figure 3). Samples from the Norwegian Sea transect show no significant relationship between Mg/Ca and $\Delta[CO_3^{2-}]$ at temperatures from -1.0 to 0.5°C (R^2 = 0.164; P- value = 0.29; slope of 0.026; Figure 3). Likewise, samples from the Gulf of Mexico homo-thermal transect do not exhibit any significant covariance between Mg/Ca and $\Delta[CO_3^{2-}]$ at temperatures of ~4.3°C (R^2 = 0.030; P- value = 0.34; Figure 3). The absence of a depth-related trend in both homo-thermal transects apparently argues against a significant $\Delta[CO_3^{2-}]$ effect on ostracodal Mg/Ca leading *Farmer et al.* [2012] to attribute the offset between the Norwegian samples and the global data set to iner-species variability between K. glacialis and all other *Krithe* species. Here we follow the conclusions of *Elderfield et al.* [2006], which are
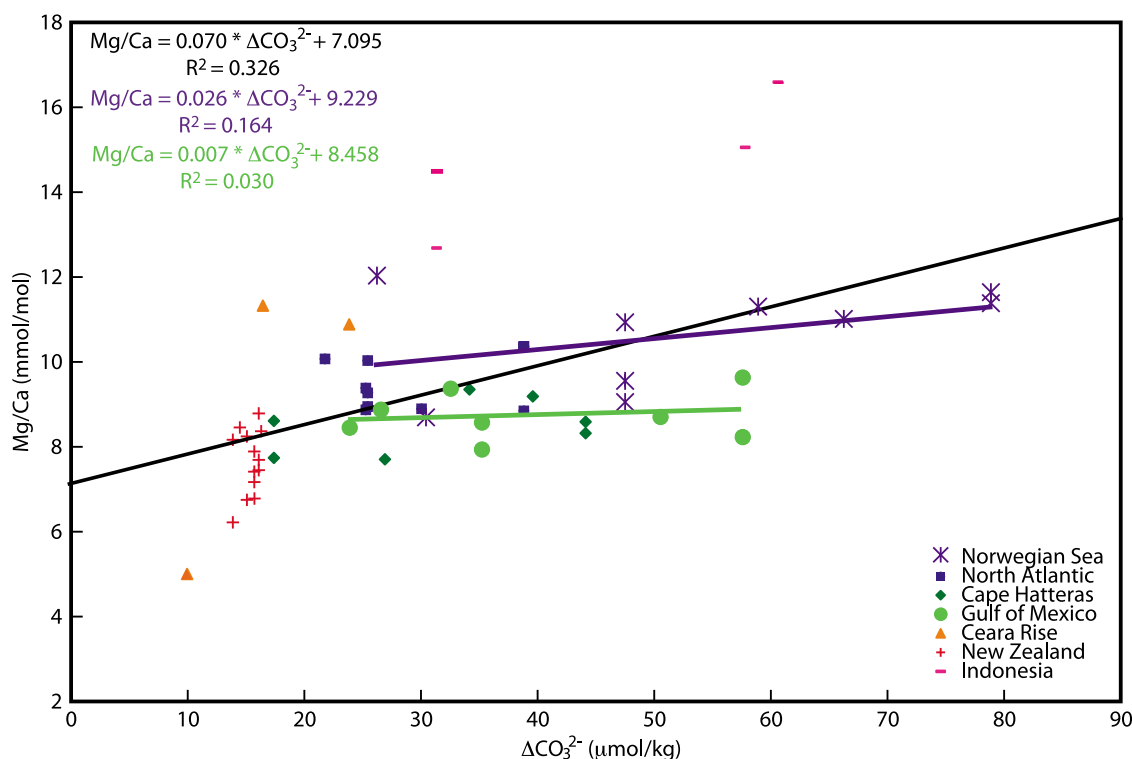
Figure 3. Core top Mg/Ca data versus $\Delta[CO_3^{2-}]$ from this study; Norwegian Sea (purple), North Atlantic Ocean (blue), Cape Hatteras shelf (dark green), Gulf of Mexico (light green), Ceara Rise (orange), New Zealand shelf (red), and Sulawesi Margin, Indonesia (pink) sites plotted versus $\Delta[CO_3^{2-}]$. A linear regression for all the data is shown in black. Linear regressions for the cool, homo-thermal, homo-haline transect of the Norwegian Sea (purple) and for the warm, homo-thermal, homo-haline transect of the Gulf of Mexico (light green) are also shown.

based on their calibration of Mg/Ca ratios in benthic foraminifera, to suggest that the offset in Mg/Ca ratios in Norwegian Sea and New Zealand ostracods from the global calibration is due to a 'carbonate ion effect' on *Krithe* that only occurs at low temperatures (Figure 3), similar to the carbonate ion effect in benthic foraminifera [*Elderfield et al.*, 2006].

3.2. Temperature Calibration

[24] Previously published core top calibrations of *Krithe* Mg/Ca ratios have identified temperature as the main control on magnesium incorporation (Table 1) [e.g., *Dwyer et al.*, 1995; *Farmer et al.*, 2012]. Core top Mg/Ca ratios from this study are combined with all previously published core top data [*Cadot et al.*, 1972; *Cadot and Kaesler*, 1977; *Dwyer et al.*, 1995; *Cronin et al.*, 1996; *Corrège and De Deckker*, 1997; *Dwyer et al.*, 2002] (auxiliary material, Appendix 2) in order to more completely examine factors that may affect the incorporation of magnesium into the carapaces of ostracods. A compilation of core top data from this study and published core top data yields a

statistically significant positive linear regression between Mg/Ca ratios and temperature, defined by the equation Mg/Ca$_{Krithe}$ = (0.689 mmol/mol/°C * BWT) + 9.677 mmol/mol (R^2 = 0.448; P- value ≪ 0.05; Figure 4). Scatter is especially prevalent at low temperatures, particularly from Norwegian Sea data from this study, and from the Arctic Ocean data from *Cronin et al.* [1996], as was noted by those authors (Figure 4). Deep Pacific sites have Mg/Ca ratios that are lower than the global regression (Figures 2 and 4).

