



# Increased dissolved terrestrial input to the coastal ocean during the last deglaciation

### G. P. Klinkhammer and A. C. Mix

College of Oceanic and Atmospheric Sciences, Oregon State University, Ocean Administration Building 104, Corvallis, Oregon 97331, USA (gklinkhammer@coas.oregonstate.edu)

#### B. A. Haley

Leibniz Institute of Marine Sciences, IFM-GEOMAR, Wischhofstrasse 1-3, D-24148 Kiel, Germany

[1] Here we present the first downcore results for a new paleoproxy, the Mn/Ca ratio of foraminiferal calcite, applied to sediment accumulated in the extreme Eastern Tropical North Pacific (ETNP) over the last 30,000 years. The Mn/Ca results are compared to oxygen isotopes and sea surface temperature calculated from Mg/Ca. We determined metal ratios using flow-through time-resolved analysis to minimize the effects of secondary mineralization. The foraminiferal species used for this study calcify at different depths. Core top ratios of these variant species change in proportion to the concentration of dissolved manganese in the water column at the depth of calcification. Since terrestrial input and oxidation reduction reactions control the levels of dissolved Mn in the oceans today, it therefore should be possible to use the Mn/Ca ratios of foraminifera as a proxy for these processes in the past. Mn/Ca of a mixed-layer species (G. ruber) suggest that dissolved terrestrial input to the surface waters of the ETNP during the last glacial maximum was lower than today but began to increase with initial sea level rise and reached a maximum at 15 ka B.P. before coming down to present-day levels at the end of sea level rise in the mid-Holocene (7– 5 ka). Ratios of a deeper calcifying species (N. dutertrei) mimic those of G. ruber over this same time period, consistent with shoaling of the 18°C thermocline. Mn/Ca of a benthic species (U. peregrina) does not show a maximum at 15 ka, suggesting that Mn was efficiently remineralized in the water column during deglaciation. Assuming that the period from the last glacial until the mid-Holocene was a time of increased productivity, as elevated Mn might imply, the oxygen minimum zone (OMZ) was at least as well developed during deglaciation as it is today. Expansion of the OMZ may have contributed to the Mn/Ca trends we observe through time.

Components: 7220 words, 6 figures, 1 table.

Keywords: manganese; paleoproxy.

**Index Terms:** 4924 Paleoceanography: Geochemical tracers; 4936 Paleoceanography: Interglacial; 4954 Paleoceanography: Sea surface temperature.

Received 28 August 2008; Revised 26 January 2009; Accepted 4 February 2009; Published 18 March 2009.

Klinkhammer, G. P., A. C. Mix, and B. A. Haley (2009), Increased dissolved terrestrial input to the coastal ocean during the last deglaciation, *Geochem. Geosyst.*, *10*, Q03009, doi:10.1029/2008GC002219.

KLINKHAMMER ET AL.: DISSOLVED TERRESTRIAL INPUT TO THE OCEAN 10.1029/2008GC002219

# 1. Introduction

Geochemistry

Geophysics Geosystems

[2] Dissolved Mn is present at low nanomolar levels in the oceans but has a moderately high crustal abundance (850 ppm) and high dissolved concentrations in rivers, reducing sedimentary pore fluids and hydrothermal fluids relative to seawater. Dissolved Mn has a distinctive profile in the oceanic water column [Klinkhammer and Bender, 1980; Klinkhammer, 1980]. While Fe and most other transition elements are nutrient-like and depleted at the surface, dissolved Mn concentrations are elevated in the mixed layer (2-5 nM), decrease through the thermocline, increase again in the oxygen minimum zone (OMZ), and decrease in deep water (Figure 1). Mn has a short residence time in surface waters ( $\sim$ 50 years) being readily removed as oxyhydroxide coatings during scavenging. These coatings are susceptible to reduction in suboxic conditions [Froelich et al., 1979] and Mn scavenged from the surface is efficiently remobilized in an intense OMZ [Klinkhammer and Bender, 1980; Balakrishnan Nair et al., 1999; Lewis and Luther, 2000]. Its short residence time and relatively high crustal abundance make Mn a sensitive tracer of terrestrial input on a basin scale. The direct relationship between Mn levels and terrestrial supply produces a distinct N-S gradient in surface waters of the Pacific Ocean consistent with lower inputs south of the equator [Klinkhammer and Bender, 1980].

[3] Since terrestrial input and oxidation reduction reactions control its distribution in today's oceans we might hope to better understand these processes by looking at changes in dissolved manganese through time. This study looks at the possibility of using the Mn/Ca ratio of planktonic and benthic foraminiferal calcite as a proxy for dissolved Mn by examining this record at one site in the eastern tropical north Pacific (ETNP) from 30 ka, through the last glacial maximum (LGM) to present.

[4] Transition from the LGM brought about major changes to the biogeochemistry of the adjacent coastal ocean [*Clark et al.*, 2004]. Our study helps quantify these changes by examining Mn/Ca and other paleoproxies in calcic foraminifera from sediment cores taken in the Pacific Ocean on the margin of Central America (Figure 2). Today's sediments and water column of the ETNP are highly impacted by a heavy rain of organic carbon from the surface driven by high productivity supported by coastal upwelling [*Karstensen et al.*, 2008]. The high carbon rain rate supports a welldeveloped OMZ, one of the deepest and most intense oxygen minimum zones in the world.