[25] According to the method outlined in *Elderfield et al.* [2006], since some of the scatter at low temperatures may result from secondary calcification effects, an initial paleotemperature equation was generated by compiling data from this study and published data from locations with bottom water temperatures above ~3°C (Figure 4). This critical temperature was selected for a variety of reasons; (1) 3°C is the temperature below which carbonate ion changes significantly in the modern ocean, (3) a larger amount of scatter is seen in the combined *Krithe* Mg/Ca data set at low temperatures below 3°C, (3) there is a statistically stronger relationship
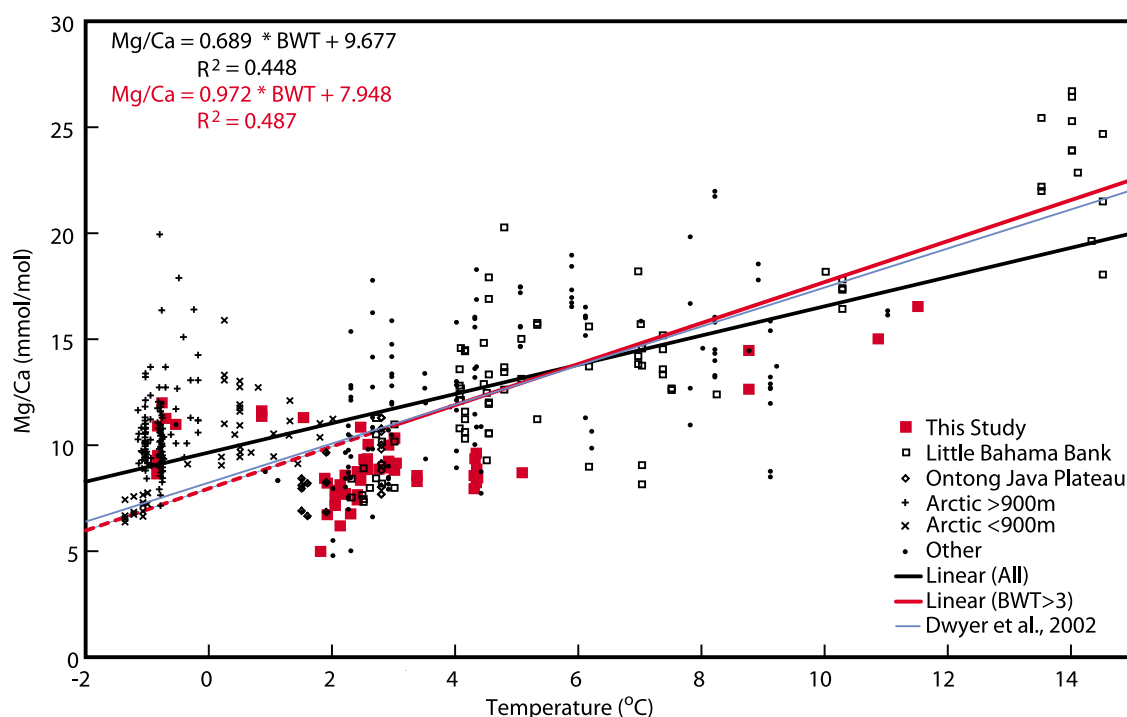
Figure 4. Mg/Ca data from core top sites from this study (red squares) plotted against temperature. Data from Little Bahama Bank ([*Dwyer et al.*, 1995] black squares), Ontong-Java Plateau ([*Dwyer et al.*, 2002] black diamonds), Arctic Ocean <900 m ([*Cronin et al.*, 1996] black x-s), the Arctic Ocean >900 m ([*Cronin et al.*, 1996] black crosses), and all other sources ([*Cadot et al.*, 1972; *Cadot and Kaesler*, 1977; *Corrège*, 1993b; *Corrège and De Deckker*, 1997] small black circles) are also shown. The black line represents a linear regression of all of the data, and the red line represents a linear regression of data from sites where BWT >3°C. The linear Mg/Ca- temperature equation from *Dwyer et al.* [2002] (Mg/Ca = 0.931 * BWT + 8.14) is shown by the thin blue line. The difference between our Mg/Ca-temperature relationship for BWT >3°C and the *Dwyer et al.* [2002] equation is minimal because that regression included only a small amount of data in the lower temperature range.

between Mg/Ca and BWT above 3°C (correlation coefficient = 0.698), suggesting temperature is a dominant control on Mg/Ca, rather than below 3°C (correlation coefficient = 0.084), suggesting a non-temperature control on Mg/Ca at low temperatures, and 4] 3°C is the threshold below which carbonate ion effects have been observed in benthic foraminifera [*Elderfield et al.*, 2006]. A linear regression of all available core top data above 3°C yields the equation

$$Mg/Ca_{Krithe} = (0.972 \pm 0.152) * BWT + (7.948 \pm 1.103)$$
(3)

where Mg/Ca is in mmol/mol and BWT is in °C, reported with standard error (R^2 = 0.487; P- value ≪ 0.05). Extrapolation of this regression to lower temperatures confirms that the Mg/Ca ratios of Norwegian Sea samples from this study and in Arctic Ocean samples from *Cronin et al.* [1996] fall consistently above the trend line (Figure 4).

The Mg/Ca temperature sensitivity for *Krithe*, 0.972 mmol/mol/°C, is higher than published temperature sensitivities for benthic foraminifera that range from 0.11 to 0.50 mmol/mol/°C [*Healey et al.*, 2008, and references therein], which is reasonable given that the concentration of Mg/Ca found in *Krithe* is an order of magnitude higher than benthic foraminiferal concentrations.

3.3. Carbonate Ion Effects

[26] Results from this study and published studies suggest that temperature is the primary control on Mg/Ca incorporation in *Krithe* carapaces (Figure 4) [*Dwyer et al.*, 1995; *Cronin et al.*, 1996], but our data also highlight the large scatter in the Mg/Ca – BWT regression at low temperatures and suggest that carbonate ion concentration might control Mg incorporation at low temperatures (Figure 3). Therefore, the dominant temperature effect must be removed to better understand the secondary relationship between Mg/Ca and $\Delta[CO_3^{2-}]$ [*Elderfield*

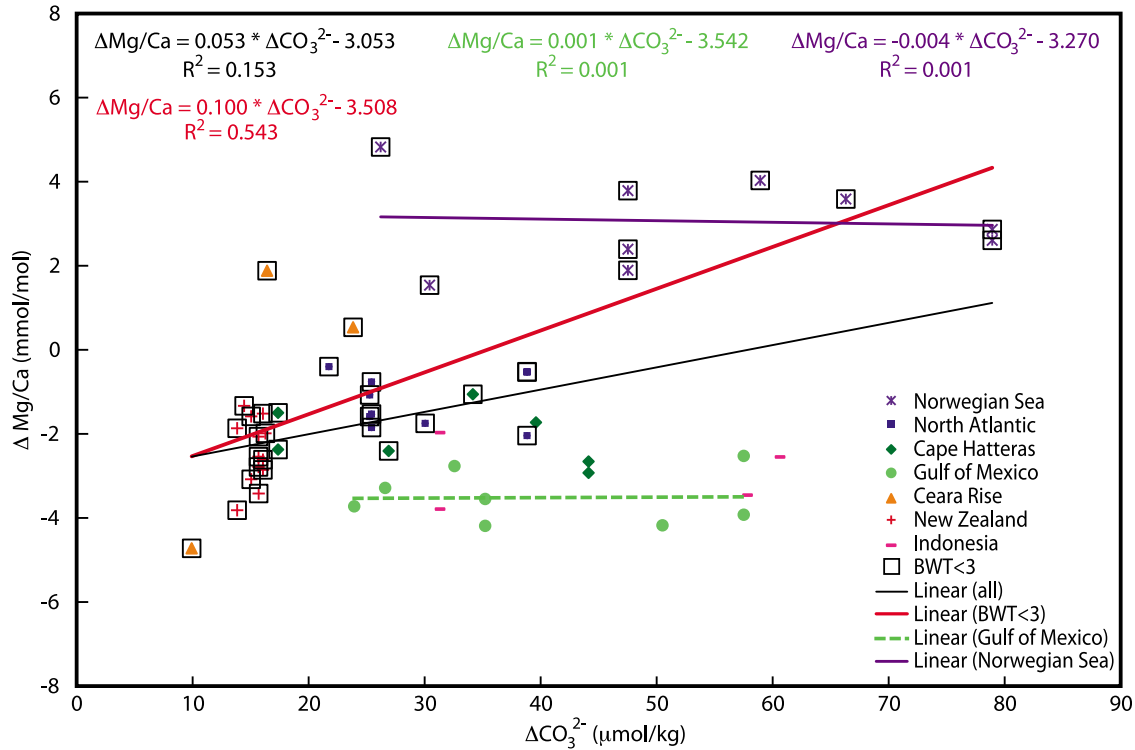**Figure 5.** The deviation between measured Mg/Ca and temperature based upon expected Mg/Ca (ΔMg/Ca) from equation (4) plotted versus $\Delta[CO_3^{2-}]$ for core top sites from the Norwegian Sea (purple; regression shown as purple line), North Atlantic Ocean (blue), Cape Hatteras shelf (dark green), Gulf of Mexico (light green; regression shown as dotted green line), Ceara Rise (orange), New Zealand shelf (red), and Sulawesi Margin, Indonesia (pink). The black line represents a linear regression of all of the data. Core top sites with BWT $\leq 3°C$ are identified by outer squares, and defined by the red linear regression.

et al., 2006]. To examine secondary effects other than temperature on Mg/Ca ratios, a predicted Mg/Ca ratio was calculated for each location using the measured bottom water temperature and equation (3). The difference (ΔMg/Ca) between the measured Mg/Ca ratio and the predicted Mg/Ca ratio quantifies the Mg/Ca that is not explained by the Mg/Ca-temperature relationship above $3°C$.

[27] A linear regression of ΔMg/Ca ratio and $\Delta[CO_3^{2-}]$ from all of the sites in this study reveals a wide scatter of data, suggesting that the carbonate ion effect for *Krithe* is not linear (linear correlation $R^2 = 0.153$; P- value = 0.24; Figure 5). Since a large deviation from the temperature-expected Mg/Ca ratio is observed from our Norwegian Sea sites (ΔMg/Ca > 3 mmol/mol), which cover a wide range of $\Delta[CO_3^{2-}]$ values (30 to 80 μmol/kg; Figure 5), we follow the methodology described in *Elderfield et al.* [2006] and suggest that the carbonate ion effect occurs at low temperatures. After reexamination of the relationship between $\Delta[CO_3^{2-}]$ and ΔMg/Ca for sites only where bottom water temperature was less than or equal to $3°C$, we

find a linear correlation defined by the equation (Figure 5)

$$\Delta\text{Mg/Ca} = (0.100 \pm 0.030) * \Delta[CO_3^{2-}] - (3.508 \pm 1.023)$$
(4)