[5] Ocean Drilling Program (ODP) Site 1242 of Leg 202 was located on the Cocos Ridge (7° 51.35N, 83° 36.42W) in the extreme ETNP close to the Panama Basin and margin of Costa Rica (Figure 2) [*Shipboard Scientific Party*, 2003]. The water depth at Site 1242 is 1364 m, above the regional lysocline. Surface waters at Site 1242 are warm (Figure 1) with relatively low salinity [*Benway et al.*, 2006] lying at the northern extent of the present-day North Equatorial Countercurrent. Bottom waters originate as North Pacific Deep water and remnants of North Pacific Intermediate Water and are associated with the lower parts of the thick oxygen minimum zone.

[6] Sediment samples from Core 1242A and another core taken at the same place were processed for this study. Core ME0005A-43JC was taken at almost the same location (7° 51.35N 83° 36.50'W; 1,368m). Sedimentation rates at this hemipelagic site range between 10 and 12 cm ka<sup>-1</sup>. Age models for these cores are based on six <sup>14</sup>C accelerator mass spectrometry dates for *N. dutertrei* from ME0005A-43JC from 0 to 20 ka, and  $\delta^{18}$ O stratigraphy [*Grootes and Stuiver*, 1997; *Shackleton et al.*, 2000]. Further details are given by *Benway* [2005].

## 2. Methods

[7] In this report we present data for multiple proxies (Mg/Ca, Mn/Ca and  $\delta^{18}$ O) from two sediment cores, two species of planktonic foraminifera (Globigerinoides ruber; Neogloboquadrina dutertrei), and one benthic species (Uvigerina peregrina). Twenty to thirty specimens of foraminifera (250-355 micron size fraction) were picked every 2-4 cm, sonicated in ethanol without crushing and split into two equal fractions. One fraction was processed for stable isotope analysis using standard procedures and the other was set aside for metal analysis. Isotope analyses were carried out at Oregon State University using a Finnigan-MAT 252 stable isotope ratio mass spectrometer equipped with a Kiel-III device. Data are reported relative to Pee Dee Belemnite standard calibrated against NBS-19 and NBS-20. Isotope, Mg/Ca and other results from these cores have been discussed previously as they relate to paleosalinity and climate [Benway, 2005; Benway et al., 2006].



Geochemistry

Geophysics Geosystems

Figure 1. Profile of Mn and T in the Guatemala Basin near ODP Site 1242. The two species of planktonic foraminifera used in this study, *G. ruber* and *N. dutertrei*, calcify in the surface mixed layer and in the thermocline (50-200 m), respectively. Mn profile modified from *Klinkhammer* [1980]. Elevated dissolved Mn in the OMZ is produced by reduction of Mn oxyhydroxides scavenged from the surface. Mn oxyhydroxides are reduced at the same intensity as nitrate [*Froelich et al.*, 1979]. The dissolved Mn profile therefore looks like the profile of nitrate reduction, not oxygen, as explained by *Klinkhammer and Bender* [1980].

[8] The second picked fraction, approximately ten specimens of foraminifera were transferred to 13 mm PTFE disposable filter units (Whatman: 1.0  $\mu$ M). These units were loaded into a leaching module [*Haley and Klinkhammer*, 2002] linked to a PQ ExCell inductively coupled mass spectrometer (ICP-MS) made by VG Elemental. Samples were run with a 25-min program using flow-through time-resolved analysis (FT-TRA).

[9] In previous studies, the Mn associated with foraminiferal tests was thought of as a contaminant from diagenetic manganese carbonate overgrowths [*Boyle*, 1983] or clay detritus [*Barker et al.*, 2003]. FT-TRA helps mitigate contamination

by separating the Mn in biogenic calcite from that associated with secondary phases using differences in their susceptibilities to chemical leaching [*Haley and Klinkhammer*, 2002; *Benway et al.*, 2003; *Klinkhammer et al.*, 2004]. Each FT analysis produces over 8500 elemental ratios for each sample as the foraminiferal calcite and associated diagenetic phases dissolve in a highly controlled chemical attack using a gradient pump.

[10] The FT method used for these samples began with a 10-min rinse with deionized water and ended with dissolution in 10 mM HNO<sub>3</sub> [*Klinkhammer et al.*, 2004]. In this method labile phases are removed with the deionized water and more refractory phases like clay are left undisturbed until the end of the leaching procedure. Biogenic calcite dissolves at the beginning of the dissolution sequence. FT software is used to develop plots of concentrations and metal/ Ca ratios during the leaching process (dissolution curves) as well as graphs of one element against another (El-El plots). Dissolution curves and El-El plots for Mn/Ca from representative samples analyzed for this study are shown in Figure 3. Mg/Ca ratios are determined in the same way.

[11] Not all 8500 ratios developed during the FT-TRA analysis are used to calculate the proxy ratio. Rather ratios in the biogenic calcite are isolated in the software using cursor lines like those shown in Figure 3. The proxy ratio is taken as the slope in the best fit line thorough these selected data. Shown in the El-El plots are spreads in ratios found for each representative depth interval represented by two divergent lines. These lines are drawn to pass through the origin while encompassing all the data and are meant to show that the ratio varies downcore even within the widest limits. This



Figure 2. Map of the location of ODP Site 1242 showing the extent of exposed shelf at the LGM.