where Mg/Ca has units of mmol/mol and $\Delta[CO_3^{2-}]$ has units of μmol/kg ($R^2 = 0.543$; P- value = 0.000076). The low P- value, <0.05, indicates that the relationship is significantly different that random and therefore suggests that $\Delta[CO_3^{2-}]$ is a secondary factor in the incorporation of magnesium into *Krithe* carapaces at temperatures at or below $3°C$. The $\Delta[CO_3^{2-}]$ sensitivity of 0.100 mmol/mol/ μmol CO_3^{2-}/kg from equation (4) is an order of magnitude higher than the published $\Delta[CO_3^{2-}]$ sensitivities for benthic foraminifera of 0.0086 mmol/mol/ μmol CO_3/kg [*Elderfield et al.*, 2006], 0.0090 mmol/ mol/μmol CO_3/kg [*Yu and Elderfield*, 2008], and 0.0083 mmol/mol/μmol/kg [*Healey et al.*, 2008]; this order of magnitude difference is consistent with the 10 fold higher Mg/Ca ratios in *Krithe* compared to benthic foraminifera.
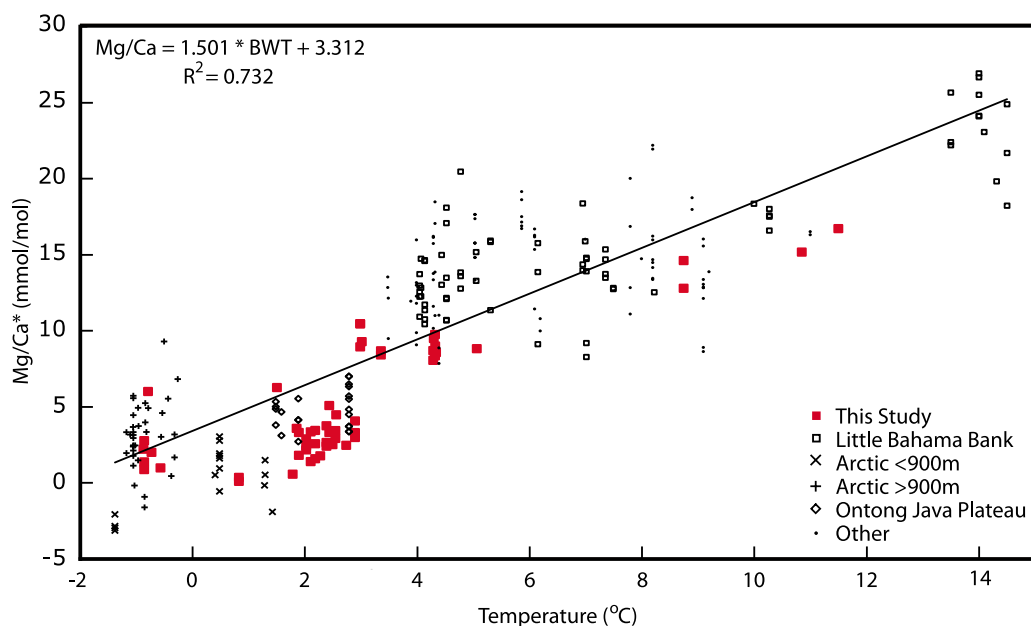
Figure 6. Mg/Ca data corrected for carbonate ion effects from this core top study (red squares) plotted against temperature. Data from Little Bahama Bank ([*Dwyer et al.*, 1995] black squares), Ontong-Java Plateau ([*Dwyer et al.*, 2002] black diamonds), Arctic Ocean <900 m ([*Cronin et al.*, 1996] black x-s), and the Arctic Ocean >900 m ([*Cronin et al.*, 1996] black crosses) are also shown. The black line represents a linear regression of all data.

[28] Next we apply equation (4) to all of the cold temperature (BWT $\leq 3°C$) core top sites within the compilation and found a strong correlation between $\Delta[CO_3^{2-}]$-corrected Mg/Ca ratios (henceforth marked Mg/Ca*) and BWT ($R^2 = 0.732$; P- value $\ll 0.05$; Figure 6). This correlation is improved from the initial correlation between Mg/Ca and BWT for core top sites with bottom water temperatures above 3°C ($R^2 = 0.485$; Figure 4). The application of this correction factor to the Norwegian sites, which were previously offset from the initial global linear regression (Figure 4), greatly reduces the difference between the corrected Mg/Ca* and the measured Mg/Ca core top relationship (Figure 6). Mg/Ca ratios from Arctic Ocean sites, even those below 900 m water depth that were previously excluded from calibrations, are also much improved by the application of the carbonate ion effect correction (Figure 6).

3.4. Global Paleotemperature Equation

[29] A revised global paleotemperature equation for *Krithe* Mg/Ca ratios can now be constructed using data from this study and previously published data that takes into account the secondary carbonate ion saturation effects (Figure 4). Mg/Ca values for sites where bottom water temperature during calcification was less than or equal to 3°C were corrected

for carbonate ion effects according to equation (4) to yield Mg/Ca*. The combination of equations (3) and (4) yields a new paleotemperature equation for bottom water temperatures at or below 3°C:

$$
\begin{aligned}
Mg/Ca_{Krithe} = {} & (0.972 \pm 0.152) * BWT \\
& + (0.100 \pm 0.030) * \Delta[CO_3^{2-}] \\
& + (4.440 \pm 1.103) \qquad\qquad (5)
\end{aligned}
$$

where Mg/Ca has units of mmol/mol, BWT has units of °C, and $\Delta[CO_3^{2-}]$ has units of μmol/kg. For bottom water temperatures above 3°C, Mg/Ca$_{Krithe} = (0.972 \pm 0.152)* BWT + (7.948 \pm 1.103)$ (equation (3)).

[30] Analytical error (~1%) explains a small fraction of the scatter observed in this global calibration; other possible errors, including: post-depositional dissolution, non-modern core tops, vital/biologic effects, variation in $\Delta[CO_3^{2-}]$ due to organic matter respiration, and differences in cleaning procedure, have been identified for benthic foraminiferal paleotemperature calibrations [e.g., *Rosenthal et al.*, 1997; *Elderfield et al.*, 2006; *Greaves et al.*, 2008] and may also effect ostracodal calibrations. As with any core top study, some scatter within this calibration may be due to the availability of truly modern core top samples due to bioturbation, low sedimentation rates, or issues during coring. The depth transects for Norwegian Sea, Gulf of Mexico,

Cape Hatteras, and the New Zealand shelf were cored using box- and multi corers that aim to preserve the sediment-water interface, some of the North Atlantic and Ceara Rise cores were retrieved by piston coring, which has been shown to disturb the uppermost sediments [*Ross and Riedel*, 1967; *Skinner and McCave*, 2003]. Additionally, it is possible that surface sediments were removed prior to coring by downslope processes that exposed older sediments at the surface, or remobilizing ostracod carapaces that were originally living at shallower depths. For example, late Holocene sediments have been winnowed from the top of northern North Atlantic core KN166–14 15JPC [*Neitzke and Wright*, 2007]; this core top was still included in this calibration since minimal BWT changes are expected at this site through the late Holocene. However, since some of the core tops used in this calibration have not been independently dated, they may not be modern, which could result in disparities between the in situ hydrographic information and the mean Holocene calcification conditions.

[31] Calibration error may also be derived from variability between carapaces due to vital effects [e.g., *Dwyer et al.*, 1995; *Corrège and De Deckker*, 1997; *Holmes*, 2008]. *Dwyer et al.* [1995] identified significant scatter in their single *Krithe* carapace measurements, which corresponded to a temperature error estimate of $\pm 1.3°C$ when single carapaces were analyzed. The error was reduced by $1/n^{0.5}$ when 'n' carapaces were analyzed [*Dwyer et al.*, 1995]. In order to minimize these effects, multiple carapaces were analyzed for this study whenever available, however large samples sizes were not typically available (see auxiliary material, Appendix 3).

[32] Studies of foraminifera [*Rosenthal et al.*, 2004; *Greaves et al.*, 2008] and lacustrine ostracods [*Holmes*, 1992; *Jin et al.*, 2006] have shown that inter-laboratory differences in cleaning and analytical techniques can yield differences in measured Mg/Ca ratios; however, differential cleaning on *Krithe* has not been thoroughly studied and this compilation data set encompasses over 35 years of analyses [*Cadot and Kaesler*, 1977]. The cleaning procedure used for this study involves oxidatively and reductively cleaning the carapaces, which results in the removal of clays, as well as secondary calcite and ferromanganese coatings [*Boyle and Keigwin*, 1987]; previously published Mg/Ca *Krithe* measurements were made without oxidatively or reductively cleaning. In foraminifera, samples that were not oxidatively and reductively cleaned were shown to have anomalously high

Mg/Ca ratios [*Rosenthal et al.*, 2004; *Elderfield et al.*, 2006]. *Krithe* carapaces have ~10 times higher concentration of magnesium than benthic foraminifera, and thus the magnesium concentration in secondary calcite may be less apt to affect ostracodal Mg/Ca ratios than foraminiferal Mg/Ca ratios. According to *Jin et al.* [2006], the maximum difference in Mg/Ca ratios resulting from oxidative and reductive cleaning for lacustrine ostracod is ~3.0 mmol/mol. A cursory interlaboratory comparison of *Krithe* from a homogenized sample between our laboratory at Rutgers (used in this study, with oxidative and reductive cleaning) and Duke University (with oxidative cleaning only) was conducted in the Fall of 2010 and suggested no substantial inter-laboratory offsets, though more work on cleaning protocols and inter-laboratory calibration for *Krithe* are recommended.

[33] Despite the possible errors in this calibration due to post-depositional dissolution, non-modern core tops, vital effects, and differences in cleaning procedure measurements, the global calibration has an error of $\sim\pm 0.3°C$ at 1 Standard Error, though the $\Delta[CO_3^{2-}]$ estimate would add additional error. Analytical error ($\sim1\%$) has a small effect on the calibration error, while I propose that an evaluation due to cleaning protocols on *Krithe* may have the largest effect and thus should be systematically examined.

3.5. Comparison to Published Calibration Studies

[34] The results of this core top calibration suggest a possible $\Delta[CO_3^{2-}]$ control on *Krithe* Mg/Ca ratios at low temperatures ($>3°C$). In contrast, *Dwyer et al.* [2002] concluded that carbonate ion concentration does not affect *Krithe* Mg/Ca ratios. The main difference is in the interpretation of the cause for the offset of data from cold temperatures (e.g., Nordic Seas) from the global calibration. *Dwyer et al.* [2002] measured *Krithe* Mg/Ca ratios from four core top sites on the Ontong Java Plateau and found Mg/Ca ratios that were consistent with the expected Mg/Ca ratios calculated from in situ bottom water temperatures (1.5 to 2.8°C) using their Mg/Ca-temperature equation (equating to ΔMg/Ca near 0 mmol/mol; auxiliary material, Appendix 2). However, the reported Mg/Ca ratios from Ontong Java Plateau have lower Mg/Ca ratios than the expected Mg/Ca ratios according to equation (5). Thus the Ontong Java Plateau samples have a small negative ΔMg/Ca (−0.04 to−3.66 mmol/mol; Figure 6). According to equation (4), this ΔMg/Ca

is explainable given the $\Delta[CO_3^{2-}]$ range of these samples, -3.3 to 8.8 μmol/kg. The $\Delta[CO_3^{2-}]$ correction increased the Mg/Ca values from the Ontong Java Plateau sites, which then conform closer to the linear Mg/Ca-temperature relationship (equation (5)). Therefore, even the previously published Ontong Java Plateau data are consistent with the carbonate ion effect identified by this study (Figure 6).

[35] A recent paper by *Farmer et al.* [2012] also examined the elevated Mg/Ca ratios from *Krithe* at low temperatures in the Nordic Seas and suggested that carbonate ion saturation was not a controlling factor. The *Farmer et al.* [2012] study proposed some other possible mechanisms for the elevated ratios in Nordic samples, including: nutrient availability, calcification rate [after *Dwyer et al.*, 1995; *Corrège and De Deckker*, 1997; *Dwyer et al.*, 2002], and species differences, instead of $\Delta[CO_3^{2-}]$. Consequently, they propose two different calibrations, one for the North Atlantic and another for the Nordic-Arctic Seas. Results from this study showing a linear relationship between Mg/Ca and BWT are consistent with *Farmer et al.* [2012] for the temperature range above $3°C$, however we propose that elevated Mg/Ca at low temperatures result from $\Delta[CO_3^{2-}]$ variations, rather than species differences.