KLINKHAMMER ET AL.: DISSOLVED TERRESTRIAL INPUT TO THE OCEAN 10.1029/2008GC002219



Geochemistry

Geophysics

is not to say that ratios are always constant within the envelope. It is well established using laser ablation and SEM that foraminiferal shells can contain various Mg/Ca ratios for a variety of reasons [Eggins et al., 2003; Sadekov et al., 2005] and that Mn/Ca and Mg/Ca can be affected by kutnohorite-type phases [Pena et al., 2005]. The FT method used here does not have the resolving power of these microtechniques but rather organizes this material according to its susceptibility to dissolution [Benway et al., 2003] and presents the most common ratio on average in a selected part of the sample. But FT has a couple of advantages over microtechniques: samples can be rapidly analyzed, at a rate similar to isotopic analysis, and FT provides data on a statistically significant number of specimens in the same analysis. The FT technique is also robust for samples from all settings and ages. Batch cleaning methods [e.g., Barker et al., 2003; Pena et al., 2005] on the other hand typically produce a single ratio. Batch analysis therefore relies on the assumption that susceptibility of phases is the same from place to place and downcore, otherwise the net effect of chemical cleaning will vary. Over cleaning during batch analysis can lead to partial dissolution of the biogenic calcite, which can exaggerate the effects of contamination by more resistant phases. Contamination by residuals is particularly difficult to address in batch processing because secondary phases tend to become more resistant to leaching as they age. Mixtures of different phases can also affect FT-TRA results but FT produces a more complete picture of sample composition, which in turn creates an opportunity to isolate ratios of primary biogenic calcite from those of remnants and other phases.

[12] The observation that most Mn in the tests used for this study can be reasonably represented by a single relationship to Ca throughout the selected part of the dissolution process (bottom graphs in

**Figure 3.** Dissolution curves and El-El plots from FT-TRA. The lines on the El-El plots are envelopes of ratios encompassing data between the two cursors (dashed lines) and passing through the origin. The ranges of ratios for each example are 0.164-0.204 (0.184), 0.252-0.303(0.267), and 0.104-0.144 (0.124) for the top, 15K, and the LGM, respectively. The values in parentheses are the best fit ratios. Ca concentrations were calculated from the average of two isotopes (43 and 48), while Mn is monoisotopic. Aluminum was undetectable in all samples used in this study, eliminating the possibility of significant influence from clays.



Geochemistry

Geophysics Geosystems

**Figure 4.** Mn/Ca of the planktonic foraminiferal species *G. ruber* and *N. dutertrei* and the benthic species *U. peregrina*. Also shown are  $\delta^{18}$ O ratios for *U. peregrina* from ODP Core 1242A. The most distinct feature is the prominent maximum at 15 ka shared by *G. ruber* and *N. dutertrei*. A maximum in Mn/Ca also occurs in the benthic foraminifera, but some 3,000 years later.

Figure 3) suggests that Mn was incorporated into the calcite as the shells were formed and not added later. Homogeneity of these samples with respect to Mn is also consistent with how well the dissolution curves correlate with those of Ca (top graphs in Figure 3). Such close interdependence is not seen in samples with significant overgrowths where dissolution peaks from secondary phases offset minor and trace element peaks from Ca.

[13] Other observations support the FT result that the Mn in these shells is primary. First, in today's ocean ODP Site 1242 underlies a productive surface ocean that maintains an intense OMZ (Figure 1). It seems unlikely on the basis of the results of this and other studies [Hendy and Pedersen, 2006; Karstensen et al., 2008] that this situation has changed over the last 30 ka. At sites like ODP 1242 that underlie well-developed oxygen minima, Mn scavenged from the surface is reduced in the OMZ before the host particles reach the seafloor [Balakrishnan Nair et al., 1999; Lewis and Luther, 2000]. Sediment below the OMZ is thus void of the labile Mn that dissolves during diagenesis forming Mn carbonate overgrowths [Alagarsamy et al., 2005]. Second, if a significant amount of the Mn in these samples were diagenetic, we would expect the Mn/Ca ratios of the three foraminiferal species to be similar and show the same trends downcore, which is not the case (Figure 4; see data in Appendix A, Table A1).

#### 3. Results

[14] The planktonic foraminiferal species G. ruber and N. dutertrei are thought to have distinctly different ecologies. G. ruber calcifies in the mixed layer, while N. dutertrei prefers thermocline depths, 50-200 m [Benway, 2005; Benway et al., 2003; and references therein]. This difference in the depth of calcification is reflected in the  $\delta^{18}{\rm O}$  of their tests, as illustrated in Figure 5 (data in Table A1). Also shown in Figure 5 are data for Mg/Ca for the two planktonic species and estimated sea surface temperature (SST) calculated using Mg/Ca data for G. ruber and a calibration curve derived from sediment trap samples [Anand et al., 2003]. SST at the core top is consistent with the present-day temperature at this site (28.5°C). As shown calculated  $\triangle$ SST (present–LGM) is 4.5°C. This  $\triangle$ SST is higher than the  $1-2^{\circ}C$  estimated by *Climate*: Long-Range Investigation, Mapping, and Prediction Project Members [1981] on the basis of ecological studies, and on the high end of other KLINKHAMMER ET AL.: DISSOLVED TERRESTRIAL INPUT TO THE OCEAN 10.1029/2008GC002219



Geochemistry

Geophysics Geosystems

> estimates from Mg/Ca [*Barker et al.*, 2005]. Applying the same calibration to *N. dutertrei* (Figure 5) indicates that this species has lived at a relatively constant thermocline temperature  $(18.3 \pm 0.4^{\circ}C)$ throughout the last 30 ka. The change in  $\delta^{18}O$  for *N. dutertrei* then, by inference, would be related to changes in ice volume and water mass isotopic composition.