[36] Whether the proposed paleotemperature calibration equation is linear or exponential is particularly important for paleoceanographic reconstructions. Inorganic, empirical, culture, and core top foraminiferal studies have shown that the Mg/Ca – temperature relationship could be either linear [*Mucci*, 1987; *Toyofuku et al.*, 2000; *Healey et al.*, 2008] or exponential [*Katz*, 1973; *Rosenthal et al.*, 1997; *Lea et al.*, 1999]. However, the *Krithe* paleotemperature equation has typically been described as linear [*Cadot and Kaesler*, 1977; *Dwyer et al.*, 1995; *Cronin et al.*, 1996; *Corrège and De Deckker*, 1997; *Dwyer et al.*, 2000, 2002], though an improved statistical representation from an exponential relationship was suggested [*Dwyer et al.*, 2002]. Prior to correcting for carbonate ion effects, an exponential regression of the entire data set yielded an R^2 value of 0.379 (not shown), whereas a linear regression of the data yielded an improved R^2 value of 0.448 (Figure 4). Similarly, an exponential regression of the data from sites where temperature is above $3°C$ yielded an R^2 values of 0.419 (not shown), whereas linear regressions of the same data yielded an improved R^2 value of 0.487 (Figure 4). Thus, before accounting for secondary calcification effects, initial statistical analysis suggests that the relationship between Mg/Ca and BWT is better described by a linear relationship (Figure 4). The identification of a carbonate ion effect on *Krithe* Mg/Ca at low temperatures has the added result of decreasing the apparent Mg/Ca ratios at many cold temperature sites (Figure 6); these elevated Mg/Ca ratios at cold temperatures may have contributed to *Dywer et al.*'s [2002] description of the paleotemperature equation as exponential. Since many of the low temperature, high Mg/Ca values can be explained by $\Delta[CO_3^{2-}]$ effects, instead of by temperature effects, there is no statistical reason to describe the Mg/Ca-temperature relationship as exponential (Figure 6). This indicates that *Krithe* may be particularly useful as a paleothermometer, when combined with an independent $\Delta[CO_3^{2-}]$ proxy.

[37] In addition to explaining much of the variability in Mg/Ca ratios at low temperatures, applying the $\Delta[CO_3^{2-}]$ correction to sites with bottom water temperatures at or below $3°C$ changes both the slope (i.e., the temperature sensitivity of Mg/Ca) and the intercept of the paleotemperature equation (Table 1). The y-intercept of the paleotemperature equation from this study (7.948 mmol/mol; equation (5)) is higher than the intercepts published by *Cadot and Kaesler* [1977], *Corrège and De Deckker* [1997], *Dwyer et al.* [1995], and the Atlantic equation of *Farmer et al.* [2012] (Table 1). Equations that were generated using data only from the Arctic Ocean core tops [*Cronin et al.*, 1996], or from a compilation of sites that included the Arctic Ocean [*Cronin et al.*, 1996; *Dwyer et al.*, 2002; *Farmer et al.*, 2012] had higher y-intercepts than the equation generated by this study, since a $\Delta[CO_3^{2-}]$ correction had not been applied (Table 1). The y-intercept defined by this study is similar to that defined by *Dwyer et al.* [2002], since the majority of their locations have BWT $>3°C$ and therefore a $\Delta[CO_3^{2-}]$ correction factor was not needed (Table 1 and Figure 4). Additionally, the *Dwyer et al.* [2002] calibration is similar to the equation from this study due in part to the small carbonate ion effect on the cold temperature Ontong Java Plateau, as mentioned previously (Figure 6). The y-intercept of the *Corrège and De Deckker* [1997] equation is the lowest of all published equations (Table 1); however, within the temperature range of their data ($2.3–5.9°C$), their equation is similar to the equation generated by this study (Figure 6).

[38] Paleotemperature equations from *Dwyer et al.* [1995], *Cronin et al.* [1996], and *Dwyer et al.* [2002] have similar Mg/Ca versus temperature relationships at the warmer temperature range

(BWT = 13–15°C) because the Mg/Ca ratios for this temperature range are determined from the same core top locations on the Little Bahama Bank. However, Little Bahama Bank samples used in benthic foraminiferal Mg/Ca versus temperature calibrations have been shown to be contaminated by high Mg-calcite overgrowths [*Lear et al.*, 2002; *Marchitto et al.*, 2007]; this would have a smaller effect on the ostracod data, due to their higher Mg/Ca ratios, but nonetheless can account to some offsets from the previous calibration, which did not include oxidative and reductive cleaning steps; it has been shown that the reductive step lowers Mg/Ca ratios in foraminifera [*Rosenthal et al.*, 2004]. However, the core tops presented here from Sulawesi Margin, Indonesia (BWT = 9 to 12°C) support this warm end of the paleotemperature equation (Figure 6).

[39] Despite the strong correlation between residual Mg/Ca and $\Delta[CO_3^{2-}]$ shown for the global data set that herein is proposed to indicate a carbonate ion effect, the samples from the Norwegian Sea region do not show an obvious trend with $\Delta[CO_3^{2-}]$ (Figures 3 and 6). This is counterintuitive, as the Norwegian Sea sites are cold, homo-thermal, and homo-haline, and would therefore be an obvious location for examining the carbonate ion effect at low temperature. Interestingly, when applying the same statistical methodology to benthic foraminifera in which the same global carbonate ion effect was found, the relationship between Mg/Ca and $\Delta[CO_3^{2-}]$ in the Norwegian Sea was also absent [*Elderfield et al.*, 2006]. Unlike for ostracods, the benthic foraminiferal calibrations compared the same species (e.g., *P. wuellerstorfi* and *O. umbonatus*) in core tops from the Nordic Seas and sites elsewhere, so it is difficult to argue for species-specific effect [*Elderfield et al.*, 2006].