> [15] Mn/Ca data for the three species used in the study are shown in Figure 4. The Mn/Ca ratios are consistent with  $\delta^{18}$ O and the idea that *N. dutertrei* calcify deeper in the water column than *G. ruber* (Figures 1 and 5). Core top Mn/Ca ratios for *G. ruber* from this study are on average 2.5 times higher than those of *N. dutertrei*, which is approximately the same as the ratio of Mn concentrations at their depths of calcification (~3; Figure 1). Core top Mn/Ca ratios of benthic foraminifera *U. peregrina* are intermediate (Figure 4, bottom), again consistent with what we would expect from the water column profile in the ETNP [*Klinkhammer*, 1980].

[16] The covariance of water column Mn and core top Mn/Ca suggests that the partition coefficients for Mn ( $K_{Mn}$ ) of the three species are similar. This somewhat surprising result may be related to the fact that Mn, unlike most other metals, is not strongly associated with organic carbon [*Klinkhammer and Bender*, 1980]. The finding of a constant  $K_{Mn}$  needs to be verified at other sites with more species but if proven out would make foraminiferal Mn/Ca a straightforward and widely applicable paleoproxy.

#### 4. Discussion

[17] As shown in Figure 4, the Mn/Ca ratios of thermocline-calcifying *N. dutertrei* began to mimic those of surface-calcifying *G. ruber* in the LGM, before 19 ka B.P. Concurrence was not the case after the mid-Holocene (7-5 ka) when the ratios of the two species diverge. Since the Mg/Ca ratios of *N. duter*-

**Figure 5.** Oxygen isotopes ( $\delta^{18}$ O), Mg/Ca, and calculated SST from two cores at the same site near the Costa Rican margin. The results for Core 43J and ODP 1242A are in good agreement except for the Mg/Ca data for *N. dutertrei* in Core 43J. Several TRA-ICP-MS runs during this time produced poor Mg standard curves that led to unusually high errors, and these data are not presented. These data are presented in Table A1 but are not plotted in Figure 5. SST was calculated using the Mg/Ca ratios for *G. ruber* and a published calibration curve from plankton tow data [*Anand et al.*, 2003].



Geochemistry

Geophysics Geosystems

**Figure 6.** Changes in sea level, meltwater, and Mn/Ca. (top) The relationship between  $\delta^{18}$ O and Mn/Ca for the higher-resolution data set (core 1242A). The minima in Mn/Ca and  $\delta^{18}$ O at 5 ka B.P. coincide with a cooling event identified by land-based climatic studies in Costa Rica [*Islebe and Hooghiemstra*, 1997]. The same overlay shows that the timing and duration of the Mn spike at 15 ka B.P. is closely associated with a plateau in  $\delta^{18}$ O. Since there is no associated SST anomaly (Figure 5), we interpret this feature to be the Bolling-Allerod melt pulse event common in records from the Northern Hemisphere. (bottom) The relative rise in sea level estimated from corals in Bermuda [*Bard et al.*, 1990; *Fairbanks*, 1990, 1992; *Stanford et al.*, 2006].

*trei* indicate that this species has been calcifying in  $18^{\circ}$ C water for at least the last 30 ka (Figure 5), the change at the LGM may be related to an upward shift in the depth of the thermocline. Modeling of oceanatmosphere interactions during the LGM suggests that the  $18^{\circ}$ C thermocline may have been 30 m higher in the water column in the Eastern Equatorial Pacific than it is today [*Bush and Philander*, 1998]. At Site 1242 this shoaling would have translated to a glacial thermocline depth of ~40 m [*Benway et al.*, 2006]. This being the case, the calcification depth of N. *dutertrei* would have been well within the Mn gradient between surface and intermediate waters (Figure 1) thereby linking the Mn/Ca of the two species.

[18] Assuming this is the case, Mn/Ca indicates that the thermocline was at a shallow position before 19 ka (Figure 4), which coincides with the onset of gradual warming of the surface ocean (Figure 5). The 19 ka time period was also when the first deglacial meltwater pulse in the North Atlantic (Figure 6 and data in Table A1) [*Clark et al.*, 2004]. In fact, these investigators identified a close linkage between the onset of deglaciation at northern latitudes and warming in the tropics, an observation supported by this data set (Figure 5).

[19] While shoaling of the thermocline might explain the coupling of Mn/Ca in G. ruber and N. dutertrei, it does not explain the maxima centered at 15 ka B.P. In today's ocean Mn is lower below the mixed layer (Figure 1) and higher concentrations at the surface cannot be explained by increased upwelling. Moreover, while the ratios of N. dutertrei were higher during deglaciation, they were still lower than those of G. ruber, suggesting a gradient similar to today existed between surface water and the thermocline, although somewhat reduced. If we rule out upwelling as a source then the 15 ka excursion in Mn/Ca requires an increased supply of terrestrial material. All things being equal, the Mn/Ca pattern indicates that terrestrial input at 15 ka was as much as 1.5 times higher than today and 2.5 times minimal glacial levels at this site, assuming minimal compression of the mixed layer.

[20] Since Mn is supplied to the oceans from the same sources as iron, Mn/Ca suggest that the last deglaciation was generally a time of increased productivity. This conclusion needs to be proven out by wider application of Mn/Ca and other proxies but is consistent with anomalously high accumulation rates of barium and redox-sensitive metals on the Mexican margin [*Nameroff et al.*, 2004] at this same time as well as widespread observations of generally stronger denitrification during interglacial periods [*Altabet et al.*, 1999, 2002; *Ganeshram et al.*, 2007].

[21] Increased productivity would have led to deglacial expansion of the OMZ as postulated by *Hendy and Pedersen* [2006]. Mn/Ca ratios of the benthic species *U. peregrina* (Figure 4) also sup-



port the idea of an expanded OMZ during the last interglacial. That is, if the water column were oxidizing increased productivity would have enhanced the fluxes of Mn and organic carbon from the surface to the bottom, which should have produced elevated sedimentary pore water levels through diagenesis and a spike in the Mn/Ca of Uvigerina peregrina contemporaneous with the maximum at the surface. The absence of such an anomaly in benthic foraminifera indicates that parts of the water column must have been reducing at this time and Mn scavenged from the surface efficiently recycled in overlying water and thus decoupled from diagenesis in the sediment, as seen in the modern ocean under intense oxygen minimums [Balakrishnan Nair et al., 1999; Lewis and Luther, 2000; Alagarsamy et al., 2005].

[22] While Mn/Ca ratios of the benthic foraminifera show a maximum in the Holocene, this feature lags the maxima in the planktic species by some 3000 years (Figure 4). This lag and the tight coupling with shifts in  $\delta^{18}$ O shown in Figure 4 suggest that the Mn/Ca maximum in the benthic foraminifera is most probably related to a change in bottom water circulation.

[23] Detailed information about the source of the deglacial maximum in dissolved Mn would require an extended study, but one clue may lie in the relationship of the anomaly to trends in  $\delta^{18}$ O. The heart of the Mn/Ca maximum in the planktic foraminifera occurs at 15-13 ka and is closely linked to a plateau in  $\delta^{18}$ O (Figure 6, top), a feature normally attributed to increased freshwater input during the Bolling-Allerod warming event in the northern hemisphere. The concurrence of these anomalies is consistent with the overall strong linkage of elevated Mn/Ca with sea level rise, also shown in Figure 6 (bottom). It seems unlikely that the increase in Mn/Ca in surface water at Site 1242 during deglaciation was a response to local inundation because the paleoshelf off Costa Rica is relatively modest (Figure 2). It seems more probable that the deglacial maximum is a manifestation of a basinwide coastal phenomenon related to sea level rise, this scale being more compatible with the 50-year residence time of Mn in the surface ocean [Klinkhammer and Bender, 1980]. A basinwide increase in terrestrial input to the coastal ocean and associated increase in productivity centered at 15 ka as deduced from Mn/Ca is consistent with increases in the Thnormalized particle flux and mass accumulation rate of organic carbon in the Panama Basin [Kienast et al., 2007] as well as the faster accumulation of redoxsensitive metals [*Nameroff et al.*, 2004; *Hendy and Pedersen*, 2006] during the last deglaciation.

## 5. Conclusions

[24] Changes in the Mn/Ca of planktonic foraminifera from the extreme ETNP over the last 30 ka are consistent with higher dissolved terrestrial input to coastal surface waters during deglaciation than today or during the LGM. The influence of this input at the surface extended down to the 18°C isotherm beginning in the LGM and continuing through deglaciation, as indicated by the matched response of surface-calcifying G. ruber and thermocline-calcifying N. dutertrei. Increased chemical communication between the surface and 18°C water can be most easily explained by shoaling of the thermocline in the ETNP during the LGM, similar to that previously postulated by Bush and Philander [1998] from ocean-atmosphere modeling. Changes in the Mn/Ca ratio of planktonic foraminifera suggest that productivity peaked during the last deglaciation, which is consistent with several other studies that looked at isotopes of nitrogen [Altabet et al., 1999, 2002; Ganeshram et al., 2000, 2002; Kienast et al., 2002; Robinson et al., 2007] or thorium-normalized particle flux in the Panama Basin [Kienast et al., 2007]. Increased productivity may have led to a thickening and intensification of the OMZ that would have contributed to even greater communication between surface and thermocline. An increase in the Mn/Ca of the benthic foraminifera U. peregrina during the Holocene lags that of planktonic species by several thousand years and seems to be associated with a shift in bottom water circulation. The absence of an anomaly in the Mn/Ca of benthic foraminifera contemporaneous with that of surface species suggests that the oxygen minimum zone of the ETNP during the last deglacial was at least as intense as today, supporting work by other investigators [Nameroff et al., 2004; Hendy and Pedersen, 2006]. Further sorting of circulation and productivity effects through time will require wider application of foraminiferal Mn/Ca in combination with other paleoproxies.