[40] While the examination of carbonate ion effects in ostracods presented here closely mirrors the benthic foraminiferal studies [*Elderfield et al.*, 2006] and is statistically robust, we also acknowledge that there are other factors that may also be at play in the elevated Mg/Ca values at low temperatures or in particular regions. One possibility is that cold temperature-preferring species, namely *K. glacialis*, incorporate Mg differentially [*Farmer et al.*, 2012]. Additionally, the histology and physiology of the molting process and the formation of the cuticle from epidermal layer via the ecdysial fluids, and changes in fluid volume and osmotic pressure, are highly complex [*Okada*, 1982; *Keyser*, 2005] and thus could be related to metabolism, temperature (indirectly or directly),

food resources, and/or other factors (T. Cronin, personal communication, 2011).

3.6. Paleoceanographic Applications

[41] The paleotemperature equation generated by this study for sites with BWT above 3°C is similar to many published equations, in part because those equations were generated by using mainly sites with bottom water temperatures above 3°C, thus a $\Delta[CO_3^{2-}]$ correction was not required (Table 1). However, much of the modern deep ocean has bottom water temperatures at or below 3°C [*Levitus and Boyer*, 1994], with estimated glacial temperatures of 0 to 1°C [e.g., *Labeyrie et al.*, 1987; *Adkins et al.*, 2002]. Given that this cold temperature range is typical of the deep glacial ocean, the use of a paleotemperature equation that also incorporates carbonate ion effects is important for most paleoceanographic reconstructions.

[42] The determination of paleotemperatures is critical to the understanding of past oceans and climate; however, the suggestion of carbonate ion effects in addition to the temperature effects on Mg/Ca ratios of *Krithe* poses a problem for the use of *Krithe* as paleothermometer since few paleo-carbonate ion concentration records exist. Foraminiferal shell weights [*Lohmann*, 1995; *Broecker and Clark*, 2001; *Barker and Elderfield*, 2002; *Broecker and Clark*, 2002], benthic foraminiferal boron to calcium ratios (B/Ca; [e.g., *Yu and Elderfield*, 2007]), and benthic foraminiferal boron isotopes [e.g., *Sanyal et al.*, 1995; *Rae et al.*, 2008] provide proxies for estimating paleo-carbonate ion concentrations; however, these proxies have shown that the carbonate ion system is highly complex [*Yu and Elderfield*, 2008; *Yu et al.*, 2008]. While several ostracod Mg/Ca studies have yielded convincing paleotemperature estimates without applying a carbonate ion effect correction [*Corrège and De Deckker*, 1997; *Dwyer et al.*, 1995; *Farmer et al.*, 2011], our carbonate ion corrected equation may provide improved paleotemperature estimates.

[43] Here, I calculate paleotemperatures according to three different methods for comparison; (1) using the Mg/Ca:temperature relationship exclusive of a carbonate ion effect, (2) using the Mg/Ca:temperature relationship with an included carbonate ion effect suggested here in, utilizing estimated paleo-carbonate ion concentrations, and (3) using paleo-temperature estimates from benthic foraminiferal $\delta^{18}O$ values. Since Last Glacial Maximum (LGM) sediments are missing from 11JPC [*Elmore and Wright*, 2011], average values of *Krithe* Mg/Ca

and *P. wuellerstorfi* $\delta^{18}O$ were calculated for the Holocene (Mg/Ca = 10.02 mmol/mol; $\delta^{18}O$ = 3.50 ‰ V-PDB) and for the late Marine Isotope Chron (MIC) 3 (~33–43 ka; Mg/Ca = 8.95 mmol/mol; $\delta^{18}O$ = 4.95 ‰ V-PDB; Table 2).

[44] Paleotemperatures from measured Mg/Ca ratios were first estimated for the Holocene and late MIC 3, without taking carbonate ion concentrations into account, according to equation (3) (Table 2). This method yielded bottom water temperatures of 2.1 and 1.0°C for the Holocene and Late MIC 3, respectively (Table 2). The Holocene average estimated in this manner is reasonable when compared with observed modern temperature at this water depth on Gardar Drift, 3.00°C, since the Mg/Ca data represent an average throughout the Holocene (auxiliary material, Appendices 1 and 2). However, the glacial value of 1.0°C represents a fairly small deglacial temperature warming.

[45] Next, taking into account carbonate ion concentrations, paleotemperatures were estimated from Mg/Ca ratios for the Holocene and late MIC 3 according to equation (5) (Table 2). The modern $\Delta[CO_3^{2-}]$ value of 38.8 μmol/kg was used for the Holocene (see Methods section and auxiliary material, Appendix 1) and an estimated $\Delta[CO_3^{2-}]$ change of ~25 μmol/kg from late MIC 3 to the Holocene was used according to estimates of $\Delta[CO_3^{2-}]$ for this period from a similar water depth in the northeastern North Atlantic, calculated from B/Ca ratios [*Yu and Elderfield*, 2008; *Yu et al.*, 2008]. *Yu et al.* [2008] suggested that waters shallower than 2400 m had higher $\Delta[CO_3^{2-}]$ during the LGM than during the Holocene; a site at 2777 m also appears to show elevated glacial $\Delta[CO_3^{2-}]$, though to a lesser degree than at the shallower sites [*Yu et al.*, 2008]. Higher LGM $\Delta[CO_3^{2-}]$ at sites shallower than 2800 m may be due to lower atmospheric CO_2 and an increased biologic pump [*Barker and Elderfield*, 2002; *Curry and Oppo*, 2005; *Yu and Elderfield*, 2008; *Yu et al.*, 2008]. By correcting for the $\Delta[CO_3^{2-}]$ effect, temperatures of 1.7 and −1.9°C were estimated for the Holocene and Late MIC 3, respectively (Table 2).