# Appendix A

[25] Mn/Ca and Mg/Ca ratios plotted in Figures 3– 6 as well as core depths, ages and  $\delta^{18}$  results are given in Table A1. Core information, ages and oxygen isotope data were taken from *Benway* [2005]. Mg/Ca data from this thesis were reproc-

Core	Species	Section	Interval (cm)	mbsf	Age (ka B.P.)	$\delta^{18} \mathrm{O}$	Mg/Ca (mmol/mol)	Mn/Ca (mmol/mol)	Species	Section
ODP-1242A	G.ruber	1H-1	6	0.05	1.222	-2.75	4.71	0.210	N. dutertrei	1H-1
			14	0.13	2.133	-2.68	4.89	0.188		
			22	0.21	2.498	-2.37	4.66	0.170		
			30	0.29	3.373	-2.03	4.50	0.165		
			38	0.37	3.865	-2.49	4.54	0.151		
			46	0.45	5.148	-2.73	4.51	0.175		
			50	0.49	5.635	-2.26	4.43	0.193		
			54	0.53	5.967	-2.66	4.44	0.199		
			62	0.61	6.591	-2.57	4.50	0.220		
			70	0.69	7.001	-2.62	4.42	0.228		
			78	0.77	7.976	-2.58	4.40	0.226		
			86	0.85	8.269	-2.58	4.41	0.229		
			94	0.93	8.513	-	4.40	0.221		
			98	0.97	8.659	-2.36	4.36	0.222		
			102	1.01	8.727	-2.29	4.34	0.225		
			110	1.09	9.088	-2.77	4.30	0.228		
			118	1.17	9.508	-2.52	4.32	0.225		
			126	1.25	9.781	-2.51	4.31	0.219		
			134	1.33	10.122	-2.54	4.29	0.211		
			142	1.41	10.610	-1.30	4.07	0.210		
		1H-2	5	1.55	11.370	-1.43	3.95	0.225		1H-2
			13	1.63	11.599	-1.82	3.94	0.222		
			21	1.71	12.088	-1.44	3.76	0.244		
			29	1.79	12.954	-1.53	3.64	0.276		
			33	1.82	13.819	-1.74	3.56	0.240		
			37	1.87	13.819	-1.36	3.53	0.252		
			45	1.90	14.173	-1.57	3.45	0.256		
			53	2.03	14.726	-1.62	3.51	0.244		
			61	2.11	15.404	-1.37	3.47	0.211		
			69	2.18	15.740	-1.16	3.35	0.175		
			77	2.27	16.244	-1.15	3.40	0.182		
			85	2.34	16.640	-0.77	3.39	0.147		
			93	2.43	17.423	-0.70	3.46	0.135		
			101	2.51	18.035	-0.88	3.49	0.126		
			109	2.59	18.350	-0.88	3.38	0.119		
			113	2.62	18.440	-0.98	3.44	0.134		
			117	2.67	18.593	-0.96	3.42	0.111		
			125	2.75	18.890	-0.60	3.40	0.105		
			133	2.83	19.475	-0.92	3.48	0.113		
			141	2.91	20.060	-1.08	3.39	0.108		
			145	2.94	20.240	-0.78	3.33	0.112		
			149	2.99	20.510	-0.93	3.38	0.117		
		1H-3	9	3.10	21.022	-0.73	3.44	0.125		1H-3
			13	3.14	21.242	-0.79	3.39	0.134		
			21	3.22	21.864	-0.41	3.48	0.140		
			29	3.30	22.297	-0.79	3.54	0.130		
			37	3.36	22.887	-1.02	3.57	0.139		
			45	3.46	23.300	-0.86	3.55	0.129		
			53	3.54	23.650	-1.08	3.55	0.122		
			61	3.60	24.000	-0.81	3.62	0.118		
			69	3.70	24.345	-0.94	3.59	0.150		
			77	3.78	24.574	-0.56	3.58	0.132		
			85	3.86	25.149	-1.00	3.60	0.133		
			93	3.94	25.723	-0.91	3.59	0.144		
			101	4.02	26.642	-0.93	3.57	0.146		
			109	4.10	28.653	-0.78	3.61	0.132		
			117	4.18	29.227	-1.18	3.58	0.138		

**Table A1** (Sample). Oxygen Isotope and Metal Ratio Data for Three Species of Foraminifera Collected at ODP Site1242<sup>a</sup> [The full Table A1 is available in the HTML version of this article]

<sup>a</sup>Depths are given in meters below seafloor (mbsf).

Geochemistry Geophysics Geosystems

**.**3

] [

essed for this study. Mn/Ca data were not formulated in the Benway thesis.

#### Acknowledgments

Geochemistry

Geophysics Geosystems

[26] We acknowledge the excellent technical support of Andy Ungerer, Manager of the Keck Collaboratory at Oregon State University, and the many hours spent by June Wilson and Maziet Cheseby preparing samples. This work was supported by a grant from the Marine Geology and Geophysics unit in the Ocean Sciences Division of the U.S. National Science Foundation to Alan Mix and Gary Klinkhammer: OCE-0426410. This paper benefited greatly by comments made by the Editor (V. Salters), Associate Editor (A. Spivack), and two anonymous reviewers.