[46] Finally, paleotemperatures were independently estimated from average benthic foraminiferal $\delta^{18}O$ for both time periods according to the *Shackleton* [1974] equation:

$$BWT = 16.9 - 4.0 \left(\delta^{18}O_{calcite} - \left(\delta^{18}O_{SW} - 0.27‰ \right) \right) \quad (6)$$

where $\delta^{18}O_{calcite}$ is the measured value benthic foraminiferal calcite (values from *Elmore and*

Wright [2011]), in units of ‰ V-PDB, corrected by 0.64 ‰ to adjust to equilibrium seawater [*Shackleton and Hall*, 1984], $\delta^{18}O_{SW}$ is the oxygen isotopic composition of the overlying seawater, in units of ‰ V-SMOW (0.3 ‰ for the Holocene and 0.6 ‰ for late MIC 3; *Waelbroeck et al.* [2002], after *Shackleton* [2000]), and 0.27 ‰ is the correction factor between V-SMOW and V-PDB [*Bemis et al.*, 1998]. The $\delta^{18}O_{SW}$ value for late MIC 3 was estimated assuming that Antarctic Bottom Water did not bathe this site during late MIC 3. This method yielded temperature estimates of 3.02 and −1.58°C for the Holocene and late MIC 3, respectively (Table 2).

[47] All three methods yield paleotemperature estimates for the Holocene that are within error limits of each other, and are consistent with modern bottom water temperature measurements (3.00°C, Table 2 and auxiliary material, Appendices 1 and 2), indicating that our calibration is effective in characterizing modern temperatures (Table 2). The carbonate corrected Mg/Ca and $\delta^{18}O$ methods yield late MIC 3 paleotemperatures that are also within error limits of each other (Table 2). In contrast, the paleotemperatures estimated from Mg/Ca by equation (3), which does not include carbonate ion effects, are significantly warmer than paleotemperatures generated according to the other two methods for Late MIC 3, and do not effectively characterize modern bottom water temperatures (Table 2); this demonstrates that carbonate ion effects must be accounted for when using *Krithe* Mg/Ca as a paleothermometer. Additionally, the modern BWT at this site of 3.00°C (auxiliary material, Appendices 1 and 2), is likely significantly higher than the MIC 3 BWT at this site, and therefore, following this core top calibration study, carbonate ion effects must be taken into account throughout the record.

[48] A published down core record from CHN82 4PC, in the midlatitude North Atlantic, identified a change in *Krithe* Mg/Ca ratios from ~7.5 to 10.5 mmol/mol from the LGM to the Holocene [*Dwyer et al.*, 1995]. When interpreted without carbonate ion effects, this Mg/Ca record was proposed to represent a change of ~3°C and a >1.5 ‰ change in $\delta^{18}O_{SW}$ due to ice volume changes [*Dwyer et al.*, 1995]. However, it has been estimated that $\Delta[CO_3^{2-}]$ was ~12 μmol/kg higher at this site during the LGM than during Holocene [*Sosdian*, 2008], consistent with previous estimates of 10 to 15 μmol/kg $\Delta[CO_3^{2-}]$ change [*Marchitto et al.*, 2002]. Reanalysis of the LGM CHN82 4PC data incorporating carbonate ion effects, using

equation (5) from this study, results in a LGM bottom water temperature ~1°C lower than that suggested that *Dwyer et al.* [1995]. This resulted in an underestimation of the LGM-Holocene temperature change, and therefore overestimated the change in $\delta^{18}O_{SW}$. A lower $\delta^{18}O_{SW}$ change LGM-Holocene would make this record more consistent with other records that suggest changes in $\delta^{18}O_{SW}$ from the LGM to Holocene of 1.1 ‰ [*Labeyrie et al.*, 1987], 1.2 ‰ [*Fairbanks*, 1989], 1.0 ‰ [*Waelbroeck et al.*, 2002; *Shrag et al.*, 1996], or 0.75–1.17 ‰ [*Adkins et al.*, 2002]. Thus, the development of a paleotemperature equation that includes carbonate ion effects affords the ability to generate reasonable estimates of ice volume variations and shows the usefulness of this proxy for paleoceanographic reconstructions for deep ocean temperatures.

4. Conclusions

[49] Mg/Ca ratios of ostracods from globally distributed core tops indicate that the incorporation of magnesium into the calcium carbonate lattice of *Krithe* carapaces is not strictly temperature dependent, as was suggested previously. Just as benthic foraminiferal Mg/Ca calibration studies have identified carbonate ion effects at temperatures below 3°C [*Elderfield et al.*, 2006], this study has shown that $\Delta[CO_3^{2-}]$ exerts a role on *Krithe* Mg/Ca ratios below the same temperature threshold. Based on these results a new temperature calibration is proposed that incorporates a carbonate ion effect.

[50] The acknowledgment of a carbonate ion effects on the Mg/Ca ratios of *Krithe* below 3°C, creates previously unknown problems for the interpretation of most down core *Krithe* Mg/Ca records since BWT is less than 3°C in much of the global oceans. In order to use Mg/Ca as a paleotemperature proxy, $\Delta[CO_3^{2-}]$ must first be carefully considered, through the use of foraminiferal shell weights [*Lohmann*, 1995; *Broecker and Clark*, 2001, 2002], benthic foraminiferal B/Ca ratios [e.g., *Yu and Elderfield*, 2007], benthic foraminiferal boron isotopes in benthic foraminifera [e.g., *Sanyal et al.*, 1995; *Rae et al.*, 2008], or by other means. Alternatively, Mg/Ca of *Krithe* may be useful in conjunction with an independent temperature proxy such as benthic oxygen isotopes or by using pore water fluid analysis [*Adkins et al.*, 2002] to calculate paleo-carbonate ion saturation [e.g., *Elderfield et al.*, 2006].

[51] In summary, down core *Krithe* Mg/Ca may be useful as a paleothermometer in warmer locations,

in agreement with *Farmer et al.* [2012], or when combined with an independent proxy for carbonate ion concentration. This calibration provides an alternate method for estimating paleotemperatures in sediment cores that do not have a sufficient quantity of benthic foraminifera for trace metal analysis, such as some North Atlantic drift sites [*Elmore*, 2009].

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