#### References

- Alagarsamy, R., G. A. Wolff, and R. Chester (2005), Partitioning and speciation of trace metal diagenesis in differing depositional environments of the Oman margin, *Aquat. Geochem.*, *11*, 195–213, doi:10.1007/s10498-004-3944-5.
- Altabet, M. A., D. W. Murray, and W. L. Prell (1999), Climatically linked oscillations in Arabian Sea denitrification over the past 1 m.y.: Implications for the marine N cycle, *Paleoceanography*, 14, 732–743, doi:10.1029/1999PA900035.
- Altabet, M. A., M. J. Higginson, and D. W. Murray (2002), The effect of millennial-scale changes in Arabian Sea denitrification on atmospheric CO<sub>2</sub>, *Nature*, 415, 159–162, doi:10.1038/415159a.
- Anand, P., H. Elderfield, and M. H. Conte (2003), Calibration of Mg/Ca thermometry in planktonic foraminifera from a sediment trap time series, *Paleoceanography*, 18(2), 1050, doi:10.1029/2002PA000846.
- Balakrishnan Nair, T. M., V. Ramaswamy, R. Shankar, and V. Ittekkot (1999), Seasonal and spatial variations in settling manganese fluxes in the northern Arabian Sea, *Deep Sea Res.*, *Part I*, *46*, 1827–1839, doi:10.1016/S0967-0637(99)00029-1.
- Bard, E., B. Hamelin, R. G. Fairbanks, and A. Zindler (1990), Calibration of the <sup>14</sup>C timescale over the past 30,000 years using mass spectrometric U-Th ages from Barbados corals, *Nature*, 345, 405–410, doi:10.1038/345405a0.
- Barker, S., M. Greaves, and H. Elderfield (2003), A study of cleaning procedures used for foraminiferal Mg/Ca paleothermometry, *Geochem. Geophys. Geosyst.*, 4(9), 8407, doi:10.1029/2003GC000559.
- Barker, S., I. Cacho, H. Benway, and K. Tachikawa (2005), Planktonic foraminiferal Mg/Ca as a proxy for past oceanic temperatures: A methodological overview and data compilation for the Last Glacial Maximum, *Quat. Sci. Rev.*, 24, 821–834, doi:10.1016/j.quascirev.2004.07.016.
- Benway, H. M. (2005), Modern and Past Climate Variability in the Eastern Pacific Warm Pool, Ph.D. thesis, 116 pp., Oregon State Univ., Corvallis.
- Benway, H. M., B. A. Haley, G. P. Klinkhammer, and A. C. Mix (2003), Adaptation of a flow-through leaching procedure for Mg/Ca paleothermometry, *Geochem. Geophys. Geo*syst., 4(2), 8403, doi:10.1029/2002GC000312.
- Benway, H. M., A. C. Mix, B. A. Haley, and G. P. Klinkhammer (2006), Eastern Pacific Warm Pool paleosalinity and climate variability: 0–30 kyr, *Paleoceanography*, 21, PA3008, doi:10.1029/2005PA001208.

- Boyle, E. A. (1983), Manganese carbonate overgrowths on foraminiferal tests, *Geochim. Cosmochim. Acta*, 47, 1815–1819, doi:10.1016/0016-7037(83)90029-7.
- Bush, B. G., and S. G. H. Philander (1998), The role of oceanatmosphere interactions in tropical cooling during the last glacial maximum, *Science*, 279, 1341–1344, doi:10.1126/science. 279.5355.1341.
- Clark, P. U., A. M. McCabe, A. C. Mix, and A. J. Weaver (2004), Rapid rise of sea level 19,000 years ago and its global implications, *Science*, *304*, 1141–1144, doi:10.1126/science. 1094449.
- Climate: Long-Range Investigation, Mapping, and Prediction Project Members (1981), Seasonal reconstructions of the Earth's surface at the last glacial maximum, *Map Chart Ser., MC-36*, Geol. Soc. of Am., Boulder, Colo.
- Eggins, S., D. P. De, and J. Marshall (2003), Mg/C variation in planktonic foraminifera tests, *Earth Planet. Sci. Lett.*, *212*, 291–306, doi:10.1016/S0012-821X(03)00283-8.
- Fairbanks, R. G. (1990), The age and origin of the "Younger Dryas Climate Event" in Greenland ice cores, *Paleoceano-graphy*, 5, 937–948, doi:10.1029/PA005i006p00937.
- Fairbanks, R. (1992), Barbados sea level and Th/U <sup>14</sup>C calibration, *World Data Cent. Paleoclimatol. Data Contrib. Ser.*, 92-020, Paleoclimatol. Program, Natl. Geophys. Data Cent., Natl. Oceanic and Atmos. Admin., Boulder, Colo.
- Froelich, P. N., et al. (1979), Early oxidation of organic matter in pelagic sediments of the Eastern Equatorial Atlantic: Suboxic diagenesis, *Geochim. Cosmochim. Acta*, 43, 1075–1090, doi:10.1016/0016-7037(79)90095-4.
- Ganeshram, R. S., T. F. Pedersen, S. E. Calvert, G. W. McNeill, and M. R. Fontugne (2000), Glacial-interglacial variability in denitrification in the world's oceans: Causes and consequences, *Paleoceanography*, *15*, 361–376, doi:10.1029/1999PA000422.
- Ganeshram, R. S., T. F. Pedersen, S. E. Calvert, and R. Francois (2002), Reduced nitrogen fixation in the glacial ocean inferred from changes in marine nitrogen and phosphorus inventories, *Nature*, *415*, 156–159, doi:10.1038/415156a.
- Grootes, P. M., and M. Stuiver (1997), Oxygen 18/16 variability in Greenland snow and ice with 10<sup>3</sup>- to 10<sup>5</sup>-year time resolution, *J. Geophys. Res.*, *102*, 26,455–26,470, doi:10.1029/97JC00880.
- Haley, B. A., and G. P. Klinkhammer (2002), Development of a flow-through system for cleaning and dissolving foraminiferal tests, *Chem. Geol.*, *185*, 51–69, doi:10.1016/S0009-2541(01)00399-0.
- Hendy, I. L., and T. F. Pedersen (2006), Oxygen minimum zone expansion in the eastern tropical North Pacific during deglaciation, *Geophys. Res. Lett.*, 33, L20602, doi:10.1029/ 2006GL025975.
- Islebe, G. A., and H. Hooghiemstra (1997), Vegetation and climate history of montane Costa Rica since the last glacial, *Quat. Sci. Rev.*, 16, 589–604, doi:10.1016/S0277-3791(96)00051-0.
- Karstensen, J., L. Stramma, and M. Visbeck (2008), Oxygen minimum zones in the eastern tropical Atlantic and Pacific oceans, *Prog. Oceanogr.*, 77, 331–350, doi:10.1016/j.pocean. 2007.05.009.
- Kienast, S. S., S. E. Calvert, and T. F. Pedersen (2002), Nitrogen isotope and productivity variations along the northeast Pacific margin over the last 120 kyr: Surface and subsurface paleoceanography, *Paleoceanography*, 17(4), 1055, doi:10.1029/2001PA000650.
- Kienast, S. S., M. Kienast, A. C. Mix, S. E. Calvert, and R. François (2007), Thorium-230 normalized particle flux and sediment focusing in the Panama Basin region during

the last 30,000 years, *Paleoceanography*, 22, PA2213, doi:10.1029/2006PA001357.

Geochemistry

Geophysics Geosystems

- Klinkhammer, G. (1980), Observations of the distribution of manganese over the East Pacific Rise, *Chem. Geol.*, 29, 211–226, doi:10.1016/0009-2541(80)90021-2.
- Klinkhammer, G., and M. Bender (1980), The distribution of manganese in the Pacific Ocean, *Earth Planet. Sci. Lett.*, 46, 361–384, doi:10.1016/0012-821X(80)90051-5.
- Klinkhammer, G. P., B. A. Haley, A. C. Mix, H. M. Benway, and M. Cheseby (2004), Evaluation of automated flowthrough time-resolved analysis of foraminifera for Mg/Ca paleothermometry, *Paleoceanography*, 19, PA4030, doi:10.1029/2004PA001050.
- Lewis, B. L., and G. W. Luther III (2000), Processes controlling the distribution and cycling of manganese in the oxygen minimum zone of the Arabian Sea, *Deep Sea Res.*, *Part II*, 47, 1541–1561, doi:10.1016/S0967-0645(99)00153-8.
- Nameroff, T. J., S. E. Calvert, and J. W. Murray (2004), Glacialinterglacial variability in the eastern tropical North Pacific oxygen minimum zone recorded by redox-sensitive trace metals, *Paleoceanography*, 19, PA1010, doi:10.1029/ 2003PA000912.
- Pena, L. D., E. Calvo, I. Cacho, S. Eggins, and C. Pelejero (2005), Identification and removal of Mn-Mg-rich contami-

nant phases on foraminiferal tests: Implications for Mg/Ca past temperature reconstructions, *Geochem. Geophys. Geosyst.*, *6*, Q09P02, doi:10.1029/2005GC000930.

- Robinson, R. S., A. Mix, and P. Martinez (2007), Southern Ocean control on the extent of denitrification in the southeast Pacific over the last 70 ka, *Quat. Sci. Rev.*, 26, 201–212, doi:10.1016/j.quascirev.2006.08.005.
- Sadekov, A. Yu., S. M. Eggins, and P. De Deckker (2005), Characterization of Mg/Ca distributions in planktonic foraminifera species by electron microprobe mapping, *Geochem. Geophys. Geosyst.*, 6, Q12P06, doi:10.1029/2005GC000973.
- Shackleton, N. J., M. A. Hall, and E. Vincent (2000), Phase relationships between millennial time scales events 64,000 to 24,000 years ago, *Paleoceanography*, *15*, 565–569, doi:10.1029/2000PA000513.
- Shipboard Scientific Party (2003), Site 1242, Ocean Drill. Program Initial Rep., 202, 74 pp., doi:10.2973/odp.proc. ir.202.113.
- Stanford, J. D., E. J. Rohling, S. E. Hunter, A. P. Roberts, S. O. Rasmussen, E. Bard, J. McManus, and R. G. Fairbanks (2006), Timing of meltwater pulse 1a and climate responses to meltwater injections, *Paleoceanography*, 21, PA4103, doi:10.1029/2006PA001340.